

Elemental Release Patterns of Low-level Pb-Zn Dolomitic Tailings in Missouri

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Abstract: Lead and zinc tailings are common in the Ozark region of Missouri and constitute an environmental hazard, particularly to soil and water resources. This study investigated the elemental release patterns of low-level Pb-Zn dolomitic waste-rock along Bee Fork Creek in Reynolds County, Missouri, to determine whether these tailings are releasing sufficient metal concentrations to adversely impact water and adjacent riparian resources. Aqua-regia digestion of control and impacted sites confirm the presence of substantial concentrations of As, Cd, Pb, Zn and other metals. Hot water and 0.01 M NaNO₃ extractions recovered small portions of the total elemental pool and that only a very small portion of the total metal pool is labile. The EDTA extraction recovered greater concentrations of Ca, Mg, Pb, Zn and Cd than the hot water extraction. The Ca and Mg concentrations recovered by the EDTA extraction suggest partial dissolution of the dolomitic waste rock, thus promoting metal release. The EDTA Pb, Zn and Cd concentrations reflect recovery of these metals from the organic, exchangeable and waste rock fractions. Long-term weathering of the dolomite waste rock may promote the continuous, but low level, release of metals to Ozark streams.

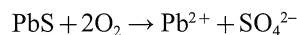
Key Words: lead, cadmium, mine tailings, EDTA extraction

Introduction

Tailings are milled or washed ores that have insufficiently low metal contents to be considered of commercial value and are commonly stored at the mine site. Lead tailings are common in Missouri, a state with a long history of Pb and Zn mining. These tailing piles, tailing ponds and other mining products are frequently adjacent to streams, predisposing the tailing water leachate to negatively impact the surface water quality, soil quality, and the surrounding ecosystem.

Missouri Pb deposits reside primarily in the Bonnetterre Formation; which is, a light-gray, medium to finely crystalline, medium bedded dolomite of the Cambrian system (Thompson, 1995). Lead occurs primarily as galena (PbS), with sphalerite

(ZnS) and other metal sulfides as important auxiliary minerals. Sulfur oxidizing bacteria (*Thiobacillus thiooxidans*, *Ferrobacillus ferrooxidans* and *Thiobacillus ferrooxidans*) appreciably advance the oxidation and hydrolysis of galena (Essington, 2004), which may be characterized as:



The direct oxidation of PbS by O₂, as a purely inorganic reaction, does not produce acid mine drainage; however, secondary reactions, especially when microbially mediated and involving FeS oxidation, may produce considerable quantities of acid mine drainage (Essington, 2004).

PbS oxidation produces Pb²⁺ and hydrolysis in a near-neutral pH environment commonly involves Pb(OH)⁺ adsorption on quartz, clay, and Fe-Mn oxyhydroxide substrates (Essington, 2004). Langmuir (1997), in a review, reported that oxyanion (SeO₄²⁻, SO₄²⁻, CrO₄²⁻, VO₄³⁻, AsO₄³⁻) and cation (Cr³⁺, Pb²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺ and Ca²⁺) adsorption on many variable charge substrates is pH dependent. Oxyanion adsorption is favored in acidic environments on net-positively charged surfaces and cation adsorption is favored in neutral or alkaline environments on net-negatively charged surfaces. Sidle et al. (1992), Dorransoro et al. (2002), and Pueyo et al. (2003) demonstrated that metals have differing mobility, with Pb²⁺ considered to be a relatively immobile species.

Selective sequential extractions attempt to fractionate elements into discrete chemical environments, with each protocol allowing element mobility and biological availability estimates (Tessier et al., 1979; Shuman, 1985; Levy et al., 1992; Ostergren et al., 1999; Lim et al., 2002; Roussel et al., 2000; Pueyo et al., 2003; Mbila and Thompson, 2004). In broad context, selective extractions are semi-quantitative estimates of element partitioning into distinctive chemical environments, which may suffer because of incomplete metal extraction, metal precipitation, and the inadvertent extraction of metals from non-target fractions (Shuman, 1991). Single (non-sequential) selective extractions have less potential to describe metal partitioning in the soil environment; however, their simplicity is an attractive advantage.

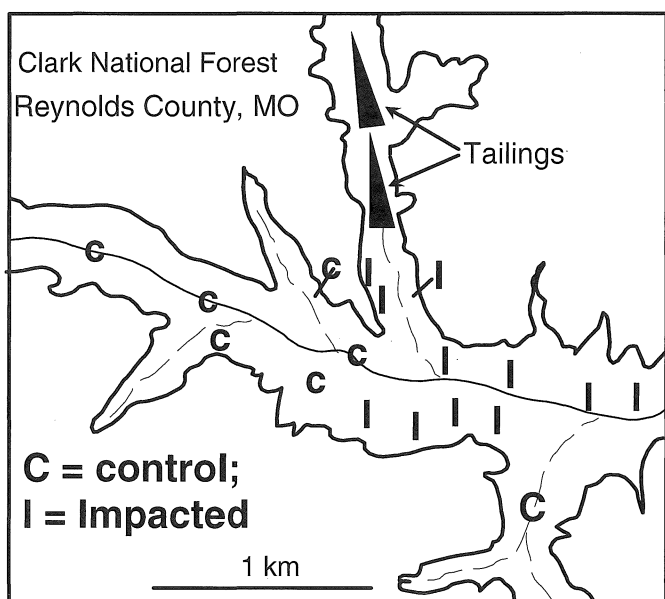
The objectives of this research are: (1) to estimate element release potentials of waste-rock containing small concentrations of Pb, Zn, Cd and other elements, and (2) to assess the threat to the waters and sediments of a small Missouri Ozark stream. In essence, we wish to determine if waste-rock enters the stream from its upland confinement area and to elucidate whether or not waste-rock has the potential to release metals to stream waters.

Study Area and Sampling Protocols

Lead-zinc mine tailings are located adjacent and along the Bee Fork Creek in Reynolds County, MO and in the Clark National Forest. A rock dam, spanning the sides of a descending ephemeral stream channel restrains the tailings from entering Bee Fork Creek. Sampling occurred in the dry bed load of Bee Fork Creek, both above (control) and below (impacted) the Pb-Zn tailings (Fig. 1). One control sample site was located downstream, but was topographically elevated above the high water level of Bee Fork Creek and resided on a descending, ephemeral stream bottom. Eight control sites consisted of cherty sandy loam to cherty loamy sand material, composed primarily of quartz sand and silt with small quantities of clay. Ten impacted sites consisted of similar materials, coupled with secondary quantities of carbonate materials washed from the tailings areas. Thus, the labeling of “control sites” and “impacted sites” was based on the likelihood of rock-waste incorporation by a combination of mass wasting and stream processes.

Sampling consisted of 0.25 meter \times 0.25 meter wide and 0.05 meter deep excavations, each geo-referenced with a global positioning system. Samples were placed in plastic bags and oven-dried at 110°C for 48 hours. Samples were lightly crushed

Figure 1. An illustration showing the relative placement of the control and impacted sites and the locations of the tailings.



and sieved through a 10 Mesh sieve to obtain the fine earth fraction; that is, material finer than 2mm equivalent spherical diameter. All procedures were performed using the fine earth fraction. Visual estimations of the gravel content were made.

Laboratory Protocols

Soil pH was measured using equal volumes of water and sediment with a pH meter equipped with a combination pH electrode (Carter, 1993). We measured the particle size distribution using the hydrometer method and sieves (Carter, 1993). Two *M* acetic acid extractable $\text{SO}_4\text{-S}$ was determined by the University Missouri-Columbia soil testing service.

An aqua-regia (AR) digestion was performed to estimate the baseline concentrations of Pb, Cd, Zn and other elements. The AR digestion procedure completely recovers elements residing in soluble, exchangeable, carbonate, organic, Fe and Al oxide environments and partially recovers elements from phyllosilicate and calcic dominated feldspar environments. Quartz, orthoclase, albite, anatase barite, monazite, sphene, chromite, ilmenite, rutile and cassiterite are largely unaffected by the AR digestion (communication from chief analyst at SGS Laboratory). The AR procedure was performed by SGS Laboratories (Toronto, Canada). In this procedure, 0.25 g of finely ground fine earth fraction was digested in 0.01 liter of aqua regia (1 HCl:3HNO₃) for one hour, followed by 0.45 μm filtration. Digest solutions were analyzed using inductively coupled plasma — atomic emission spectroscopy (ICP-AES using ARL 3560 and Optima 4300 instruments). Selected duplicates and reference samples having known metal concentrations were performed.

A hot water extraction was performed to recover only the most labile or potentially labile fractions. The hot water extraction involved equilibrating 0.5 g samples in 0.02 L distilled-deionized water at 80°C for one hour followed by 0.45 μm filtration and aqueous elemental analysis using ICP-MS (Inductively coupled plasma — mass spectroscopy using an Optima 4300 instrument). The hot water extraction was performed by activation laboratories (Toronto, Canada).

A (i) NaNO₃ extraction and a (ii) NaNO₃ — EDTA extraction were performed by the authors to further characterize element availability. Samples were extracted using 10⁻² M NaNO₃ and a second sample set was extracted using 10⁻² M NaNO₃ buffered with 10⁻³ M EDTA (di-Na salt). Two grams of sediment were equilibrated with 0.02 liter of the extracting solutions (1:10 soil:solution) for two hours, with hand swirling every 20 minutes to re-suspend the equilibrating material. The suspensions were centrifuged (2000g for 10 minutes) and the decantate filtered (0.45 μm) before elemental analysis using ICP-MS.

We performed X-ray diffraction analysis using dry mount whole soil samples (<2 mm). X-ray diffractograms were obtained with a Scintag diffractometer using CuK α radiation. Samples were scanned from 20 to 90° 2 θ at 0.02° s⁻¹. Mineral identification was assisted using JCPDS International Centre for Diffraction Data, 1980).

Statistics

Mean separation between the control and impacted sites was performed using the t-test statistic employing a two-tail format. Pearson correlations were performed to estimate element associations.

Results and Discussion

Routine Site Characterization

All sites have extremely gravelly loamy sand to extremely gravelly sandy loam textures. Clay contents varied from 1.6 to 9.9 percent with an average clay content of 3 percent. Sediment pH levels range from slightly acidic (pH 6.40) to moderately alkaline (pH 7.78), with the impacted sites being slightly more alkaline (mean ± standard deviation: 7.3 ± 0.3) than the control sites (6.8 ± 0.5), a result that is attributed to the presence of dolomitic rock. Extractable sulfate-S concentrations were not significantly different between the control (23.2 mg SO₄-S kg⁻¹) and the impacted (48.9 mg SO₄-S kg⁻¹) sites.

X-ray diffraction of dry powder mounts of the fine earth fraction revealed the near absolute dominance of quartz and phyllosilicates (primarily 2:1 layer clay) in the control sites and the near dominance of quartz and phyllosilicates, with trace to small quantities of dolomite, in the impacted sites. Quartz sand and chert nodules are commonly the dominant materials in Missouri Ozark streams. X-ray diffraction failed to reveal any diffraction peaks for galena (PbS), particularly for the stronger intensity lines at 0.3429 and 0.2969 nm (Moore and Reynolds, 1989), suggesting that galena is less than 0.5%. A few hand specimens from the impacted sites revealed tiny (hand-lens) galena crystals.

Aqua-Regia Digestion of the Control and Impacted Sites

Aqua-regia digestion was used to estimate the near-total element content of the control and impacted sites. Elements not discussed in the following narrative and showing no significant differences between the control and impacted sites are listed as a footnote in Table 1. Calcium and Mg concentrations were dramatically greater in the impacted sites. Interestingly, the Mg and Ca concentrations on a mole basis are present in nearly a one to one correspondence, suggesting the presence of small quantities of dolomitic waste-rock. Impacted sites had significantly greater Sr, As, Cd, Pb, Mn, Fe, Ni, Cu, Zn and Ag concentrations (Table 1).

Zinc concentrations in the control sites ranged from 11.3 to 85.8 mg Zn kg⁻¹, whereas Zn concentrations in the impacted sites ranged from 178 to 658 mg kg⁻¹. Similarly, lead concentrations in the control sites ranged from 8.9 to 214 mg Pb kg⁻¹, whereas the impacted sites ranged from 188 to 371 mg Pb kg⁻¹. Cadmium concentrations in the control sites ranged from 0 to 0.7 mg Cd kg⁻¹, whereas the Cd concentrations in the impacted sites ranged from 1.2 to 13.2 mg Cd kg⁻¹. The relatively modest coefficients of variance from the control sites reflect the small and somewhat variable geochemical background levels and the possibility that air-borne waste-rock dust may have slightly impacted the entire study area. The relatively large coefficients of variance from the impacted sites reflect the variable quantities of waste-rock incorporated into the stream's bed load.

As an example, Ag is an element commonly associated with Missouri's Pb deposits. The mean Ag concentrations of the impacted sites (0.22 mg Ag kg⁻¹) are substantially greater than those of the control sites (0.005 mg Ag kg⁻¹). The greatest Ag concentration from the control sites (0.04 mg Ag kg⁻¹) is smaller

Table 1. Aqua-regia digestion of soil samples selected from tailings impacted sites on Bee Fork Creek, Missouri.

	Mg	Ca	Sr	As	Cd	Pb	Mn	Fe	Co	Ni	Cu	Zn	Ag
	mg kg ⁻¹												
Control Sites (8 sites)													
Mean	4330.00	8080.00	6.0	4.00	0.4	74.00	675.00	10510.00	16.0	12.00	13.00	48.00	0.005
Standard Deviation	4940.00	9540.00	4.0	3.00	0.3	67.00	367.00	3340.00	16.0	5.00	7.00	28.00	0.014
CV	1.14	1.18	0.7	0.75	0.8	0.9	0.54	0.31	1.0	0.43	0.53	0.58	2.80
Impacted Sites (10 sites)													
Mean	71900.00	133000.00	32.0	30.00	6.2	274.00	2226.00	15320.00	26.0	49.00	52.00	390.00	0.22
Standard Deviation	48510.00	91070.00	19.0	23.00	3.3	84.00	951.00	4740.00	7.0	22.00	21.00	163.00	0.18
CV	0.67	0.67	0.6	0.8	0.5	0.3	0.4	0.31	0.3	0.45	0.41	0.42	0.83
Detection Limits	100.00	100.00	0.5	0.1	0.01	0.01	1.0	100.00	0.1	0.1	0.01	0.1	0.002
Mean T-test Probability	**	**	**	**	**	**	**	*	NS	*	**	**	**

* is significant (P < 0.05) and ** is highly significant (P < 0.01), NS is not significant. CV is the coefficient of variation (standard deviation/mean)

The elements Li, Al, K, Sc, V, Ga, Se, Rb, Y,Zr, Mo, Sn, Sb, Te, Cs, Ba, Au, Tl, Bi, Th and the rare earth elements were not significantly different between the control and impacted sites.

than any Ag concentration from the impacted sites (0.07 mg Ag kg⁻¹), suggesting that most of the impacted sites have accumulated Ag.

Arsenic concentrations from the control sites ranged from 0.5 to 8.2 mg As kg⁻¹, whereas the As concentrations from the impacted sites ranged from 4.1 to 76.5 mg As kg⁻¹. Mean As concentrations for the control and impacted sites were significantly different; however, the large impacted site As variance infers that a least one of the impacted sites has accumulated As and some of the sites may be considered pristine.

Zinc shows significant Pearson correlations with Pb and Cd. Pooling of the control and impacted sites shows that Pb is positively correlated with Zn ($r=0.89$) and Cd is positively correlated with Zn ($r=0.98$). The implication is that waste-rock incorporation acts as an “element provider” and that the elemental ratios are largely preserved.

Impacted sites were selected in the downstream portion of the creek, whereas the control sites were selected from the upstream portions of the creek. Elemental differences between the control and impacted sites imply greater metal accumulation in the downstream portion of the stream. No spatial distribution patterns were observed among the ten impacted sites; that is, the likelihood of a site adjacent to the confined rock-waste being impacted is identical to that of a site at some downstream distance. It is speculated that waste-rock entering the stream is segregated in the bed load.

Hot-Water Extraction

Elemental recovery by the hot-water extraction revealed that only a small portion of the total element pool is labile or potentially labile. Greater total element recoveries were observed from the impacted sites (Table 2). Mean As, Cd, Pb,

Co, Ni, Cu and Zn concentrations from the impacted sites are greater than the corresponding concentrations from the control sites. Control site Pb and Zn concentrations recovered by the hot water extraction averaged 64 μg Pb kg⁻¹ and 70 μg Zn kg⁻¹, whereas the impacted sites averaged 857 μg Pb kg⁻¹ and 2700 μg Zn kg⁻¹. Cadmium averaged 1.5 μg Cd kg⁻¹ in the control sites and averaged 32.6 μg Cd kg⁻¹ in the impacted sites. The large standard deviation in the impacted sites for Pb, Zn and Cd likely reflects different amounts of waste-rock incorporation. Considering only the impacted sites, two samples having decidedly smaller hot water Zn, Pb and Cd recoveries were the same sites having smaller Zn, Pb, and Cd aqua-regia recoveries, inferring that these two sites have smaller amounts of waste-rock. The substantial metal concentrations corresponding to the hot-water extractions from the impacted sites suggest that: (1) at least a portion of the total pool of these elements resides in potentially labile forms, and (2) continued weathering of the waste rock may slowly release elements.

NaNO₃ and NaNO₃-EDTA Extractions from Impacted Sites

Impacted sites were further characterized to estimate the metal release potential. The NaNO₃ extraction attempts to recover salt-displaceable (exchangeable) metals, whereas the NaNO₃-EDTA extraction attempts to recover exchangeable plus EDTA-chelatable metals. Iron showed similar recoveries between the NaNO₃ and NaNO₃-EDTA extractions (Table 3). Calcium, Mg and Mn show substantially greater EDTA recoveries, underscoring the capability of EDTA to partially recover Ca and Mg from dolomitic materials.

Cadmium was not detected in the NaNO₃ extraction, whereas Pb, Ni, Cu and Zn exhibited modest NaNO₃ concentrations (Table 3). The EDTA extraction recovered substantially

Table 2. Hot water extract of soil samples from control and impacted sites on Bee Fork Creek, Missouri.

	Mn	As	Cd	Pb	Co	Ni	Cu	Zn
	mg kg ⁻¹			μg kg ⁻¹				
Control Sites (8 sites)								
Mean	1.3	14.00	1.5	64.00	12.00	31.00	92.00	70.00
Standard Deviation	2.1	6.00	0.4	53.00	4.00	12.00	76.00	28.00
CV	1.6	0.46	0.28	0.81	0.33	0.39	0.82	0.40
Impacted Sites (10 sites)								
Mean	1.5	140.00	33.00	854.00	85.00	400.00	422.00	2550.00
Standard Deviation	1.0	120.00	20.00	387.00	70.00	352.00	200.00	1776.00
CV	0.7	0.87	0.60	0.45	0.82	0.88	0.47	0.69
Detection Limits	10.0	1.00	0.2	1.00	1.00	1.00	1.00	1.00
Mean T-test Probability	NS	**	**	**	**	*	**	**

* is significant ($P < 0.05$) and ** is highly significant ($P < 0.01$), NS is not significant.

CV is the coefficient of variation (standard deviation/mean)

The elements Li, Mn, Sr, Cs, Ba, Ti, Y, Zr, Nb, Hf, Ta, Br, I, V, Se, Mo, Sb, Th, U, Ga, Sn and the rare earth elements were not significantly different between the control and impacted sites.

Table 3. Sodium nitrate and sodium nitrate-EDTA extractions from impacted sites on Bee Fork Creek, Missouri.

	Ca	Mg	Fe	Mn	Cd	Pb	Ni	Cu	Zn
	mg kg ⁻¹								
0.01 M NaNO ₃ Extractions of Impacted Sites									
Mean	79.00	36.00	13.00	0.58	<0.1	0.33	0.24	0.14	2.1
Standard Deviation	39.00	16.00	8.5	0.55	0.38	0.22	0.05	1.2	
CV	0.49	0.44	0.65	0.94	1.15	0.92	0.34	0.58	
0.01 M NaNO ₃ buffered with 10 ⁻³ M EDTA Extractions of Impacted Sites									
Mean	280.00	117.00	18.00	9.1	1.6	33.00	4.0	3.1	71.00
Standard Deviation	128.00	60.00	7.1	1.6	1.2	20.00	4.3	1.8	73.00
CV	0.46	0.51	0.39	0.18	0.7	0.62	1.06	0.60	1.03

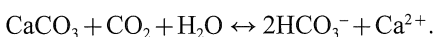
Arsenic was below detection limits (< 1 mg As/kg) for both the sodium nitrate and sodium nitrate-EDTA extractions. CV is the coefficient of variation (standard deviation/mean)

greater concentrations of Cd, Pb, Ni, Cu, and Zn than the NaNO₃ extraction. The effectiveness of EDTA rests with: (1) the affinity of EDTA to complex Ca and Mg, and (2) the ability of EDTA to form strong complexes with metals and prevent their subsequent re-adsorption or precipitation (Norvell, 1991). Both extractions infer that long term contact with surface waters will likely result in the low-level release of these elements, especially if the surface waters are buffered with natural chelating agents, e.g., fulvic acid and low molecular weight organic acids.

Conclusions

Dolomitic rock-waste was assessed to determine if metals leaching from these tailings were impacting a small Missouri Ozark stream. Aqua-regia extractions showed substantial reserves of Pb, Cd, Zn and other elements. Hot water and NaNO₃ extracts show that these materials have a small fraction of the total element pool that is labile or potentially labile. Lead, Cd and Zn recovered by EDTA suggests that dolomite weathering may allow a long-term, although at a low level, release of selected metals into the environment.

The severity of the elemental release would increase if soil or water conditions were to favor the congruent weathering of the dolomite, such as, microbial enhanced carbonation reactions:



Soil organic matter complexation may also augment the congruent weathering of the dolomitic waste-rock, as simulated by EDTA extraction. Thus, soil and geologic weathering processes may permit the continual release of metals; however, the kinetics of such releases is likely to be quite slow. The continual and slow release of Pb, Zn and Cd may not necessarily pose an appreciable threat to the environment because stream flow may effectively disperse these metals. However, further

research may elucidate chronic toxicity to aquatic organisms depending upon annual stream flow differences, the presence of particularly sensitive organisms, the presence of additional tailing spillage or other appropriate factors.

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