FRACTIONATION OF HEAVY METALS IN ORGANICALLY AMENDED MINE LANDS¹

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<u>Abstract:</u> Sequential extraction was used in this U.S. Bureau of Mines study to determine the fractions of Cd, Pb, and Zn in abandoned Pb-Zn mill tailing amended with four types of organic residues, applied at three levels, with and without inorganic fertilizer. Trace element fractions selected for sequential chemical extraction were: (1) exchangeable, (2) dilute-acid extractable (bound to carbonates), (3) iron-manganese oxide bound, (4) organically bound, and (5) residual. Metal fractions in lead-zinc mill tailing change dependent upon organic residue type and rate of application. For all organic residue types, concentrations of Cd, Pb, and Zn in the Fe-Mn oxide and organically bound fractions increased as the rate of organic residue application increased, while concentrations of Cd, Pb, and Zn in the exchangeable and dilute-acid extractable fractions decreased as the rate of residue application increased. The results suggest that Cd, Pb, and Zn in abandoned Pb-Zn mill tailing will be prevalent in the weakly mobile, nonbioavailable forms as the rate of organic residue application is increased.

Additional Key Words: sequential extraction, trace elements, bioavailability, compost.

Introduction

The surface waste materials or tailing discarded from mineral processing activities results in a unique environment which potentially can severely inhibit vegetation stabilization. Mineral tailing materials contain residues from metal ore processing operations and are often characterized by high concentrations of heavy metals, alkaline or acid conditions, or toxins from the chemicals used to process the ore (Chambers and Sidle 1991).

Tailing materials associated with mineral processing activities are of environmental concern because of the potential for heavy-metal contamination in the mining-related wastes, and in both surface and shallow ground water flowing under, through, and into a tailing disposal area. Elevated trace element concentrations in tailing materials can also lead to human and animal health risks owing to exposure through ingestion of wind-blown material, through ingestion of the tailing directly, through uptake and accumulation by vegetation, and through various food chains. There are also concerns of trace element contamination due to sedimentation of river channels and reservoirs and the impact of contaminated sediment on floodplain soils (Moore and Luoma 1990).

Reclamation of mineral-related processing wastes contaminated with trace elements has not been successful using conventional agricultrual techniques owing to high concentrations of metal elements and other edaphic factors. Treatment technologies available for contaminated soils have been discussed by Gilbertson (1992); however, mineral mine wastes, particularly tailing materials, differ from soil in terms of chemical, physical, and biological properties. As a result, there is a need for development of treatment technologies applicable to mineral-related waste sites contaminated by trace elements. Abandoned Pb-Zn chat tailing, associated with the Tri-State Mining District consisting of portions of southwest Missouri, southeast Kansas, and northeast Oklahoma, offers an opportunity to study various environmental problems associated with tailing contaminated with trace elements and methods of physical, chemical, and vegetative stabilization.

In a 1989 record of decision (ROD), the U.S. EPA selected a remedial action plan for southeastern Kansas based on the following considerations: (1) surface mine wastes contain high levels of trace elements, particularly Cd, Pb, and Zn; (2) human ingestion through exposure to these elements and leaching of these elements into the shallow ground water and surface waters are of major concern; and (3) the shallow ground water system and surface waters are contaminated with trace elements.

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The goal of this U.S. Bureau of Mines study was to evaluate the concentration and chemical fractionation of Cd, Pb, and Zn in Pb-Zn chat tailing that had been amended with organic residues. A sequential extraction procedure based on work by Tessier et al. (1979) was used to partition these trace elements into five fractions to determine occurrence and bioavailability.

Materials and Methods

The study was conducted within the Galena subsite of the Cherokee County Superfund Site in southeastern Kansas. In April 1990, a 4x3x3 unbalanced factorial experiment arranged in a randomized complete block design with three replications was initiated. The design included four organic waste materials, three levels of application, and three types of fertilizer application. Control plots were included in the design. Treatment combinations were assigned to 2.5- by 4-mtest plots at random within each replication.

Four locally available or potentially available organic residues were applied at the surface to experimental plots. The organic residues used were: (1) composted cattle manure, (2) composted yard waste, (3) spent mushroom compost, and (4) turkey litter. Each of the organic amendments were applied at rates of 22.4, 44.8, and 89.6 Mg/ha on a dry weight basis. Fertilizer applications were based on recommendations by the Cherokee County Extension Agriculture Agent for new plantings of native grass and a fescue-legume mixture. The applications of fertilizer consisted of none, 22.4 kg/ha N + 29.4 kg/ha P + 74.4 kg/ha K (recommended rate for the establishment of native grasses), and 44.8 kg/ha N + 48.9 kg/ha P + 130.1 kg/ha K (recommended rate for the establishment of a fescue-legume mixture). The control plots consisted of no organic amendment or fertilizer applications; no organic amendment but fertilizer applied at the recommended rate for native grass establishment; and no organic amendment but fertilizer applied at the recommended rate for fescue-legume establishment.

Table 1 contains a complete list of the grass and forb species selected for study and the rates of each within the mix. The species selected for the seed mix, its percentage in the seed mix, and the rate of application were based on the results of a species trial experiment conducted on chat tailing adjacent to the current study area (Norland and Veith 1990). Recommendations by the Soil Conservation Service (1987) as to the minimum and maximum percentage for each species in a mixture for critical area planting were used as a guideline. The seed mix was formulated based on the rate of pure live seed (PLS) in kilograms per hectare.

TADLE 1. Species selected for use in the se	ed mix.		
Species	Percent in	Ord at m2	Amount of seed
DPECTES	mrycure-	<u>OLIGIN-</u>	(FLS Kg/ha)
Cool-season grasses	_	_	
Smooth brome (<u>Bromus</u> <u>inermis</u>)	5	I	1.4
Tall fescue (<u>Festuca</u> <u>arundinacea</u>)	5	I	1.7
Warm-season grasses			
Big bluestem (Andropogon gerardi)	20	N	3.4
Little bluestem (Schizachvrium scoparium).	20	N	3 4
Switch grass (Panicum wirgatum)	20	N	2.4
Switch glass (lanicum virgacum)	20	14	2.7
Sand bluestem (<u>Andropogon hall11</u>)	10	N	1.3
Leguminous forbs			
Partridge pea (<u>Cassia fasciculata</u>)	5	N	1.7
Crownyetch (Coronilla varia)	5	Ι	1.1
Alfalfa (Medicago sativa)	5	T	1 0
$\frac{1}{1}$	5	÷	1.0
iellow sweetclover (<u>Melilotus</u> <u>officinalis</u>)		T	0.8

¹Precent of each species in bulk mixture, prior to PLS correction. ²I=Introduced, N=Native.

During the 1992 growing season, tailing samples were collected in each organic residue type and rate of application treatment plot from nonrhizosphere locations. Three randomly located subsamples were taken to a depth of 15 cm in each plot using a soil recovery probe. Subsamples were composited, based on treatment combination, into 13 samples for analysis.

A five-step sequential fractionation scheme was used to partition the trace elements into exchangeable; dilute, acid-extractable; Fe-Mn oxide bound; organically bound; and residual fractions. The scheme (table 2) was based on work by Tessier et al. (1979), Pickering (1986), and Elliot et al. (1990). All samples were submitted to MVLT Laboratories, Inc., Bismarck, ND, for sequential extraction and analysis. The procedures used by MVLT Laboratories followed those established by Elliot et al. (1990). Reagents were added to 1.0-g samples of oven-dried chat tailing, which were then agitated on a shaker for the specified time and centrifuged at 1,500 rpm for 20 min. The centrifugate was decanted into a plastic bottle and set aside for analysis.

Fraction	Reagent conditions ¹	Shaking time, h
Exchangeable	16 mL 1 <u>M</u> MgC1 ₂ (pH 7.0)	1
Dilute acid-extractable	l6 mL 1 <u>M</u> NaOAc adjusted to pH 5 with HOAc	. 5
Fe-Mn oxide bound	40 mL of $0.175\underline{M}$ (NH ₄) ₂ C ₂ O ₄ and $0.1\underline{M}$ H ₂ C ₂ O ₄	4
Organically bound	40 mL of $0.1\underline{M} \operatorname{Na}_4 P_2 O_7 \dots$	24
Residual	Dry (in oven) 0.1 g of material remaining after previous step. Add 4 ml HNO_3 1.0 mL $HCIO_4$, and 6.0 mL HF and heat at 140 °C for 3.5 h. Add 5.0 g boric acid and dilute to 100 ml volume.	

Table 2. Chemical extraction scheme for trace element fractionation.

¹These volumes are for 1.0 g oven-dried chat tailing.

The next extracting solution was added, and the extraction process was repeated. After the first four extractions, 100 mg (dry wt.) of the remaining material was transferred to a Teflon decomposition bomb, and a hot triple-acid digestion was performed (Elliott and Shields 1988). Cadmium, Pb, and Zn analysis was performed using flame atomic absorption spectroscopy.

Results and Discussion

The total concentrations of Cd, Pb, and Zn in the Galena subsite tailing materials are extremely high (table 3). For comparative purposes, the trace element concentration action levels established by the U.S. EPA for the Galena subsite of the Cherokee County Superfund Site are included. Trace element concentration action levels are used to identify surface-deposited mine wastes (waste rock, chat tailing, and slag) for selective placement in disposal sites such as open subsidences, pits, and shafts within the Galena subsite. This action will through proper disposal essentially eliminate human exposure via ingestion of contaminated surface-deposited mine wastes (dust or direct) and will reduce long-term shallow ground water and surface water trace element loading resulting from mine wastes (Black and Veatch 1990).

Trace element concentration action levels established are: (1) Pb - 1,000 mg/kg, (2) Zn - 10,000 mg/kg, and (3) Cd - 25 mg/kg. According to the U.S. EPA, chat tailing characterized above the action level for Pb and below the action level for Cd and Zn may be mixed with plus 5-cm waste rock and buried in wet voids. Chat tailing containing Cd and/or Zn above the action level must be buried in dry voids. This chat tailing may be mixed with waste rock that is also placed in dry voids to minimize settlement after backfilling. Chat tailing below the action level for Cd, Pb, and Zn may be used as cover material or material for recontouring mine waste areas.

Table 3. Trace element concentrations of chat tailing and uncontaminated soils, mg/kg, dry wt.

	<u> Chat tailing </u>		Soils		Action	
Trace element	Range	Mean ¹	Range ²	Typical ³	levels	
Cd	6- 86	27	0.01- 7	0.4	25	
Pb	191- 2,432	800	2 -200	15	1.000	
<u> Zn</u>	898-31,940	11,939	10 -300	40	10.000	

¹Means are given for 14 chat tailing samples.

²Lindsay, 1979.

³Berrow and Reaves, 1984.

The mean total concentration of Cd and Zn exceed established action levels, while the mean value for Pb was below the action level. All three trace elements have ranges that fall above and below their specific action levels, but are above levels typically found in uncontaminated soils. This indicates that before the chat tailing is used as cover material or material for recontouring mine waste areas, x-ray fluorescence spectrometry or other U.S. EPA approved field detection methods must be used to determine the concentration of each trace element.

Without proper classification, the material used for cover may continue to be a human and animal health risk and lead to revegetation failures due to increased plant concentration of trace elements (phytotoxicity) or trace element chlorosis, which limits plant productivity. Trace element concentrations exceeding 8 mg/kg Cd, 100 to 400 mg/kg Pb, and 70 to 400 mg/kg zinc (Kabata-Pendias and Pendias 1984) can render soils nonproductive due to trace element phytotoxicity. Concentrations of Cd, Pb, and Zn are far above the apparently safe soil concentrations of 7, 200, and 300 mg/kg, respectively, and should be considered phytotoxic (Bowen 1979, Lindsay 1979, Bresler et al. 1982, Bohn et al. 1985). In light of these data, the toxic tailing concentrations of Cd, Pb, and Zn may be playing a large role in limiting vegetation establishment on the site. When taken up by the plant, these trace elements compete with and displace iron and other ions in enzyme systems, resulting in the alteration of the sterostructure and operation of the enzyme in plant metabolism (Lagerwerff 1967, Lagerwerff and Specht 1971).

Concurrent with surface mine waste classification and removal, all mine waste areas on the Galena subsite will be recontoured to eliminate closed basins (ponded areas) and vegetated to control erosion. The revegetation plan of the Galena subsite includes the native grasses listed in table 1 and the use of organic residues as the primary tailing amendment. Indiangrass (<u>Sorghastrum nutans</u> (L.) Nash) has been added to the native grass seed mix at a rate of 2.7 kg/ha PLS.

Treatment effects on the distribution and concentration of trace elements determined by chemical fractionation are shown in tables 4 and 5. For convenience, Elliot et al. (1990) placed the fractions evaluated into two broad categories which were distinguished by whether or not solid-phase dissolution is required to release the trace elements. Trace elements displaced without substrate dissolution are nondetrital (labile), while solid-phase dissolution is essential to solubilize detrital (nonlabile) trace elements. Nondetrital trace elements are those that are water soluble, exchangeable, or adsorbed onto solids phases and would correspond to the exchangeable and dilute acid-extractable fractions in table 4. Exchangeable trace elements would likely represent those most readily mobilized in tailing-water systems, whereas low pH (<5) would be required to release the dilute acid-extractable trace elements (Elliot et al. 1990). The detrital fraction (moderately labile to nonlabile) includes trace elements present as precipitated compounds (hydroxides, sulfides), fixed within the silicate matrix, or bound to hydrous oxides through occlusion, chemisorption, or coprecipitation (Elliot et al. 1990). The lability of organically bound trace elements is questioned, but because this fraction is evaluated after oxide-bound metals (table 2), it will be considered as part of the nonlabile trace elements (Elliot et al. 1990).

		Fraction				
	Trace		Acid	Fe-Mn	Organically	
<u>Treatment¹</u>	element	Exchangeable	<u>soluble</u>	oxide bound	bound	Residual
YW - 1	Cd	17.1	14.5	15.1	19.8	33.4
	РЪ	2.2	21.3	66.6	1.0	8.9
	Zn	1.3	43.3	18.3	15.9	21.1
YW - 2	Cd	14.9	13.4	11.6	27.0	33.0
	РЪ	1.5	20.6	64.3	1.4	12.1
	Zn	1.2	32,9	14.8	24.1	26.9
YW - 3	Cd	9.0	15.2	20.5	37.0	18.2
	РЪ	0.9	14.0	75.4	1.3	8.4
	Zn	0.7	26.2	27.5	32.5	13.2
CM - 1	Cđ	16.8	19.5	14.6	16.3	32.8
	РЪ	1.5	22.5	65.2	1.5	9.3
	Zn	0.8	41.6	14.5	15.2	27.9
CM - 2	Cd	17.9	17.4	14.4	21.2	29.1
	РЪ	1.1	25.3	63.1	1.3	9.2
	Zn	1.3	43.3	15.7	17.7	22.0
CM - 3	Cd	13.9	15.1	25.1	33.4	12.4
	РЪ	1.6	18.0	71.5	1.7	7.2
	Zn	2.0	32.0	29.2	27.5	9.4
MC - 1	Cd	16.3	22.1	16.3	17.7	27.5
	РЬ	1.6	20.2	54.7	4.4	19.1
	Zn	1.3	41.3	13.7	18.8	24.9
MC - 2	Cd	9.3	13.9	17.7	40.6	18.5
	РЬ	0.9	19.3	68.0	1.1	10.7
	Zn	0.7	31.1	24.7	30.0	13.5
MC - 3	Cd	7.2	13.1	14.1	56.1	9,5
	РЪ	0.9	15.5	74.2	1.0	8.4
	Zn	0.8	22.2	15.5	53.3	8.1
TL - 1	Cđ	15.1	23.6	23.4	15.1	22,9
	РЪ	2.1	25.6	63.5	1.4	7.4
	Zn	1.1	52.4	20.2	11.6	14.7
TL - 2	Cd	8.6	22.1	23.5	24.6	21.3
	РЪ	1.4	23.4	63.7	1.7	10.0
	Zn	1.0	38.3	16.6	25.0	19.1
TL - 3	Cd	6.2	18.9	26.6	40.7	7.7
	Pb	0.4	9.3	55.1	3.7	31.5
	Zn	0.8	24.2	19.5	34.8	20.7
Control	Cd	21.4	17.2	14.2	23.9	23.4
	Pb	2.3	25.8	62.5	1.3	8.2
	Zn	1.1	41.8	20.8	21.8	14.6

Table 4. Organic residue treatment effects on Cd, Pb, and Zn chemical fractionation, % of total trace element in each fraction.

¹YW=composted yard waste, CM=composted cattle manure, MC=spent mushroom compost, TL=turkey litter; 1=22.4 Mg/ha, 2=44.8 Mg/ha, 3=89.6 Mg/ha.

		Fraction						
	Trace		Acid	Fe-Mn	Organically			
<u>Treatment¹</u>	element	Exchangeable	<u>soluble</u>	oxide bound	bound	Residual	<u> </u>	
1		·········		mg/kg-				
YW - I	Cđ	8.7	7.4	7.7	10.1	17.0	50.9	
	РЬ	19.5	193.0	602.3	9.2	80.6	904.6	
	Zn	214.0	6,930.0	2,930.0	2,540.0	3,380.0	15,994.0	
YW - 2	Cđ	9.1	8.2	7.1	16.5	20-1	61.0	
	Pb	10.8	147.6	460.1	9.9	86.8	715 2	
	Zn	206.0	5,470.0	2,460.0	4,010.0	4,460.0	16,606.0	
VU - 3	Cđ	48	8 1	10.9	10.7	07	52 0	
10 9	Ph	6.8	102 9	554 3	1)./ Q S	<i>5.7</i>	725 0	
	Zn	94.6	3.720.0	3 900 0	4 620 0	1 870 0	14 204 6	
			5,,20.0	5,70070	4,020.0	1,0/0.0	14,204.0	
CM - 1	Cd	, 10.5	12.3	9.1	10,2	20.5	62.5	
	Pb	9.2	136.9	396.8	9.4	56.4	608.7	
	Zn	143.0	7,220.0	2,520.0	2,630.0	4,840.0	17,353.0	
СМ - 2	Cđ	12.7	12.3	10.2	15.0	20.6	70.8	
	РЪ	8.2	191.1	475.7	9.6	69.5	754 1	
	Zn	283.0	9,360.0	3,400.0	3,820.0	4,750.0	21.613.0	
					,		,-2010	
CM - 3	Cd	6.7	7.3	12.1	16.1	6.0	48.2	
	РЪ	9.0	101.0	401.8	9.6	40.7	562.1	
	Zn	298.0	4,700.0	4,290.0	4,040.0	1,380.0	14,708.0	
MC - 1	Cd	12.0	16.2	12.0	13.0	20.2	73.4	
	Рb	18.3	237.4	641.3	52.2	224.1	1.173.3	
	Zn	221.0	6,930.0	2,290.0	3,150.0	4,180.0	16,771.0	
MC - 2	Cd	5.9	8.8	11 2	25 7	11 7	63 3	
	Pb	8.4	170.4	601.0	10 0	94.5	884 3	
	Zn	127.0	5,430.0	4,320.0	5,250.0	2,360.0	17,487.0	
MC - 3	Cđ	4 2	7.6	8.2	32 6	5 5	. 50 1	
110 5	Ph	10.0	175 5	839.2	11 2	95 /	1 131 3	
	Zn	144.0	4,230.0	2,960.0	10,200.0	1,540.0	19,074.0	
πτ_1	Cđ	71	11 1	11 0	71	10.8	47 1	
112 - T	Ph	14.6	177 5	440 0	9.8	51 3	47.1 603.2	
	Zn	168.0	8,370.0	3,230.0	1,860.0	2,350.0	15,978.0	
тт Э	Cđ	6 4	16 5	17.6	18 /	15 0	7/ 0	
111 - 2	Ph	8 O	137 9	376.0	9 A	58.8	500 5	
	Zn	191.0	7,360.0	3,190.0	4,800.0	3,670.0	19,211.0	
	<u> </u>	2.6	11 0	15 5	00 7			
TL - 3	Ud D1-	3.0	11.0	LD.D	23.7	4.5	58.3	
	rd 7-	3.8 145 0	01.0 / 560 0	404.4	52.2	2/0.8	8/9.U 10 075 0	
	۷n	145.0	4,560.0	3,070.0	0,570.0	3,910.0	10,8/3.0	
Control	Cd	10.4	8.2	6.9	11.6	11.2	48,3	
	РЪ	17.9	198.2	474.0	9.5	61.0	760.6	
	Zn	149.0	5,423.0	2,777.0	2,917.0	1,950.0	13,216.0	

Table 5. Organic residue treatment effects on Cd, Pb, and Zn chemical fractionation, concentration of trace elements in each fraction.

¹YW=composted yard waste, CM=composted cattle manure, MC=spent mushroom compost, TL=turkey litter; 1=22.4 Mg/ha, 2=44.8 Mg/ha, 3=89.6 Mg/ha. The easily mobile, exchangeable Pb and Zn fractions were 2.3% and 1.1%, respectively, of the total Pb and Zn concentration in unamended chat tailing. Additionally, exchangeable Pb and Zn were not affected by organic residue type or rate of application. Exchangeable Cd was reduced compared to the control when organic residues were applied and the rate of application was increased (table 4). The unamended tailing exchangeable Cd fraction of 21.4% of the total was similar to what Sims and Kline (1991) found for unamended Atlantic coastal plain soils, 21.8% to 35.1% of the total. For each organic residue there was a progressive decrease in the exchangeable Cd fraction as the rate of application was increased. Applications of 89.6 Mg/ha of composted cattle manure, composted yard waste, spent mushroom compost, and turkey litter decreased the exchangeable Cd fraction to 13.9%, 9.0%, 7.2%, and 6.2% of the total, respectively. This agrees with Sims and Kline (1991) and Sposito et al (1983), who found that additions of 45 Mg/ha of composted sewage sludge will decrease the exchangeable Cd fraction.

The acid-soluble Cd and Pb fraction was unaffected by the application of organic residues. The relative amounts of both Cd and Pb did not show much change with increasing rates of organic amendment application, with the exception of Pb, where the acid soluble fraction decreased at the 89.6 Mg/ha rate of application for all organic residues. In unamended tailing materials, acid-soluble Zn accounted for a substantial portion (42%) of the total Zn. The Zn fraction, however, exhibited a progressive decrease as the rate of organic residue application increased, regardless of type. This suggests that if there is a sudden change in the tailing pH from the present value of 6.8 to a more acidic reaction, less Zn would be available in this fraction to be affected by change in tailing pH.

The sum of the first two fractions (exchangeable and acid soluble) represents the most labile, bioavailable fractions in the tailing system. On the basis of relative amounts of each element released from control plots in the first two extraction steps, Zn would have the greatest mobility in the tailing, followed by Cd and Pb. With the application of organic residues and increased rates of application, there was a decrease in labile (mobile), bioavailable fractions in the tailing system.

In unamended tailing, 28% of the Pb was in the labile fraction. With increasing rates of organic residue application, to 89.6 Mg/ha, there was a progressive decrease in labile Pb to 20% with composted cattle manure, 16% with spent mushroom compost, 15% with composted yard waste, and 9% with turkey litter. Most of the Pb (63%) was in the nonbioavailable Fe-Mn oxide bound fraction. With the exception of turkey litter, applications of organic residues at a rate of 89.6 Mg/ha increased the relative amount of Pb in the Fe-Mn oxide bound fraction to 72% with composted cattle manure, 74% with spent mushroom compost, and 75% with composted yard waste. This agrees with the findings of Sims and Kline (1991), who found that applications of co-composted sewage sludge (44 Mg/ha) to soil increased the relative amounts of precipitated Pb and that the majority of soil Pb was in the precipitated fraction.

The application of organic residues increased organically bound Cd and Zn. In unamended tailing, organically bound Cd and Zn accounted for 24% and 22% of the total Cd and Zn in the tailing system. At an application rate of 89.6 Mg/ha, the amount of organically bound Cd increased from 24% in unamended tailing to 33% when composted cattle manure was applied, 37% when composted yard waste was applied, 41% when turkey litter was applied, and 56% when spent mushroom compost was applied. This retention of Cd by organic matter has been documented for soils by Elliot et al. (1986). At the same rate of application, organically bound Zn increased from 22% of the total in unamended plots to 28% when composted cattle manure was applied, 33% when composted yard waste was applied, 35% when turkey litter was applied, and 53% when spent mushroom compost was applied. Organically bound Pb was not affected by applications of organic residues.

On the basis of the relative amounts of each element in the Fe-Mn oxide bound, organically bound, and residual fractions, the application of organic residues to abandoned Pb-Zn chat tailing increases the nonlabile (detrital) fractions in the tailing system. At an application rate of 89.6 Mg/ha, the relative amount of nonlabile Cd increased from 62% of the total in unamended tailing to 71% of the total when composted cattle manure was applied, 75% of the total when turkey litter was applied, 76 % of the total when composted yard waste was applied, and 80% of the total when spent mushroom compost was applied; for Pb, the nonlabile fraction increased from 72% of the total to 77% when composted yard waste was applied, 80% when composted cattle manure was applied, 84% when spent mushroom compost was applied, and 90% when turkey litter was applied at a rate of 89.6 Mg/ha; for Zn, the nonlabile faction increased from 57.2% of the total in unamended tailing to 66%, 73%, 75%, and 77% of the total in plots amended with composted cattle manure, composted yard waste, turkey litter, and spent mushroom compost, respectively, at a rate of 89.6 Mg/ha.

<u>Conclusions</u>

The application of organic residues to abandoned Pb-Zn mine tailing not only benefits plant establishment, growth, and community development (Norland 1993), but also changes the distribution of trace elements among the tailing chemical fractions. A five-step fractionation procedure identified the main trace element retention forms based on bioavailability.

Several organic residues were evaluated to determine their effect in reducing the bioavailability of Cd, Pb, and Zn in contaminated mine wastes. In unamended plots, the bioavailability (mobility) of Zn was the greatest, followed by Cd and Pb. In amended plots, the type of organic residue used had no effect on tailing chemical fractions, but the rate of application did affect the relative amount of each element in a chemical fraction. Additions of composted yard waste, composted cattle manure, spent mushroom compost, or turkey litter at a rate of 89.6 Mg/ha all reduced the labile (biovailable) Cd, Pb, and Zn fractions, while increasing the nonlabile (nonbioavailable) Cd, Pb, and Zn fractions.

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