

1 **Impact of mine waste on airborne respirable particulates in northeastern**
2 **Oklahoma, USA**

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34 List of Abbreviations Used in this Manuscript:

35 BC = Black carbon

36 CCSEM = Computer-controlled Scanning Electron Microscopy

37 EDXRF = Energy-dispersive X-ray fluorescence

38 EDX = Energy-dispersive X-ray analysis

39 LOD = Limit of detection

40 PbS = Galena (lead sulfide)

41 U.S. EPA = US Environmental Protection Agency

42 ZnS = Sphalerite (zinc sulfide)

43 **ABSTRACT**

44 Atmospheric dispersion of particles from mine waste is potentially an important route of
45 human exposure to metals in communities close to active and abandoned mining areas. In
46 this study, we assessed sources of mass and metal concentrations in two size fractions of
47 respirable particles using positive matrix factorization (EPA PMF 3.0). Weekly integrated
48 samples of PM₁₀ and PM_{2.5} were collected at three monitoring sites, varying distances
49 (0.5-20 km) from mine waste piles, for 58 consecutive weeks in a former lead (Pb) and
50 zinc (Zn) mining region. Mean mass concentrations varied significantly across sites for
51 coarse (PM₁₀-PM_{2.5}) but not fine (PM_{2.5}) particles. Concentrations of Pb and Zn
52 significantly decreased with increasing distance from the mine waste piles in both coarse
53 (p<0.0001) and fine (p<0.0005) fractions. Source apportionment analyses deduced five
54 sources contributing to PM_{2.5} (mobile source combustion, secondary sulfates, mine waste,
55 crustal/soil, and a source rich in Ca) and three sources for the coarse fraction (mine
56 waste, crustal/soil, and a Ca-rich source). In the fine fraction, mine waste contributed 1-
57 6% of the overall mass, 40% of Pb, and 63% of Zn. Mine waste impacts were more
58 apparent in the coarse fraction, and contributed 4-39% of total mass, 88% of Pb and 97%
59 of Zn. Percent contribution of mine waste varied significantly across sites (p<0.0001) for
60 both size fractions, with highest contributions in the site closest to the mine waste piles.
61 Seasonality, wind direction, and concentrations of the Ca-rich source were also
62 associated with levels of ambient aerosols from the mine waste source. Scanning electron
63 microscopy results indicated that the PMF-identified mine waste source is mainly
64 composed of Zn-Pb agglomerates on crustal particles in the coarse fraction. In
65 conclusion, the differential impacts of mine waste on respirable particles by size fraction
66 and location should be considered in future exposure evaluations.

67 **IMPLICATIONS**

68 This is the first study to use source apportionment modeling along with scanning electron
69 microscopy to quantify the impact of mine waste on respirable particles in residential
70 areas surrounding an abandoned mining site. Fugitive dust emissions from mine waste
71 were found predominantly in the coarse fraction. Impacts were most substantial in Picher,
72 the source-dominated site, and decreased with increasing distance from the mine waste
73 piles suggesting that populations living nearest to these piles may be more highly
74 exposed. These results will enable more accurate assessments of human exposure and
75 health effects in communities adjacent to active and abandoned mining areas.

76 **Keywords:** Air pollution; Chat; Metals; Mining; Positive Matrix Factorization (PMF);
77 Source apportionment; Tar Creek Superfund Site

78 **INTRODUCTION**

79 The U.S. EPA estimates there are over 200,000 inactive and abandoned hardrock mines
80 in the United States.¹ Active and abandoned mines have the potential to cause damage to
81 aquatic biota, terrestrial vegetation and wildlife, air quality, and cultural resources.
82 Seventy-two mining sites have been designated to the National Priority List (NPL) under
83 the U.S. EPA Superfund program. These sites pose an imminent threat to human or
84 ecological health and warrant federal intervention.² Both coal and hardrock mining
85 continue globally, regularly creating more abandoned mines.

86 In metal mining, less than 1% of processed material is recovered as useful metal.³
87 Mine tailings and other metal-enriched by-products of the mining process are often stored
88 in large piles that can become sources of contamination to surrounding ecosystems and
89 residential areas through wind-borne dispersal of particles. Suspended airborne particles
90 can travel offsite and infiltrate indoors where they can be inhaled directly; or deposit onto
91 soil or house dust by settling, impaction, or washout.

92 Mine waste piles represents a dispersed source of metal contamination and are
93 particularly abundant at the Tar Creek Superfund Site, a former lead and zinc mining area
94 located in rural Oklahoma. Mine waste, locally known as “chat”, is largely composed of
95 chert (SiO₂), dolomite (CaMg(CO₃)₂), and sulfide minerals including galena (PbS),
96 sphalerite (ZnS), and pyrite (FeS₂).⁴ There are approximately 30 major chat piles in the
97 Tar Creek area⁵, which contain elevated concentrations of zinc (Zn), lead (Pb), and
98 cadmium (Cd).^{6,7} Recent research suggests metal concentrations in chat particles
99 increase with decreasing particle size, and ultrafine particles (< 1µm) contain Zn, Pb, and
100 Cd at concentrations up to 20 times higher than the bulk material.⁷ Chat particles may be
101 transported into the broader environment through various mechanisms such as wind
102 erosion. Chat may also be deposited on roads, either through atmospheric settling or
103 when used as a gravel material, and then become re-suspended and dispersed with traffic.
104 In addition, local reprocessing of chat for asphalt and other transportation construction
105 projects⁶⁻⁸ may lead to increased aerosol mobilization. Variable weather conditions
106 including sporadic events such as wind storms, along with human disturbances, may lead
107 to spatial and temporal heterogeneity in airborne contaminants.

108 A large body of evidence has shown that exposure to particulate matter is harmful
109 to human health. Particle size not only determines the site and efficiency of pulmonary
110 deposition but also may be an indication of particle source and composition. Fine
111 particles (PM_{2.5}), largely generated from combustion processes, have been associated
112 with a range of adverse respiratory and cardiovascular health effects including mortality.
113 ^{9, 10} Coarse particles (PM₁₀-PM_{2.5}), generated primarily from mechanical processes, are
114 more commonly associated with respiratory and cardiovascular morbidity ¹¹ such as
115 inflammatory lung injury.¹² Additionally, experimental and epidemiologic evidence
116 suggests that metal constituents in particulate matter, such as V, Zn, Fe, and Ni, play an
117 important role in inflammatory and cardiovascular health effects.¹²⁻¹⁵ Inhalation of metals
118 may be particularly toxic since metals such as Mn, Cd, Zn, and Ni can be transported
119 directly to the brain via olfactory pathways.¹⁶⁻¹⁸

120 Since there is a potential for inhalation exposure to metal-enriched particulate
121 matter in abandoned mining areas like the Tar Creek Superfund Site, it is important to
122 quantify the impact of mine waste piles on ambient air quality. While previous studies
123 have used multivariate statistical receptor models to identify the contribution of active
124 mining operations, such as smelting, to respirable particles,^{19, 20} few studies have used
125 these techniques to quantify the impact of mine waste, a more indirect and persistent
126 source of respirable particles, in residential areas surrounding abandoned mining sites.
127 This study is part of an on-going effort to understand children's exposure to mining-
128 related metal mixtures and subsequent health effects. The goal of this study was to
129 examine the impact of chat-related sources on ambient particle concentrations at the Tar
130 Creek Superfund Site. Specifically, sources of fine and coarse particles were identified,
131 and their contributions to mass and metal concentrations were estimated using positive
132 matrix factorization. Predictors of source contributions were identified using regression
133 analysis. Lastly, the presence of unique, local sources was qualitatively confirmed using
134 scanning electron microscopy techniques.

135

136

137 **EXPERIMENTAL METHODS**

138 **Study Design**

139 Ottawa County, OK is a predominantly rural area with high humidity and abundant
140 rainfall between the months of May and November. The predominant wind direction is
141 from the south with an average wind speed of 11 Km hr⁻¹.²¹ Three stationary air
142 monitoring sites were established in the area to capture spatial variability and represent
143 potentially different human exposure scenarios. Weekly integrated samples were
144 collected at each site for 58 weeks from July 2005 to September 2006.

145 Figure 1 shows the locations of the three sites in relation to the chat piles. Sites
146 were chosen through consultation with our community partners in the area. Site 1, the
147 source-dominated site, was located in a residential yard in the town of Picher, surrounded
148 by chat piles on two sides and within a kilometer of several other piles. Site 2 was located
149 in the town of Quapaw, approximately 5 km from the bulk of the chat piles, but close to a
150 well-used county road and several dirt roads that are thought to be lined with chat
151 material.²² Site 3 was located in a suburban neighborhood within Miami, the largest town
152 in Ottawa County, and approximately 18 kilometers upwind of the Picher site with no
153 chat piles in the nearby vicinity.

154 **Analytical Methods**

155 Separate filter samples of PM_{2.5} particles and PM₁₀ particles were collected on Teflon
156 filters (2-µm pore size, 37 mm in diameter) using Harvard Impactors²³ attached to
157 MEDO air pumps (Medo, Hanover Park, IL) at 4 liters min⁻¹. Filters were exposed for
158 seven days (24 hr a day) and changed once a week. Airflow was measured and calibrated
159 at the beginning and end of every filter exposure using calibrated flow meters (Matheson
160 Tri-gas Model 603(E500)).

161 Teflon filters were weighed in a temperature- and humidity-controlled room (18 –
162 24°C, 40 ± 5% relative humidity). All filters were left to equilibrate for 24 hr prior to pre-
163 sampling weighing and 48 hr prior to post-sampling weighing. The elemental content of
164 the ambient aerosol was quantified by energy-dispersive X-ray fluorescence (EDXRF)
165 analysis, a non-destructive and moderately sensitive analytical method for determining
166 elemental concentrations of aluminum (Al) through lead (Pb).^{24, 25} Analyses were
167 performed at the U.S. EPA's National Exposure Research Laboratory (NERL) in

168 Research Triangle Park, NC, using an EDXRF spectrometer custom-built for the U.S.
169 EPA by Lawrence Berkeley Laboratory. Black carbon concentrations were estimated in
170 the PM_{2.5} fraction using reflectance analysis on the particle filters, a method that provides
171 measurements that are highly correlated with concentrations measured using
172 thermaloptical methods.²⁶ Sample absorbance values were obtained using an Optical
173 Transmissometer Data Acquisition System (Magee Scientific, Berkeley, CA). UV and IR
174 absorbance values for each sample were collected at 370nm and 880nm wavelengths,
175 respectively. A mass absorption coefficient of 16.6 was used to convert the transmittance
176 to mass concentration units.²⁷ Computer-Controlled Scanning Electron Microscopy
177 (CCSEM)²⁸ coupled with energy-dispersive X-ray analysis (EDX) (R.J. Lee Instruments,
178 Ltd., now Aspex Corporation) was conducted on specific filters to help interpret sources
179 identified from the statistical receptor models. The metals and reflectance analyses of
180 particle filters and CCSEM/EDX analyses were conducted according to standard
181 operating procedures at the U.S. EPA National Exposure Research Laboratory (Research
182 Triangle Park, NC).

183 **Quality Control and Quality Assurance**

184 Seven percent of the total samples collected were voided because they failed to meet
185 established flow or sampling time criteria. Field blanks were transported and handled like
186 regular samples, but the filters were not attached to the air pumps. Field blanks comprised
187 10% of the total samples collected and were used to determine background
188 contamination. The method limit of detection (LOD) for each species was calculated as
189 three times the average uncertainty of 23 laboratory teflon blanks divided by the median
190 volume for all samples (40 m³). If the mean field blank concentration was greater than the
191 mean plus three times the standard deviation of the lab blanks, then blank correction was
192 applied. Sample concentrations of Ca and Fe in one batch of PM_{2.5} samples were blank
193 corrected by subtracting the mean field blank concentration from the sample
194 concentrations in this batch. Precision of the method was determined by duplicate
195 samples (10% of total samples collected). Black carbon concentrations were imputed for
196 two samples using the median concentration of the sampling location. Samples collected
197 during the week of 6/30/2006 were eliminated from all analyses since these samples were
198 impacted by fireworks and had high levels of K, Cu, and Sr.

199

Meteorological Data

200 Meteorological data including daily measures of temperature, average and maximum
201 wind speed, wind direction, and precipitation was obtained from the National
202 Oceanographic and Atmospheric Administration (Washington, DC) weather station for
203 Tulsa International Airport, approximately 145 kilometers south of the study area.
204 Weekly averages for these variables were calculated and used in regression analyses.
205 Since wind direction data was originally provided in degrees, a dummy variable was
206 constructed to correspond to 90 degree directional increments (e.g. South, West, etc.).
207 Similarly, a dummy variable was constructed to correspond to the four calendar seasons.

208

Summary Statistics

209 After QA/QC criteria were implemented, a total of 156 PM₁₀ and 155 PM_{2.5} samples were
210 available for data analysis. Coarse fraction concentrations were not directly measured,
211 but were calculated as the difference between PM₁₀ and PM_{2.5} concentrations for the 150
212 samples where both PM₁₀ and PM_{2.5} measurements were available. To generate summary
213 statistics and compare concentrations across sites, a balanced dataset was created that
214 included only those samples where corresponding data was available at all three sites for
215 both size fractions (N=123). For data that fell below the method limit of detection,
216 estimated metal concentrations provided by XRF analyses were used in calculation of
217 summary statistics and statistical models. Correlations were assessed using Spearman
218 rank correlations. Statistically significant differences in metal concentrations across sites
219 were determined using the ANOVA test for differences and Scheffe's test for multiple
220 comparisons. Prior to the ANOVA analysis, the Levene's test for homogeneity of
221 variance was implemented. If the assumption of homogenous variance was not upheld,
222 the Welch's ANOVA test, which accounts for unequal group variances, was used instead.

223

Receptor Modeling: EPA PMF 3.0

224 A receptor modeling approach employing EPA Positive Matrix Factorization (PMF) 3.0
225 was used to quantify sources in both fine and coarse particulate matter. PMF uses a
226 constrained, weighted, least squares regression via the Multilinear Engine (ME-2) to
227 generate source profiles and source contributions. Further details on the algorithm can be
228 found in the PMF 3.0 user guide.²⁹ Input data includes sample concentration and
229 uncertainty estimates.

230 Calculation of uncertainty estimates varied according to chemical species and size
231 fraction. For elemental concentrations determined by XRF, sample and element specific
232 concentration uncertainties were provided that equaled one standard deviation of error
233 estimates based on analytical precision. Since sample specific uncertainty estimates were
234 not provided for particle mass or black carbon concentrations, these uncertainty estimates
235 were defined as 10% and 20% of the measured concentration, respectively.³⁰ Uncertainty
236 estimates for coarse fraction measurements were calculated as the following:

237

$$238 \quad \text{coarse } \sigma_{i,j} = \sqrt{\frac{(PM_{10}\sigma_{i,j})^2 + (PM_{2.5}\sigma_{i,j})^2}{2}} \quad (1)$$

239 where uncertainty σ is the j th species uncertainty estimated for the i th sample.

240 The model was run in default robust mode to minimize the effects of outliers and
241 included samples from all three sites since it was assumed that source profiles would not
242 vary across sites. All models were normalized to PM mass concentrations. Thirty base
243 runs were executed for each specific model, and model goodness-of-fit was evaluated by
244 examining Q (robust) values. The solution with the lowest Q value was chosen, and 100
245 bootstrap simulations were performed to estimate the stability and uncertainty of that
246 solution which involved each of the bootstrapped factors being mapped to exactly one of
247 the base case factors. The number of factors in the final solution was decided using a
248 priori knowledge about local sources and by maximizing agreement between base run
249 and bootstrapped results.

250 The source apportionment model for $PM_{2.5}$ included concentration and
251 uncertainty data from 155 samples. Fourteen possible elements and two carbon fractions
252 were considered for inclusion in the PMF model. Species were evaluated based on their
253 detection frequency, signal-to-noise ratio, and usefulness as source tracers. The following
254 analytes were included in the $PM_{2.5}$ source apportionment analysis: Al, Si, S, K, Ca, Ti,
255 Mn, Fe, Zn, Se, Br, Pb, and black carbon (BC).

256 Since coarse fraction metal concentrations were not directly measured, a more
257 conservative approach was used when conducting the coarse fraction PMF analysis. To
258 be included in the PMF analysis, elements were assessed on the following two criteria: 1)
259 well detected (>70%) in the coarse fraction and 2) had reasonably higher concentrations

260 in PM₁₀ as compared to PM_{2.5}. Based on these criteria, nine elements and 150 samples
261 were included in the coarse PMF model. This list was similar to that of the fine fraction
262 model but omitted S, Se, Br, and BC.

263 **Regression Analysis**

264 Source-specific mass concentration estimates were extracted for each sample from the
265 PMF output. Univariate and bivariate summary statistics and distributional plots were
266 examined for all variables. Mine waste estimates were positively skewed and log
267 transformed prior to regression analysis. Multiple linear regression models were used to
268 describe the relationships between PMF-estimated mine waste concentrations and
269 predictor variables of interest which included season, wind direction, wind speed,
270 precipitation, site location, and estimated mass concentration data of the other PMF
271 sources. To obtain the final model, backward elimination was used with a threshold
272 $p < 0.05$ for retaining the variable in the model. Regression analyses were conducted in
273 SAS version 9.1.

274 **RESULTS**

275 **Summary Statistics**

276 Mean (\pm SD) PM₁₀ mass concentrations in Picher ($23 \pm 6.4 \mu\text{g}/\text{m}^3$) and Quapaw (24 ± 7.6
277 $\mu\text{g}/\text{m}^3$) were significantly higher ($p=0.01$) than concentrations in Miami ($20 \pm 5.1 \mu\text{g}/\text{m}^3$).
278 Similar to PM₁₀, coarse (PM₁₀-PM_{2.5}) particle mass concentrations in Picher (12 ± 4.4
279 $\mu\text{g}/\text{m}^3$) and Quapaw ($13 \pm 6.1 \mu\text{g}/\text{m}^3$) were higher than Miami ($9.0 \pm 2.9 \mu\text{g}/\text{m}^3$)
280 suggesting a difference in local sources between these areas (Table 1). Fine (PM_{2.5})
281 particle mass concentrations did not differ by site and approximated $11 \mu\text{g}/\text{m}^3$ at all three
282 sites. PM₁₀ was more strongly correlated with coarse particles than with PM_{2.5} in both
283 Picher ($r=0.81$) and Quapaw ($r=0.85$). By contrast, in the more commercially developed
284 town of Miami, PM₁₀ concentrations were more strongly correlated with PM_{2.5} ($r=0.82$).
285 Seasonal variability was present in both PM_{2.5} and PM₁₀ with highest concentrations in
286 the summer and lowest concentrations in the winter (data not shown).

287 Mass and selected metal concentrations for coarse and fine particulates by
288 location are presented in Table 1. There was a significant spatial trend in Pb and Zn
289 concentrations, with both elemental concentrations decreasing with increasing distance

290 from the chat piles. In the more locally influenced coarse fraction, mean Pb
291 concentrations were significantly different at all three sites ((Picher: 7.9 ± 4.6) vs.
292 (Quapaw: 3.0 ± 2.4) vs. (Miami: 1.1 ± 0.75) ng/m^3 , $p < 0.0001$). Similarly, Zn
293 concentrations in coarse particles varied significantly at all three sites, with a 10-fold
294 difference between Picher ($120 \pm 69 \text{ ng/m}^3$) and Miami ($11 \pm 5.6 \text{ ng/m}^3$). Elements
295 associated with crustal sources such as Al, Si, Ca, and Fe were generally higher in
296 Quapaw and Picher compared to Miami.

297 As expected, there were fewer differences in metal concentrations across sites in
298 the fine fraction, likely due to the impact of regional pollution sources and the slower
299 deposition rate of small particles. Pb and Zn concentrations showed a similar but less
300 pronounced spatial gradient compared to the coarse fraction. Pb concentrations at Picher
301 ($3.5 \pm 2.6 \text{ ng/m}^3$) were elevated relative to Miami ($1.9 \pm 1.4 \text{ ng/m}^3$) by a factor of two. A
302 similar trend was also observed for Zn in the fine fraction.

303 **Characterization of Sources**

304 When EPA PMF was applied to $\text{PM}_{2.5}$ data, the model converged yielding a five factor
305 solution. There was good agreement between the predicted and measured $\text{PM}_{2.5}$ mass
306 ($R^2=0.75$). The R^2 values for the elements ranged from 0.50-0.99. Over 87 bootstraps out
307 of 100 were mapped to the original base factor.

308 A three factor solution was extracted from the coarse fraction data. The PMF
309 solution for the coarse data exhibited a better goodness-of-fit compared to the solution for
310 the fine fraction data. The correlation between predicted and measured PM mass yielded
311 an $R^2=0.89$, and the R^2 for the elements ranged from 0.85-0.99. All 100 bootstraps were
312 mapped to the original base factor.

313 The source profiles deduced from the PMF models for both the fine and coarse
314 fraction are presented in Figure 2. Consistent with the composition of mine waste, there
315 was a factor present in both size fractions whose source profile was dominated by Zn and
316 Pb with modest contributions of crustal elements (Al, Si, and Ca) (Figure 2). The
317 average Zn to Pb ratios in this source profile were 9 and 16 in the fine and coarse
318 fractions, respectively, which is in agreement with the ratio found in “parent” chat
319 particles $< 37 \mu\text{m}$ collected in the Tar Creek area (Zn/Pb ratio =15; unpublished data). The
320 percent mass of Zn and Pb in the PMF-deduced source profile in both fine and coarse

321 fractions were also similar to that of the “parent” chat. Zn was found in the 1-10% range
322 and Pb was found in <1% of the total mass.⁷

323 The source profile of soil and crustal materials was characterized by the
324 component loaded on Al, Si, Ti, Mn, Fe, and K. These elements have commonly been
325 used to identify crustal sources.^{31,32} In both coarse and fine fractions, there was a source
326 rich in Ca. This factor also showed contributions from Si, Al, and BC (fine fraction only)
327 and likely incorporates the impact of unpaved and paved road dust. In both size fractions,
328 the Al/Ca ratio was approximately 0.1 in the Ca-rich factor which is similar to unpaved
329 road dust as characterized by Chow et al.³¹ Also, consistent with the unpaved road dust
330 source profile³¹, the percent mass of Ca in the PMF-deduced Ca-rich profile was 15% in
331 the coarse fraction. The last two factors were only found in the fine particles. These were
332 mobile source combustion and secondary sulfates from coal combustion, and were
333 readily identified by comparison with previously reported profiles.³¹⁻³³

334 **Mass and Elemental Apportionments**

335 *Fine Fraction.* Average contributions of each source to PM_{2.5} are summarized in Table 2.
336 The majority of PM_{2.5} mass was apportioned to secondary sulfates and mobile sources
337 with less than 5% attributed to the mine waste factor. Elemental apportionment found that
338 approximately 40% of Pb and 63% of Zn were apportioned to mine waste. Variations in
339 mass apportionments were observed across sites. Average mine waste contributions
340 ranged from 1% in Miami to 6% in Picher (Figure 3a). Contributions of the Ca-rich
341 source were highest in Quapaw and mobile source contributions were highest in Miami.
342 Secondary sulfates estimates were similar at all sites. Variation was not only observed
343 across locations, but also within locations. At Picher, the source-dominated site, there
344 was a 10-fold difference between minimum and maximum estimated concentrations of
345 mine waste (0.11-1.4 µg/m³).

346
347 *Coarse Fraction.* Average contributions of each source to coarse mass concentrations are
348 also summarized in Table 2. Mean contributions of mine waste, crustal, and Ca-rich
349 across sites were 20%, 42%, and 38%, respectively. Elemental apportionments found that
350 88% of Pb and 97% of Zn were associated with mine waste. Not only were mass and
351 percent contributions of mine waste greater in the coarse fraction relative to the fine

352 fraction, but spatial differences were also more substantial with 39%, 11%, and 4%
353 percent contributions in Picher, Quapaw, and Miami, respectively (Figure 3b). Mine
354 waste was the largest contributor to coarse mass in Picher (Figure 3b), and in both Picher
355 and Quapaw, mine waste concentrations ranged two orders of magnitude - from 0.1
356 $\mu\text{g}/\text{m}^3$ to $10 \mu\text{g}/\text{m}^3$. The percent contributions of crustal and Ca-rich sources were similar
357 between Quapaw and Miami; however, the concentrations apportioned to these sources
358 were greater in Quapaw.

359 **Predictors of Mine Waste Source Contribution**

360 Predictors of mine waste attributable mass were examined using the estimated
361 concentrations ($\mu\text{g}/\text{m}^3$) from PMF source apportionment models in correlation and linear
362 regression analysis. Mine waste estimates in fine and coarse fractions were strongly
363 correlated ($r=0.76$, $p<0.0001$), but fine fraction mine waste was not significantly
364 correlated with any of the other $\text{PM}_{2.5}$ sources. Predictors of fine fraction mine waste in
365 multivariate models included sampling site, season, wind direction, and coarse fraction
366 mine waste concentrations (Table 3). These factors collectively accounted for 64% of the
367 variability in fine fraction mine waste estimates. Mine waste concentrations were highest
368 in Picher and lowest in Miami. Concentrations were highest in the fall and lowest in the
369 winter. Elevated mine waste concentrations were also associated with easterly winds.
370 Wind speed, precipitation, temperature were not associated with $\text{PM}_{2.5}$ mine waste.

371 Coarse fraction mine waste was positively correlated with coarse Ca-rich ($r=0.26$,
372 $p=0.001$) and negatively correlated with coarse crustal ($r=-0.16$, $p=0.05$). In univariate
373 analysis, precipitation was inversely associated with coarse mine waste concentrations,
374 and sampling site was a significant predictor. The final multivariate model included
375 sampling site, season, and coarse Ca-rich concentrations (Table 3). Coarse mine waste
376 concentrations were highest in Picher and lowest in Miami. Coarse mine waste levels
377 increased with increasing temperature with highest levels in the summer and lowest
378 levels in the winter. Coarse Ca-rich concentrations remained a significant predictor after
379 accounting for the other variables while precipitation was no longer significant in the
380 multivariate model. In addition, a statistically significant interaction ($p<0.0001$) was
381 observed between sampling site and Ca-rich concentrations suggesting a differential
382 relationship between Ca-rich and mine waste by location. Figure 4 shows the graphical

383 interpretation of this statistical interaction term. Coarse fraction mine waste increased
384 linearly with coarse fraction Ca-rich estimates in both Quapaw and Miami. Conversely,
385 no relationship was observed between the mine waste and Ca-rich source in Picher.
386 Collectively, these factors accounted for 79% of the variability in PMF-estimated coarse
387 mine waste concentrations. Coarse mine waste was not associated with either wind speed
388 or direction.

389 **Scanning Electron Microscopy**

390 CCSEM was used to characterize Zn- and Pb-bearing particles in a PM₁₀ sample from the
391 Picher site that had a high factor score for the mine waste source in the coarse size
392 fraction. Several hundred individual particles larger than 0.4 μm with detectable
393 concentrations of Zn or Pb were sized and analyzed for elemental composition by EDX.
394 Consistent with source apportionment modeling results, CCSEM found that these
395 particles were predominantly in the coarse fraction (mass median aerodynamic diameter
396 = 6.8 μm). Although EDX analysis does not definitively identify specific minerals, the
397 analysis showed that Zn- and Pb-rich particles were observed in two major varieties. The
398 first major type consisted of heterogeneous particles in which Zn- and Pb-rich particles
399 were co-present with sulfur, consistent with metal sulfide minerals which have been
400 identified in mine waste.^{4,6,7} Isolated particles of ZnS or PbS were rarely observed.
401 Rather, these particles were frequently attached to coarse silicate or aluminosilicate
402 particles. Figure 5 shows SEM micrographs of a typical particle of this type. The
403 secondary electron image (5a) highlights surface morphology while the backscattered
404 electron (BSE) image (5b) reveals chemical heterogeneity within the particle. Bright
405 areas in the BSE image are features associated with high average atomic number and
406 were consistent with the mineral ZnS, as seen in the upper EDX spectrum (5c). These
407 ZnS features appear to be adsorbed onto or aggregated with an aluminosilicate matrix
408 (5d) whose EDX spectrum is largely consistent with the PMF-deduced crustal/soil factor.
409 The second type of frequently occurring particle were Zn- or Pb-rich silicate particles,
410 which may be indicative of hemimorphite, a primary and secondary mineral that forms in
411 oxidic, Zn-rich conditions and has been identified in chat particles less than 37 μm.⁷

412 **DISCUSSION**

413 To our knowledge, this study is the first to use source apportionment techniques to
414 quantify the impact of mine waste on airborne respirable particulates in residential areas
415 close to an abandoned mining site. PMF results for both fine and coarse particulates
416 isolated a unique factor whose chemical profile was similar to that of particles from chat
417 piles. With a composition similar to that of chat, the PMF-deduced mine waste factor was
418 dominated by Pb and Zn and included traces of crustal elements (e.g. Al, Si, and Ca). The
419 percent mass contribution of Zn and Pb, and the Zn/Pb ratio, were also in good agreement
420 with measurements made on “parent” chat.⁷ Additionally, scanning electron microscopy
421 analysis of a filter with a high PMF-estimated mine waste concentration qualitatively
422 confirmed that the PMF-identified mine waste source corresponded to particles of mine
423 waste origin.

424 Source apportionment analysis revealed that the mine waste source predominantly
425 impacted particles in the coarse fraction. Pb and Zn concentrations as well as estimated
426 mine waste concentrations were all higher in coarse particles in comparison to PM_{2.5}.
427 Mine waste source contributions were most substantial in Picher, where mine waste was
428 the largest source of coarse mass, contributing an average of 4.5 µg/m³ (approximately
429 40% of total mass). Coarse fraction impacts were also observed at sites further away from
430 the chat piles particularly in Quapaw where average contributions exceeded 10%.
431 Particles of crustal origin and a source rich in Ca were major contributors of coarse mass
432 in Miami and Quapaw.

433 While a mine waste source was identified in the PMF solution for PM_{2.5}, its
434 contributions to PM_{2.5} mass were modest even in the source-dominated site of Picher. Our
435 results are consistent with a previous study in South Africa which found small and
436 geographically limited impacts of mine tailings on atmospheric lead.³⁴ Pb concentrations
437 in our PM_{2.5} samples were generally low and below the National Ambient Air Quality
438 Standard (0.15 µg/m³). Zinc concentrations were higher than those typically found in
439 rural areas and similar to urban areas³⁵ where respiratory effects, such as asthma, have
440 been associated with Zn PM_{2.5} levels.³⁶ Concentrations of Cd, also elevated in mine
441 waste, were all below the limit of detection in our samples. In contrast, a recent study
442 found increasing metals concentrations with decreasing particle size down to 1µm in

443 “parent” chat from the Tar Creek site.⁷ Our results suggest that while fine chat particles
444 (<2.5 μm) may be highly enriched in metals, they are low in abundance or less likely to
445 be windborne due to the presence of larger particles on the surface of the chat piles.

446 Similar to other source apportionment studies, secondary sulfates from coal
447 combustion and mobile sources were the largest contributors to $\text{PM}_{2.5}$ mass.³³ Model
448 diagnostics suggest that the factors resolved in the $\text{PM}_{2.5}$ data were less stable and more
449 uncertain than those characterized in the coarse data. $\text{PM}_{2.5}$ source apportionment results
450 may have overestimated contributions for mobile source combustion and omitted other
451 minor sources such as vegetative burning. The analysis of additional carbon fractions and
452 metals ions could have assisted in the further identification of sources and improved the
453 model fit.

454 While we were able to isolate mine waste impacts using EPA PMF source
455 apportionment, it was difficult to determine the relative importance of various sources
456 and transport mechanisms due to the dispersed, heterogeneous nature of contemporary
457 mine waste. Wind erosion of dust particles from chat piles, mechanically generated chat-
458 laden dust from paved and unpaved roads, and the ongoing removal and processing of
459 chat for construction projects may all contribute to the mine waste particles observed in
460 our air samples. For example, CCSEM/EDX analyses documented two different types of
461 particles which appeared to be of mine waste origin.

462 Additionally, linear regression results which included a statistically significant
463 interaction term between sampling site and Ca-rich concentrations in the coarse fraction
464 may suggest differential transport mechanisms by location. Mine waste estimates
465 increased linearly with Ca-rich source estimates in both Quapaw and Miami, but not in
466 Picher. One possible interpretation of this interaction is that fugitive dust from the chat
467 piles may be the predominant source of airborne mine waste in Picher. Conversely, re-
468 suspension of chat, previously deposited on paved and unpaved roads, may be a more
469 important transport mechanism at the Quapaw and Miami sites, which are farther away
470 from the chat piles. Another possible explanation for this observed interaction is that the
471 Ca-rich source concentrations are a surrogate for some other unmeasured environmental
472 factor or anthropogenic activity which varies between Picher and the other sites and is
473 positively associated with mine waste concentrations. Future studies should compare the

474 geochemical properties and particle size distribution profiles of wind blown mine waste
475 versus mechanically resuspended mine waste at relevant mining sites.

476 This study has several important strengths. The unique study design and
477 collaboration allowed us to evaluate chronic airborne exposures to mining-related metals
478 in an underserved community. While abandoned hardrock mines and associated solid
479 mine waste are increasing in a global context, limited data is available on the ambient air
480 quality at these sites. We also used a variety of methods, including receptor modeling and
481 scanning electron microscopy, to examine mine waste impacts on ambient particulate
482 matter. Another major strength of the study is the unique collaboration which included
483 university, community, and government partners. Most notably, field sampling was
484 successfully conducted by our community partners from the L.E.A.D. Agency using strict
485 QA/QC guidelines for over a year. This approach should be a model for other
486 community-based assessments of air quality.

487 There were also some weaknesses to this study. While we observed seasonal
488 variations in mine waste concentrations using regression analysis, weekly-integrated
489 samples obscured our ability to assess acute exposures, reconstruct backward trajectories,
490 and analyze relationships with wind speed. However, the longer sampling time allowed
491 for increased particle mass deposition and thus improved elemental detection limits. We
492 calculated coarse fraction concentrations indirectly by subtracting PM_{10} and $PM_{2.5}$
493 measurements, which may increase measurement error. However, the measurement error
494 in this approach did not overwhelm the data given the strong model diagnostics for the
495 PMF coarse fraction results - including excellent replication of the base factors in the
496 bootstrapping simulations. Lastly, we were only able to use scanning electron microscopy
497 methods in a qualitative manner. Future air pollution studies should expand the
498 quantitative use of geochemical techniques in source apportionment studies and compare
499 source apportionment estimates for mine waste in respirable particles to those from
500 fugitive dust models.

501 **CONCLUSIONS**

502 This study estimated the contribution of mine waste, an important local pollution source,
503 to airborne respirable particles using source apportionment techniques. Mass contribution
504 of mine waste particulates was more apparent in the coarse fraction, with average

505 contributions three-fold greater in the coarse particles compared to the fine fraction (20%
506 vs. 6%). There were also large differences observed in mine waste contribution by
507 location. Impacts were largest at the source-dominated site and decreased with increasing
508 distance from the chat piles, suggesting that populations living nearest to the chat piles
509 may be more highly exposed. In conclusion, this study characterized temporal and spatial
510 variability of metal concentrations and potential sources in two size fractions of
511 respirable, ambient particles. Future studies from our center will examine the impact of
512 mining-related sources in the indoor environment and relationships to biological
513 measures in children.

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528 **DISCLAIMER**

529 The United States Environmental Protection Agency through its Office of Research and
530 Development collaborated in the research described here. It has been subjected to Agency
531 review and approved for publication.

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Table 1. Mean (SD) mass ($\mu\text{g}/\text{m}^3$) and metal (ng/m^3) concentrations in coarse and fine particles by location.

	% <LOD ^a	Picher	Quapaw	Miami	ANOVA p-value ^b
Coarse Fraction (PM₁₀ – PM_{2.5})					
Sample Size		41	41	41	
Mass	0	12 (4.4)	13 (6.1)	9.0 (2.9)	<0.0001
Al	1	350 (140)	360 (130)	300 (130)	0.12
Si	0	1700 (610)	1600 (710)	1200 (380)	<0.0001
S	59	20 (120)	<LOD	<LOD	0.04
K	0	110 (52)	110 (44)	96 (33)	0.12
Ca	0	1200 (560)	1300 (750)	970 (400)	0.02
Ti	0	30 (14)	33 (19)	22 (8.9)	0.0003
Mn	0	7.8 (3.3)	7.7 (3.5)	6.3 (2.1)	0.02
Fe	0	290 (120)	340 (180)	220 (78)	0.0003
Cu	36	0.95 (0.56)	0.83 (0.54)	0.71 (0.55)	0.13
Zn	0	120 (69)	39 (31)	11 (5.6)	<0.0001
As	74	<LOD	<LOD	<LOD	--
Se	85	<LOD	<LOD	<LOD	0.55
Br	41	0.55 (0.60)	0.48 (0.41)	<LOD	0.03
Pb	20	7.9 (4.6)	3.0 (2.4)	1.1 (0.75)	<0.0001
Fine Fraction (PM_{2.5})					
Sample Size		41	41	41	
Mass	0	11 (4.0)	11 (3.9)	11 (3.8)	0.98
Al	49	62 (75)	67 (77)	57 (84)	0.83
Si	0	220 (150)	230 (160)	190 (170)	0.44
S	0	870 (480)	860 (490)	890 (480)	0.96
K	0	57 (21)	57 (19)	61 (20)	0.52
Ca	0	97 (44)	91 (45)	77 (33)	0.09
Ti	6	4.2 (3.7)	4.5 (3.5)	4.5 (4.1)	0.95
Mn	1	1.4 (0.64)	1.8 (0.84)	1.5 (0.71)	0.04
Fe	0	58 (38)	70 (41)	54 (43)	0.20
Cu	37	1.1 (1.2)	0.90 (0.52)	0.80 (0.61)	0.20
Zn	0	22 (10)	11 (5.0)	7.9 (3.0)	<0.0001
As	41	0.64 (0.48)	0.62 (0.32)	0.56 (0.33)	0.58
Se	23	0.58 (0.31)	0.57 (0.27)	0.58 (0.30)	0.99
Br	0	2.6 (1.1)	2.5 (0.84)	2.4 (0.88)	0.73
Pb	10	3.5 (2.6)	2.2 (1.4)	1.9 (1.4)	0.0003

^a LOD = Limit of detection.

^b Bolded values indicate significant ($p < 0.05$) differences among sites.

Table 2. Mean (SE) source contributions ($\mu\text{g}/\text{m}^3$) of coarse and fine particulate from PMF.

	Coarse (n=150)	Fine (n=155)
Mine waste	2.2 (0.20)	0.31 (0.025)
Crustal	4.6 (0.25)	1.2 (0.15)
Ca-rich	4.1 (0.24)	1.7 (0.098)
Secondary	--	2.9 (0.22)
Mobile sources	--	4.4 (0.20)

Table 3. Multivariate regression models of fine and coarse mine waste attributable mass ($\mu\text{g}/\text{m}^3$).^a

	Mass attributed to mine waste source			
	Fine Fraction ^b		Coarse Fraction ^b	
	β (SE)	<i>P</i> value	β (SE)	<i>P</i> value
Coarse mine waste mass ($\mu\text{g}/\text{m}^3$) ^b	0.42 (0.07)	<0.0001	---	---
Coarse Ca-rich mass ($\mu\text{g}/\text{m}^3$) ^b	---	---	1.01 (0.14)	<0.0001
Site		<0.0001		<0.0001
Miami ^c	0		0	
Quapaw	0.07 (0.17)		1.30 (0.24)	
Picher	0.83 (0.22)		3.33 (0.22)	
Season		<0.0001		0.0034
Winter ^c	0		0	
Spring	0.56 (0.18)		0.34 (0.16)	
Summer	0.13 (0.17)		0.77 (0.15)	
Fall	0.83 (0.17)		0.17 (0.15)	
Wind direction		0.006		---
West ^c	0		---	---
South	0.70 (0.21)		---	---
East	0.90 (0.42)		---	---
Coarse Ca-rich mass * Site interaction	---	---		<0.0001
Coarse Ca-rich * Miami	---	---	0	
Coarse Ca-rich * Quapaw	---	---	-0.14 (0.16)	
Coarse Ca-rich * Picher	---	---	-0.75 (0.16)	
Model R ²	0.64		0.79	

^a*P<0.05; ^b log-transformed; ^c reference group in parentheses.

FIGURE LEGENDS

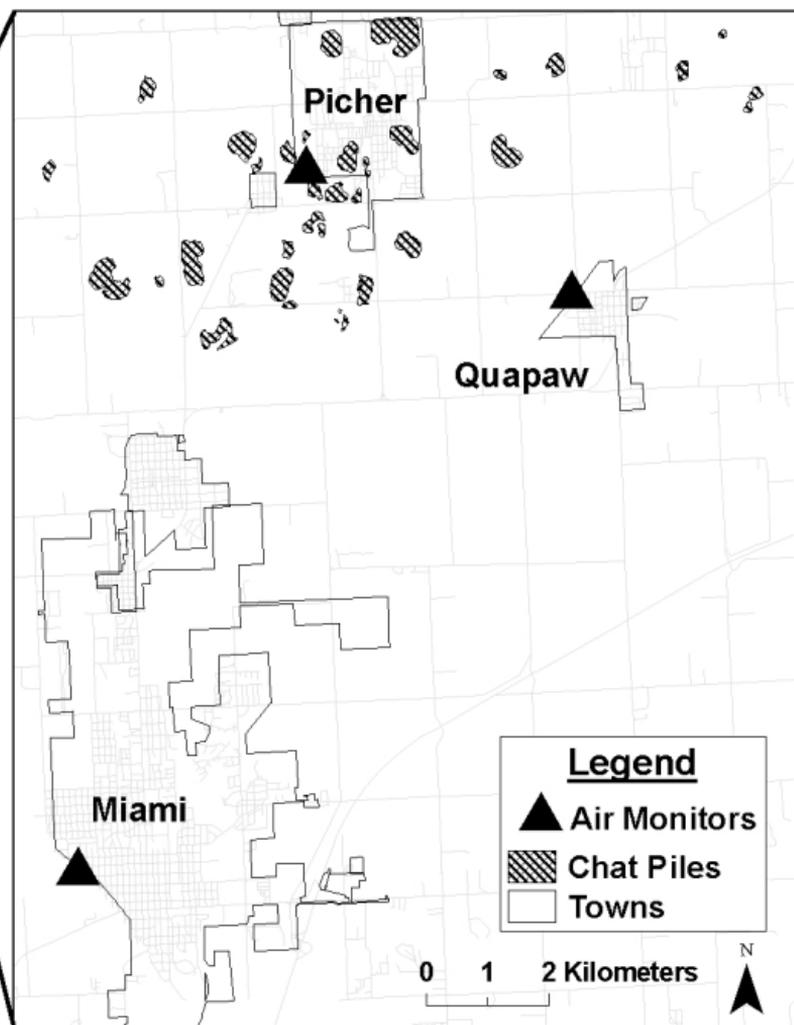
Figure 1. Location of mine waste (“chat”) piles and ambient air monitors in Ottawa County, Oklahoma.

Figure 2. Source profiles for fine and coarse fraction derived from EPA PMF 3.0

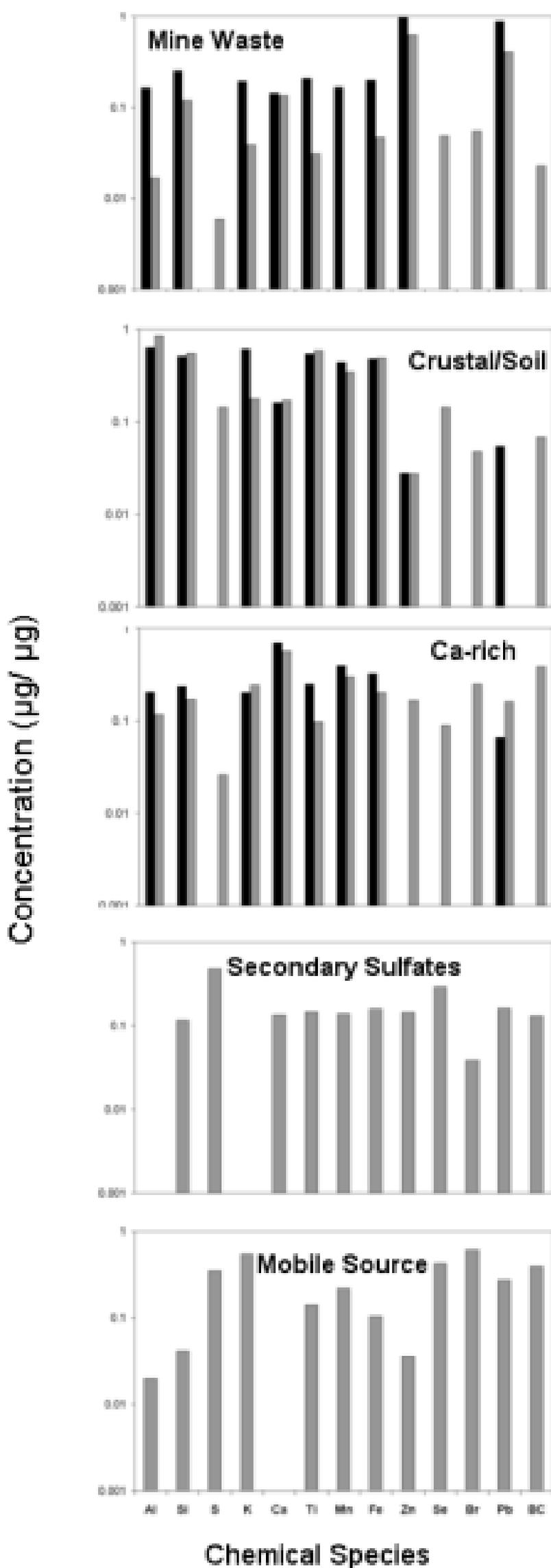
Figure 3. Mass contribution (%) of sources to (a) fine and (b) coarse mass by location.

Figure 4. Scatterplots of PMF estimated coarse mine waste concentrations versus PMF estimated coarse Ca-rich concentrations by site location. Regression lines represent the slopes of the association for the three sites and are statistically significant for Quapaw ($p < 0.0001$) and Miami ($p < 0.0001$) but not Picher ($p = 0.12$).

Figure 5. Results of CCSEM analysis from a PM_{10} particle filter identified as having a high factor score for the mine waste source in PMF models: (a) secondary electron image, (b) backscatter electron image, (c) EDX spectrum of ZnS inclusion in top of particle, and (d) EDX spectrum of aluminosilicate matrix at bottom of particle.

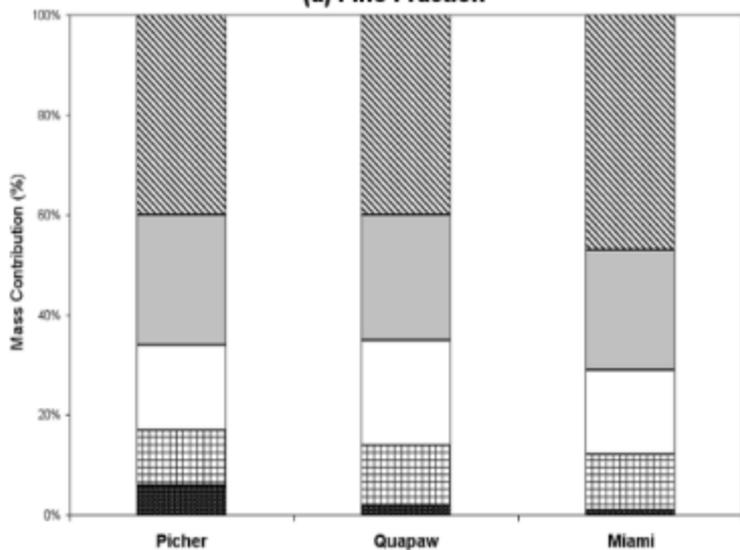


■ Coarse (PM10-PM2.5) ■ Fine (PM2.5)



Mine waste
 Crustal
 Ca-rich
 Secondary
 Mobile

(a) Fine Fraction



(b) Coarse Fraction

