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Characterization of Zinc, Lead, and Cadmium in Mine Waste: Implications for Transport, Exposure, and Bioavailability

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We characterized the lability and bioaccessibility of Zn, Pb, and Cd in size-fractionated mine waste at the Tar Creek Superfund Site (Oklahoma) to assess the potential for metal transport, exposure, and subsequent bioavailability. Bulk mine waste samples contained elevated Zn (9100 $\pm$ 2500 ppm), Pb (650 $\pm$ 360 ppm), and Cd (42 $\pm$ 10 ppm), while particles with the greatest potential for wind-borne transport and inhalation (<10 μm) contained substantially higher concentrations, up to 220 000 ppm Zn, 16 000 ppm Pb, and 530 ppm Cd in particles <1 μm. Although the mined ore at Tar Creek primarily consisted of refractory metal sulfides with low bioavailability, sequential extractions and physiologically based extractions indicate that physical and chemical weathering have shifted metals into relatively labile and bioaccessible mineral phases. In <37 μm mine waste particles, 50–65% of Zn, Pb, and Cd were present in the "exchangeable" and "carbonate" sequential extraction fractions, and 60–80% of Zn, Pb, and Cd were mobilized in synthetic gastric fluid, while ZnS and PbS exhibited minimal solubility in these solutions. Our results demonstrate the importance of site-specific characterization of size-fractionated contemporary mine waste when assessing the lability and bioavailability of metals at mine-waste impacted sites.

Introduction

Active and abandoned metal mining sites are major sources of metal contamination throughout the world. In metal mining, less than 1% of processed material is recovered as useful metal (1). Discarded metal-enriched solids are often stored in large piles that act as persistent toxic metal sources to surrounding ecosystems and residential areas through wind-borne dispersal of fine particles and waterborne transport of dissolved and particulate metals. The geochemical characteristics of this waste material, specifically size-dependent metal concentrations and solid-phase speciation, will determine the potential for metals to migrate offsite and subsequent exposure and bioavailability to humans and terrestrial and aquatic biota.

Areas surrounding mining sites are often contaminated with multiple metals, such as Pb, Zn, Cd, Cu, and Ni, that can co-occur in mineral deposits, and their bioavailability can vary considerably from site to site. While in vivo laboratory animal experiments (2, 3) and some human exposure studies (4, 5) indicate that parent minerals, such as galena (PbS) and other metal sulfides, may have limited bioavailability, over time these primary minerals in mine wastes can undergo geochemical transformations that convert metals from relatively refractory phases into phases with greater lability and bioavailability. Exposure to oxygen and moisture promotes oxidation of sulfide minerals such as galena, sphalerite (ZnS), and chalcopyrite ($CuFeS_2$) and leads to mineral dissolution and metal mobilization. A portion of solubilized metals can migrate offsite in runoff from the piles (6), while the remaining mobilized metals can reprecipitate within piles as secondary minerals such as anglesite ($PbSO_4$), cerrusite ($PbCO_3$), and plumbojarosite ($PbFe_6(SO_4)_4(OH)_{12}$), forming rinds on particle surfaces, or they can sorb to the surfaces of Fe- or Mn-hydroxides (7, 8).

The geochemical processes controlling metal lability and bioavailability in solid mine wastes are important considerations at the Tar Creek Superfund Site, formerly a zinc and lead mining area. The presence of large mine waste (chat) piles and visible contamination by acid mine seepage have led to concerns about potential impacts on humans and surrounding ecosystems. Reports of elevated blood Pb levels in children (9) and documented Zn and Pb poisoning in terrestrial fauna (10) have fueled efforts to identify and minimize routes of exposure. Despite extensive investigations at this site, questions remain about ongoing risks posed by toxic metals in chat piles, especially the extent of offsite metal migration through wind-borne and waterborne transport and related exposure and bioavailability.

Figure 1 presents a conceptual model of metal transformations and migration pathways from mine waste piles to biological receptors. Biogeochemical weathering processes within mine waste piles can solubilize metals and shift metals from parent mineral phases to secondary mineral phases. The extent of weathering varies from site to site and also changes depending on the age of the mine waste. Rates of mineral transformations and metal dissolution are dependent on particle size, since smaller particles have greater reactive surface area per unit mass. Transport of metal-rich particles away from piles and subsequent exposure are also dependent on particle size. Particles smaller than approximately 30 μm can be transported hundreds of meters by wind before settling, while smaller particles (<2.5 μm) can be distributed regionally. Smaller particles are also more important for inhalation exposure (<10 μm) and for rates of ingestion via hand–mouth contact with contaminated soils (11) and metal absorption from ingested particles (12). Therefore, size-dependent variability in metal concentration and lability has important implications for assessing human and ecological exposure and risk.

The goal of this study was to characterize the lability, bioaccessibility, and particle-size dependence of Zn, Pb, and Cd in weathered mine waste at the Tar Creek site and to explore the relationship between geochemical speciation and potential bioavailability to human and ecological receptors. We hypothesized that metals in contemporary weathered chat would have substantially greater lability and bioaccessibility than metals present in primary sulfide minerals that were the targets of mining operations. To explore this

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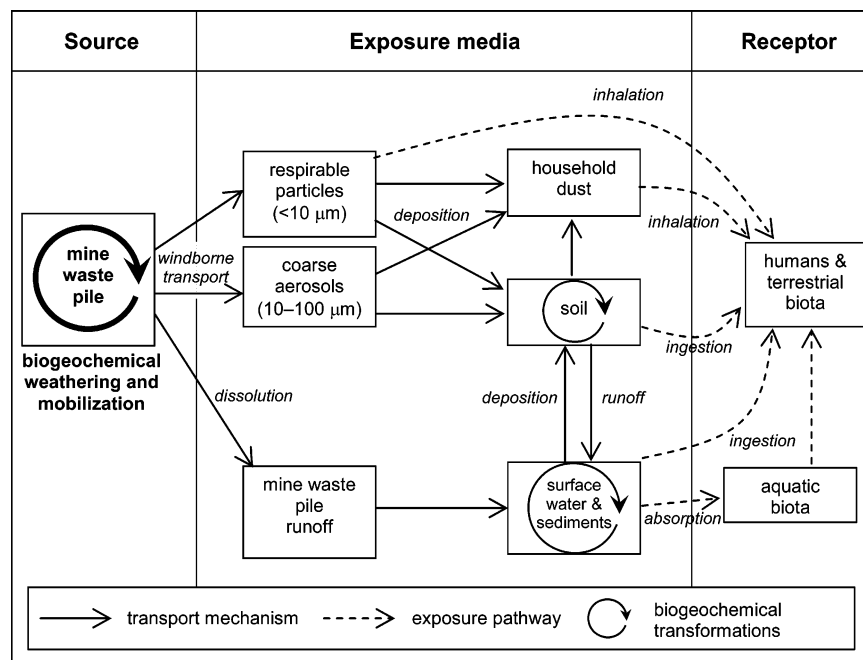
FIGURE 1. Conceptual model showing the biogeochemical cycling, fate, and transport of metals in mine waste piles and pathways of exposure. In situ biogeochemical transformations within piles can convert relatively refractory parent mineral phases into secondary mineral phases that are more labile and bioavailable. Metal transport from piles can occur via wind-borne mobilization of particles or aqueous leaching of metals into water that infiltrates the piles. In addition to human receptors, terrestrial and aquatic biota also are at risk from direct contact with waste material, inhalation of suspended particles, ingestion of contaminated soils and plants, and direct absorption of metals from contaminated surface water.
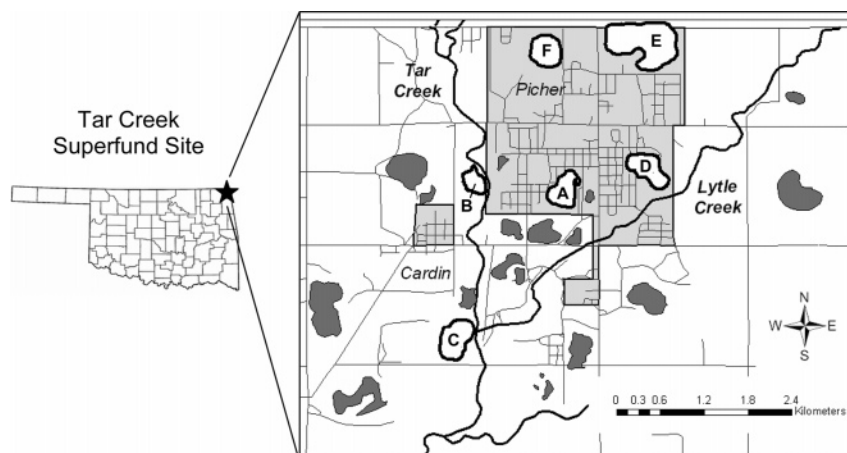
FIGURE 2. Section of Tar Creek Superfund Site in and around the town of Picher, OK. Six chat (mine waste) piles (A−F) that were sampled in January and May 2005 have dark outlines; other chat piles are shaded dark gray. Light gray areas show the towns of Picher and Cardin. Outlines of chat piles were drawn based on aerial photographs.

hypothesis, we subjected mine waste to geochemically based sequential extractions and physiologically based extractions (simulated gastric and lung fluids), and evaluated the results in both geochemical and human exposure contexts. We also investigated differences in metal concentrations and lability as functions of particle size to assess the potential for off-site migration of metal-laden particles in size fractions that are relevant to human exposure. Our results demonstrate the importance of using site-specific geochemical analyses on size-fractionated, contemporary mine waste when assessing metal exposure and risk in mining-impacted communities.

Materials and Methods

Site Description. Tar Creek Superfund Site (Oklahoma) is located in a former Pb and Zn mining area where the major mined ores were sphalerite (ZnS) and galena (PbS) (*13*). Cd is also present in sphalerite (0.3−1.4%) from this region. While mining activities ceased in the 1970s, the area remains highly impacted by metal-contaminated surface water, groundwater, sediments, and soils. There are approximately 30 major chat piles (*14*) that contain elevated concentrations of Zn, Pb, and Cd (*15*), leading to concerns about potential adverse health impacts on nearby residents and downstream ecosystems.

Sample Collection. In January and May 2005, chat samples were collected from six major piles (A−F, Figure 2) located close to residential areas and Tar Creek. Surface samples were collected because surface material is most relevant for wind-borne transport, human exposure, and direct contact with precipitation and surface runoff. Around each pile, 3−4 sampling locations were selected to assess intrapile variability in metal concentrations and grain size distributions. For each sample, gravel-sized particles in the surface layer (1−2 cm) were brushed away from a 100 cm² area and 500−1000 g of

TABLE 1. Extraction Conditions for Sequential Extractions and Physiologically Based Extractions of Mine Waste Samples[a]

extractant	target	extraction conditions	% of Pb or Zn extracted			
			ZnS	hemi–morphite	PbS	$PbCO_3$
sequential extractions						
I MgCl2	ionically–bound (ion-exchangeable) displaced by cation exchange	1 M $MgCl_2$, pH 7, 1 h, 20 °C	0	0.04	0	3.3
II HAc	carbonate–bound and other phases mobilized by slightly acidic conditions	1 M NaAcetate, pH 5, 5 h, 20 °C	0	67	0.8	82
III HCl	amorphous sulfides or amorphous Fe (hydr)oxides and Mn oxides and sorbed or coprecipitated metals	1 M HCl, 12 h, 20 °C	1.9	11	22	4.5
IV HNO3	coprecipitated with pyrite or other crystalline sulfides	concentrated HNO_3, 2 h, 20 °C	63	0.01	34	0.03
V RES	residual, including silicates and other minerals not extracted by any of the previous solutions	XRF total − Σ extracted	35	22	44	10
SBET	metals bioaccessible in gastric fluid	pH 1.5 (0.32 M HCl), 0.4 M glycine, 1 h, 37 °C	0	65	3	97
PSF	metals bioaccessible in lysosomes of alveolar macrophages	pH 4.5, salts, organic acids,[b] 5 d, 37 °C	1.7	2.8	0.4	14

[a] The sequential extraction protocol was adapted from previously described methods (27–30). Total metal concentrations were measured by XRF in separate aliquots of each sample. The simple bioaccessibility extraction test (SBET) is a simulated gastric fluid extraction (16). Phagolysosomal simulant fluid (PSF) simulates the conditions of the lysosomes of alveolar macrophages in lungs (18). The amount of Pb or Zn extracted from four pure-phase mineralogical samples added to a <37 μm mine waste sample was expressed as a percentage of total amount of spiked metal. Details of all procedures are provided in the Supporting Information. [b] Complete recipe in the Supporting Information

underlying chat was scooped from the subsequent 2–4 cm into plastic bags. Chat samples were unsaturated (<1% water content) and were assumed to have been exposed to oxygen for years to decades; therefore, no effort was made to maintain anoxic conditions during subsequent sample storage and processing.

Size Fractionation. Chat samples were air-dried at room temperature and sieved into eight size fractions ranging from <37 μm to >4 mm. The <37 μm size fraction closely corresponds to the <30 μm size fraction, the size below which particles are generally considered sufficiently small to be transported substantial distances by wind. One <37 μm sample was further separated into four smaller size fractions by aerosolizing the sample using an aspirator and then size-fractionating with a high volume cascade impactor (16) into four size ranges (0.16–1 μm, 1–2.5 μm, 2.5–10 μm, and 10–37 μm) collected onto a polyurethane foam (PUF) substrate. Total acid-soluble metals were extracted by digesting each substrate in concentrated HNO_3 at room temperature for 24 h.

Sequential Extractions. Sequential extractions employ a series of increasingly stringent solutions designed to target metals present in operationally defined solid phases. Geochemically based sequential extractions were performed on one size-fractionated chat sample from each pile using the extraction protocol described in Table 1. Particle-size dependent differences in metal speciation were assessed by analyzing two size ranges from each sample: particles most easily transported by wind (<37 μm) and a larger size range containing much of the overall mass of bulk chat (0.5–2 mm). The <37 μm samples were analyzed directly, while larger 0.5–2 mm samples were ground prior to extraction to assess the speciation throughout the entire sample rather than simply on the surface.

Although limitations to sequential extractions have been noted, including lack of specificity and potential sorption or reprecipitation of solubilized metals onto the solid sample surface (7, 17), sequential extractions provide valuable information about the geochemical phases in which metals are present and the chemical conditions that can mobilize metals from particles. To verify the ability of sequential extractions to distinguish between relevant mineral phases, additional sequential extractions were performed on <37 μm chat samples spiked with small masses of ground $PbCO_3$,

PbS, ZnS, and hemimorphite ($Zn_4Si_2O_7(OH)_2$·H_2O) mineralogical samples obtained from the Wellesley College mineral library (Table 1).

Physiologically Based Extraction Tests. Physiologically based extractions were performed on aliquots of the same <37 μm chat samples to simulate metal dissolution following ingestion and inhalation (Table 1). Simulated gastric fluid extractions followed the simple bioaccessibility extraction test (SBET) protocol (18), a pH 1.5 extraction designed to mimic gastric conditions. While the majority of in vivo metal absorption after ingestion occurs across the epithelium of the small intestine, where the pH is circumneutral, the rate-limiting step in particulate metal absorption is thought to be dissolution in acidic gastric fluids (19).

Phagolysosomal simulant fluid (PSF) (20) was used to simulate metal dissolution within the lysosomes of alveolar macrophages. Although synthetic lung lining fluid (pH 7–7.4) has been used to estimate bioaccessibility of particulate metals following inhalation (e.g., ref 21), the majority of metal dissolution from respirable particles small enough to penetrate into the alveolar regions of the lungs (<3.5 μm) is thought to occur in the lysosomes of alveolar macrophages, which have lower pH (4.5–5) and substantially longer residence times (months to years) (22).

Analytical Techniques. Total metal concentrations in each size-fractionated chat sample were determined using a Spectro XEPOS (Spectro Analytical, Kleve, Germany) polarized energy-dispersive X-ray fluorescence (pED-XRF) instrument. Total metal concentrations in extraction solutions and PUF digestions of fine particles were measured by ICP–MS (Perkin-Elmer ELAN 6100 DRC, Shelton, CT). Major Zn– and Pb-bearing mineral phases in several <37 μm samples were evaluated by X-ray diffraction (XRD) (Rigaku, Tokyo, Japan). Analytical techniques are further described in the Supporting Information.

Statistical Analyses. For the results of sequential extractions, the statistical significance of differences between metals and size fractions was tested using the Mann–Whitney U-test. Mean values are reported ±1 s.d.

Results and Discussion

Size-Fractionated Total Metal Concentrations. Total Zn, Pb, and Cd concentrations in chat samples from six major
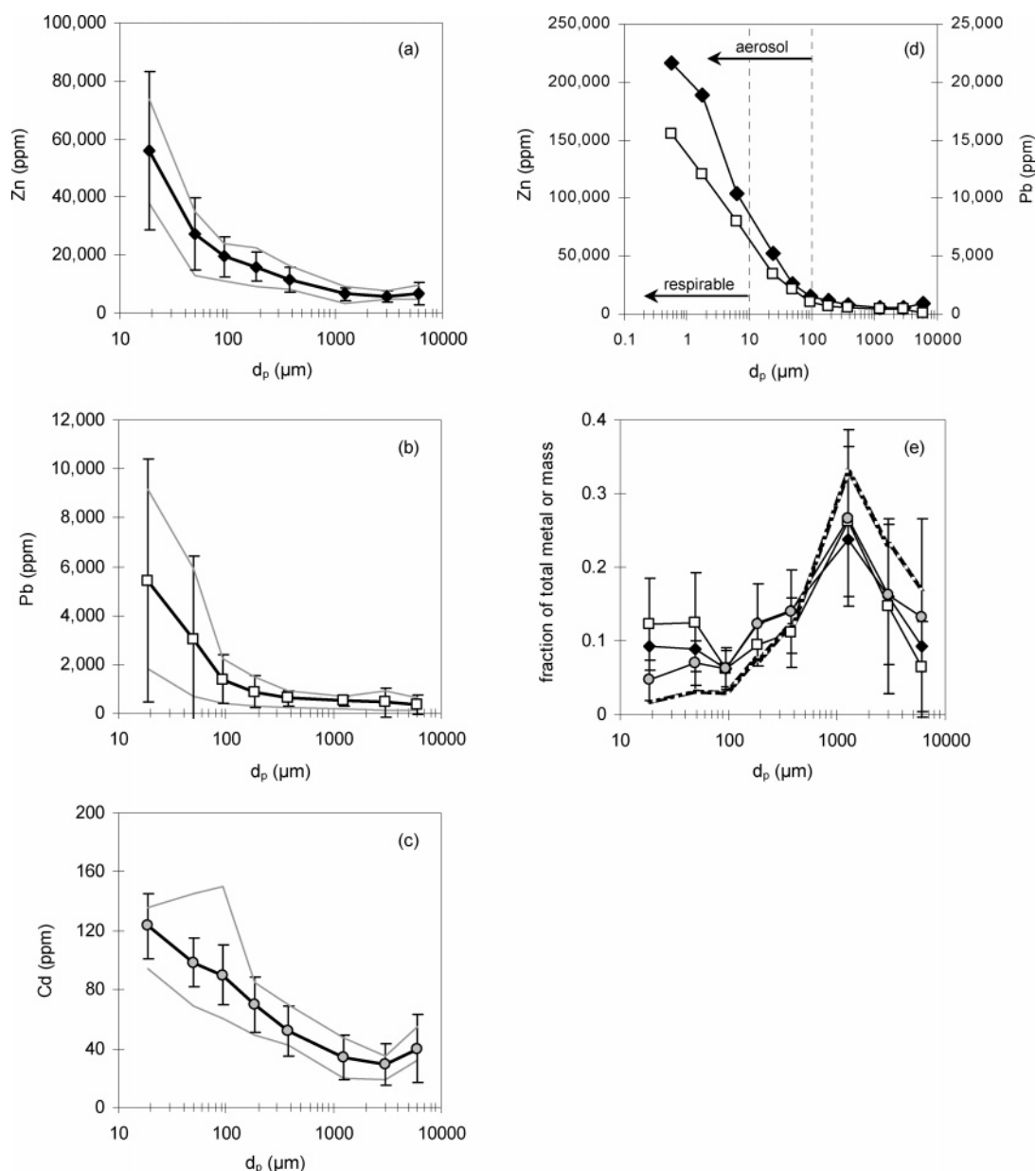
FIGURE 3. (a−c) Total Zn (◆), Pb (□), and Cd (●) concentrations in size-fractionated chat samples across six piles as a function of particle diameter (d_p). Gray lines represent the minimum and maximum values (based on pile averages). (d) Total Zn and Pb in a single size-fractionated chat sample, including four size fractions collected using a high volume cascade impactor. (e) Fraction of total metal mass as a function of particle size in chat samples. The average fraction of the sample mass present in each size fraction is depicted with the thick gray line (error bars omitted for clarity). In all graphs, particle diameters represent the midpoint of each size range, and error bars represent ±1 s.d. Note differences in *y*-axis scales.

piles were highly elevated and increased with decreasing particle size (Figure 3a−c). In bulk chat samples, average metal concentrations across all six piles were 9100 ± 2500 (4000−13 000) ppm Zn, 650 ± 360 (140−1800) ppm Pb, and 42 ± 10 (23−75) ppm Cd. These concentrations are 1 to 2 orders of magnitude above average soil and crustal abundances (60−75 ppm Zn, 14−19 ppm Pb, and 0.11−0.35 ppm Cd; ref *23*). Average metal concentrations in <37 μm particles, those with the greatest potential for long-distance wind-borne transport, were 3−9 times higher than bulk concentrations, with concentrations of 56 000 ± 28 000 ppm Zn, 5500 ± 2600 ppm Pb, and 130 ± 22 ppm Cd. In respirable particles (i.e., <10 μm), metal concentrations were even higher. Zn and Pb concentrations continued to increase with decreasing particle size (Figure 3d), up to 220 000 ppm Zn and 16 000 ppm Pb in the 0.16−1 μm size range. Cd followed a similar trend, reaching a concentration of 530 ppm in the

smallest size fraction (data not shown). Thus, the smallest respirable chat particles contained 15−22 times higher concentrations of Zn, Pb, and Cd than bulk chat samples. These size-dependent differences in metal concentrations demonstrate that using bulk mine waste characteristics, as opposed to the concentrations in exposure-relevant particle sizes, could lead to substantial underestimates of metal exposure, in some cases by more than an order of magnitude.

Although <37 μm particles constitute a small percentage of the overall sample mass, they represent a disproportionately large pool of total metals within chat piles because of their elevated metal concentrations. Across all six piles, the majority of chat mass (60−80%) was present as sand-sized (62 μm−2 mm) particles (Figure 3e). Particles <37 μm accounted for only 1.7 ± 0.8% of the total sample mass across all piles; however, these particles contained 12.3 ± 6.2%, 9.6 ± 5.5%, and 4.6 ± 2.6% of the total mass of Pb, Zn, and Cd,

respectively. Thus, substantial masses of Zn, Pb, and Cd are present at high concentrations in particles that can be readily mobilized during ongoing removal and processing of chat (e.g., to remove larger particles for use in concrete aggregate) and transported off-site by wind.

Geochemically Based Extractions. Results of sequential extractions on chat samples spiked with pure-phase mineralogical samples demonstrate the ability of the extractions to distinguish between labile forms, such as metal carbonates, and metal sulfides (Table 1). The vast majority of Pb added as $PbCO_3$ was extracted in the HAc (carbonate) fraction, while Pb added as PbS was distributed among the HCl (amorphous sulfides/oxides), HNO3 (crystalline sulfide) and RES (residual) fractions, and Zn added as ZnS was present in the HNO3 and RES fractions.

Sequential extraction results demonstrate that the majority of Zn, Pb, and Cd in chat samples are present in relatively labile mineral phases across all six piles (Figure 4a−c). If these metals had been present as metal sulfides, they would have been extracted primarily in the HCl, HNO3, and RES fractions. Instead, the majority of Zn (66 ± 9%) in <37 μm samples was present in the carbonate pool (Zn_{HAc}). Some of the apparent Zn lability may be attributable to the presence of hemimorphite, which can be both a primary mineral and a secondary mineral that forms in oxic, Zn-rich conditions. XRD analyses (discussed below) confirm the presence of hemimorphite but suggest that hemimorphite does not account for the majority of Zn in these samples. Less than 1% of Zn was extracted in the exchangeable pool (Zn_{MgCl2}), and the remainder occurred primarily in the residual fraction (Zn_{RES}, 25 ± 6%). Approximately half of Pb in <37 μm samples was present as Pb_{HAc} (49 ± 14%), implying that a substantial fraction of Pb was present as $PbCO_3$ or in other comparably labile secondary mineral phases. The remainder of Pb was primarily present as Pb_{HCl} (41 ± 17%), which can include both amorphous sulfides and Pb sorbed to or coprecipitated with amorphous hydrous ferric oxides (HFO), although XRD analyses (discussed below) indicate that PbS is a minor component of Pb speciation. Pb_{MgCl2} and Pb_{HNO3} contributed little to overall Pb speciation, and only 7 ± 5% of Pb was present as Pb_{RES}. By contrast, substantial portions of Cd in the <37 μm samples occurred in each of the fractions: 21 ± 3% Cd_{MgCl2}, 30 ± 4% Cd_{HAc}, 22 ± 8% Cd_{HCl}, 8 ± 8% Cd_{HNO3}, and 20 ± 7% Cd_{RES}.

XRD analyses of <37 μm chat samples are consistent with sequential extraction results and suggest that most Zn and Pb in <37 μm contemporary chat samples at Tar Creek occur as amorphous secondary mineral phases (Table S1). Trace amounts (<5% of total sample mass) of two Zn minerals, sphalerite (ZnS) and hemimorphite, were detected in two samples analyzed by XRD. However, based on stoichiometry, these two phases together account for only 20−35% of the total Zn present; the majority of Zn (65−80%) could not be accounted for in either of these mineral phases, suggesting that <37 μm particles primarily contain Zn in amorphous mineral phases or sorbed to particle surfaces. Pb mineral concentrations were generally too low to allow for accurate quantification of specific Pb-bearing phases, although one of the samples contained detectable PbS and cerussite ($PbCO_3$), which is likely a weathering product.

Comparing sequential extraction results for <37 μm with those of 0.5−2 mm samples, which are more representative of the bulk chat material on a mass basis, suggests that a greater proportion of metals are present in labile forms in smaller chat particles (Figure S1). The proportion of Zn and Cd present in the two most labile fractions (MgCl2 and HAc) was greater for the <37 μm particles (Zn: 66 ± 9%, Cd: 51 ± 7%) compared to the 0.5−2 mm particles (Zn: 40 ± 17%, Cd: 32 ± 22%; Zn: P < 0.05; Cd: P < 0.1). Smaller proportions of labile Zn and Cd in 0.5−2 mm particles were accompanied

by greater proportions of Zn_{HNO3} and Cd_{HNO3} (32 ± 25% and 31 ± 14%, respectively; P < 0.05). There were no size-dependent differences in the percentages of Pb present in the first two fractions; however, the percentage of Pb present as Pb_{RES} was on average 4 times higher for 0.5−2 mm particles (P < 0.1). The greater proportions of Zn, Cd, and Pb present in the HNO3 and RES fractions in 0.5−2 mm particles may indicate a greater abundance of sulfides, which could be attributable to the fact that the 0.5−2 mm particles were ground prior to analysis, which exposed unweathered sulfide mineral phases that had been in the interior of particles.

Our results indicate that throughout Tar Creek, weathering and reworking of chat have significantly altered metal speciation, converting Zn, Cd, and Pb into more labile and potentially more bioavailable solid phases than the parent sulfide minerals. The high proportion of relatively labile metals in Tar Creek chat is consistent with studies in other mine waste systems in parts of Colorado in which precipitation of secondary minerals such as metal carbonates or sulfates and sorption to Fe− and Mn− (hydr)oxides dominated Pb speciation (7, 8). However, in mine waste from metal-sulfide deposits in other areas of Colorado and Missouri, only 8−10% of Pb and 12−20% of Zn were present in the water-soluble, ion-exchangeable and carbonate fractions combined (24, 25). Thus, metal speciation and lability in mine waste can vary considerably between sites, and risk assessments of metal exposure should utilize site-specific metal speciation data.

Physiologically Based Extraction Tests. In vitro physiologically based extraction tests (PBETs) are commonly used to assess bioaccessibility (i.e., the fraction of metal that can be solubilized in relevant biological fluids) of particle-associated metals. No single chemical extraction can mimic the complex pharmacokinetic processes involved in metal absorption; however, estimates of metal bioaccessibility using PBETs have been shown to be closely correlated with in vivo bioavailability after ingestion for some metals, as measured in laboratory animal studies (18, 19). Although inhalation of particle-bound metals is another potentially important exposure pathway and several inhalation PBETs have been developed (20, 21), these techniques have not yet been validated using in vivo laboratory animal studies.

The simple bioaccessibility extraction test (SBET) is a commonly used procedure for predicting bioaccessibility of metals in ingested particles (18). Results of SBET extractions on <37 μm chat particles indicate a high degree of metal bioaccessibility in ingested chat, with 77−89% of Zn, 65−110% of Pb, and 56−69% of Cd solubilized after 2 h. By contrast, ZnS and PbS exhibited limited or no oral bioaccessibility (0−3%) (Table 1). The bioaccessibility of metals in chat was more similar to that of $PbCO_3$ (and presumably other carbonates), which was nearly 100% solubilized in the SBET extractant. These results further support the hypothesis that chat particles no longer contain Zn, Pb, and Cd primarily in sulfide form. The degree of oral bioaccessibility of metals in Tar Creek chat is similar to that found in analogous studies of Pb in mine tailings at some other sites (approximately 50%, ref 26), but is notably higher compared to others (approximately 10%, ref 18). This variability emphasizes the site-specific nature of metal speciation and lability, which depend in part on the presence or absence of carbonate minerals (26), such as dolomite, which are prevalent in Tar Creek chat.

To assess the potential bioaccessibility of metals in respired particles, Tar Creek chat samples were subjected to phagolysosomal simulant fluid (PSF). PSF is designed to simulate the chemical conditions of lysosomes in alveolar macrophages (20), where the majority of metal dissolution from small respirable particles is believed to occur. Results of PSF extractions on <37 μm chat samples suggest lower
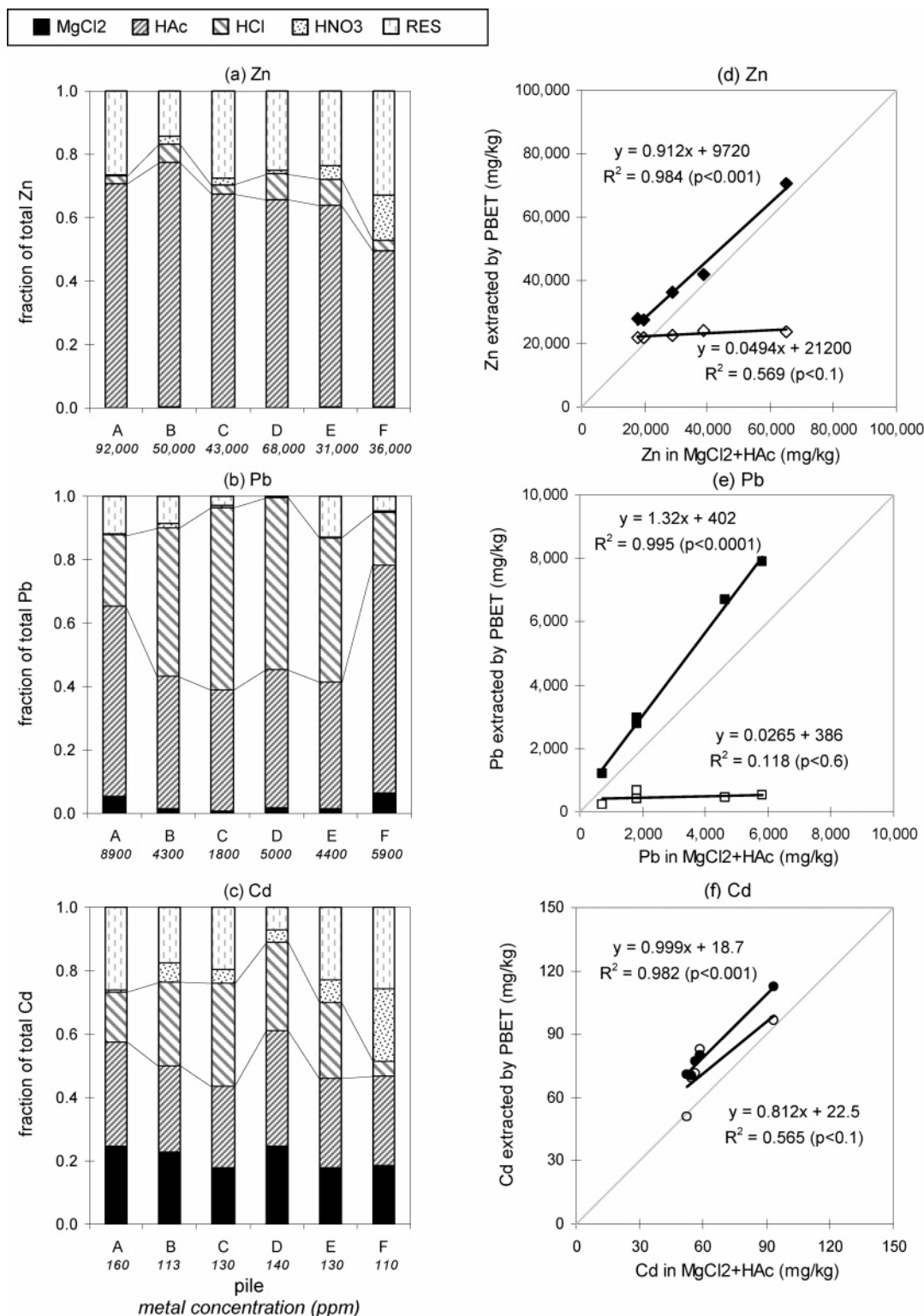
FIGURE 4. (a–c) Sequential extraction results (expressed as the fraction of solid-phase metal solubilized in each solution) for Zn, Pb, and Cd in <37 μm particles collected from six chat piles (A–F). Numbers printed in italics below each pile label represent the total metal concentration in each sample in mg/kg. (d–f) Physiologically based extraction test (PBET) results (expressed as the concentration of metal in the solid-phase solubilized in each solution) for SBET simulated gastric fluid (closed symbols) and phagolysosomal simulant fluid (PSF, open symbols), plotted as a function of solid-phase metal concentration solubilized in the exchangeable (MgCl2) and carbonate (HAc) sequential extraction fractions. PBETs are presented as the average of duplicates. The gray line shows a 1:1 correlation. All extraction conditions and abbreviations are summarized in Table 1.

metal bioaccessibility than in SBET solution. Across all samples, 26–70% of Zn, 6–16% of Pb, and 45–64% of Cd were solubilized in the PSF solution after 5 d. Chat-associated Zn and Pb were 10–40 times more soluble in PSF than were sulfide-bound Zn (1.4%) and Pb (0.4%) (Table 1).

Although sequential extractions are designed to characterize the distribution of metals among geochemically defined fractions, the agreement in our chat samples between metal lability as determined by sequential extractions and SBET results suggests that they can also provide reasonable

estimates of oral bioaccessibility (Figure 4d−f). The solubility of metals in the first two sequential extraction solutions ($MgCl_2$ + HAc) was strongly correlated with SBET bioaccessibility (adjusted $R^2 > 0.98$ for each metal), although the sequential extraction values were 10−40% lower. This consistent underestimate was likely due to a combination of differences in pH and temperature (37 °C vs 20 °C) and the potential for enhanced ligand-promoted dissolution by glycine, which forms metal complexes with 3−4 orders of magnitude higher binding strength than metal-acetate complexes. The metals extracted in the first three fractions ($MgCl_2$ + HAc + HCl) more closely approximated bioaccessibility (average ratio of ($MgCl_2$ + HAc + HCl)/SBET across all metals and piles was 1.05 ± 0.24), but the values were much less strongly correlated (adjusted $R^2 < 0.2$ for all three metals). Considering the agreement shown previously between SBET bioaccessibility and in vivo bioavailability (*18*), these results suggest that the exchangeable and carbonate sequential extraction fractions together can be used to predict oral bioaccessibility, although this relationship would need to be tested over a wider range of sample matrices.

Based on pH alone, the amount of metal extracted in these first two sequential extraction fractions (pH 5) also would be expected to predict the amount of metal solubilized in PSF (pH 4.5). This prediction appeared to hold true for Cd; the amount of Cd present in the PSF solution (Cd_{PSF}) was correlated with amount of Cd mobilized in the $MgCl_2$ and HAc extraction fractions ($Cd_{MgCl2+HAc}$), although the correlation was weaker (adjusted $R^2 = 0.57$) than for SBET. However, Zn_{PSF} and Pb_{PSF} were relatively invariable across samples despite the large range of $Zn_{MgCl2+HAc}$ and $Pb_{MgCl2+HAc}$. Equilibrium speciation calculations (MINEQL+, version 4.07, Environmental Research Software) suggest that the phosphate (1 mM) in PSF solution may have limited Pb solubility, and to a lesser extent Zn solubility, through the formation of pyromorphite ($Pb_5Cl(PO_4)_3$) and $Zn_3(PO_4)_2$, while Cd solubility was not affected by phosphate. Reprecipitation of Pb with phosphate also explains the apparently low bioaccessibility of $PbCO_3$ (Table 1) at a pH that should readily solubilize carbonates, and also could have led to underestimates of PbS, ZnS, and hemimorphite bioaccessibility (although neither PbS nor ZnS were substantially solubilized in the $MgCl_2$ or HAc fractions). Whether phosphate would limit metal solubility in phagolysosomes in vivo is unknown, since the true composition of actual phagolysosomal fluid is not known (*20*) and the ionic concentrations of PSF are based on lung lining fluid. Organic ligands in actual phagolysosomal fluid and active transport of dissolved metals out of lysosomes may enhance in vivo metal absorption even in the presence of phosphate. In any case, our results point to the fact that in vitro tests will need to be validated for each metal separately to account for potential interactions between the metal and ions in synthetic extraction solutions. Currently, a standardized in vitro technique to predict in vivo metal bioaccessibility of inhaled particle-bound metals is not available. In vivo studies are currently underway to test the bioavailability of metals from inhaled and ingested fine chat particles from Tar Creek (Molina R, personal communication) and will be used to explore the applicability of using in vitro extraction techniques for estimating bioavailability.

Broader Implications. Our results highlight the importance of performing site-specific geochemical analyses on size-fractionated mine waste when assessing metal exposure and risk in mining-impacted communities. Elevated metal concentrations in respirable and wind-mobilizable particles compared to bulk mine waste demonstrate the importance of obtaining data for particle sizes most relevant for exposure via inhalation and ingestion. In addition, the high degree of metal lability in present-day Tar Creek chat, relative to both mine waste at other sites and parent ore material, highlights the need for assessing solid-phase speciation using site-specific, contemporary mine waste. As part of ongoing remediation efforts at mining-impacted sites like Tar Creek, accurate geochemical characterizations of mine waste will be critical for predicting environmental fate and transport of metals and for understanding and minimizing important human and ecological exposure pathways.

Supporting Information Available

Details of laboratory methods; sequential extraction results for 0.5−2 mm samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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