CONSTRAINTS ON NATURAL REVEGETATION OF HARD ROCK MILLING TAILINGS IMPOUNDMENTS[1]

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Abstract: From the mid-19th through mid-20th centuries, widespread underground mining and surface milling operations deposited several hundred million tons of metals-contaminated, organic-deficient, mining waste materials on the land surface of the Tri-State Mining District of Oklahoma, Kansas and Missouri. Following metal recovery operations, fine tailings were allowed to settle in extensive impoundments often covering tens to hundreds of acres. Much of this material remains unvegetated or sparsely covered today, more than 50 years since the cessation of most mining operations. In this study, physicochemical characteristics of seven abandoned tailings impoundments were evaluated. Tailings were found to have circumneutral pH, moderate to high salinity, elevated trace metals (Cd, Fe, Pb and Zn) but limited nutrient (nitrate, ammonium, potassium and phosphate) concentrations and, overall, to demonstrate the presence of considerable barriers to vegetation establishment and growth. Five impoundments were found to be barren, but two impoundments showed substantial vegetation coverage. Physicochemical constraints (lack of moisture, organic matter, and available nutrients) and phytotoxic trace metal concentrations appeared to limit vegetation establishment on tailings impoundments.

Additional Key Words: hard rock mining, tailings, revegetation

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Introduction

Nearly 335 hectares (827 acres) of abandoned tailings impoundments lie within the Tar Creek Superfund Site, the Oklahoma portion of the historic Tri-State Lead-Zinc Mining District of OK, KS and MO. These impoundments contain approximately 7 x 10^6 m^3 of fine floatation tailings deposited predominately via hydraulic slurry techniques. Nearly all impoundments have remained completely void of volunteer vegetation, despite the more than 50 years since mining ceased.

Floatation tailings are considered to be one of the most difficult types of mining waste to reclaim, due to physical and chemical properties which inhibit vegetative establishment and growth, including poor particle size distribution, erodability, elevated heavy metal concentrations, low nutrient concentrations, and low water holding capacity (e.g., Krzaklewski and Pietrzykowski, 2002; Tordoff et al., 2000). Because tailings impoundments have characteristics limiting establishment of vegetation, they remain susceptible to wind and water erosion and have the potential to impact adjacent land areas and waterways (Ripley et al., 1996).

Natural revegetation of mining wastes can be difficult due to the drastic physical, chemical, and biological differences between native surrounding soils and the waste materials. If the waste contains toxic levels of heavy metals, natural processes that allow for future colonization by pioneer species may be limited. Stable soil structure and soil fertility are essential to plant growth, and their natural development can take centuries (Bradshaw and Chadwick, 1980). In addition, species richness and colonization rates are often limited for decades or even centuries (Shu et al., 2005).

However, research has shown that natural colonization of metalliferous mine wastes is possible through the spread of seeds and propagules by wind or water, although the process is slow and typically inadequate to meet reclamation goals (Shu et al., 2005). The process of primary succession on exposed mining waste materials may provide the opportunity for pioneer species to colonize, given that the site conditions are not toxic to vegetation (Ripley et al., 1996). Colonizing species often evolve natural adaptations to the extreme environment of mine tailings (Shu et al., 2005). The overall goal of this study was to characterize the physical and chemical properties of tailings impoundment materials in relation to plant growth and establishment.

Methods

Collection of Samples

For this initial study, floatation tailings were collected at seven sites on abandoned tailings impoundments within the Tar Creek Superfund Site in May of 2005 (Fig. 1). At each impoundment, tailings samples for chemical analyses were collected at two depths (0-20 and 20-40 cm) at three randomly selected sampling sites. If present, any O-horizon material was sampled and analyzed independently. Samples were stored in airtight bags at 4°C in the dark to inhibit potential chemical changes prior to chemical analysis. Additional tailings samples were obtained for physical analyses at the same locations and three intact 0-40 cm samples (one from each location) were mixed to make a single composite sample per impoundment which was stored in airtight bags at room temperature.

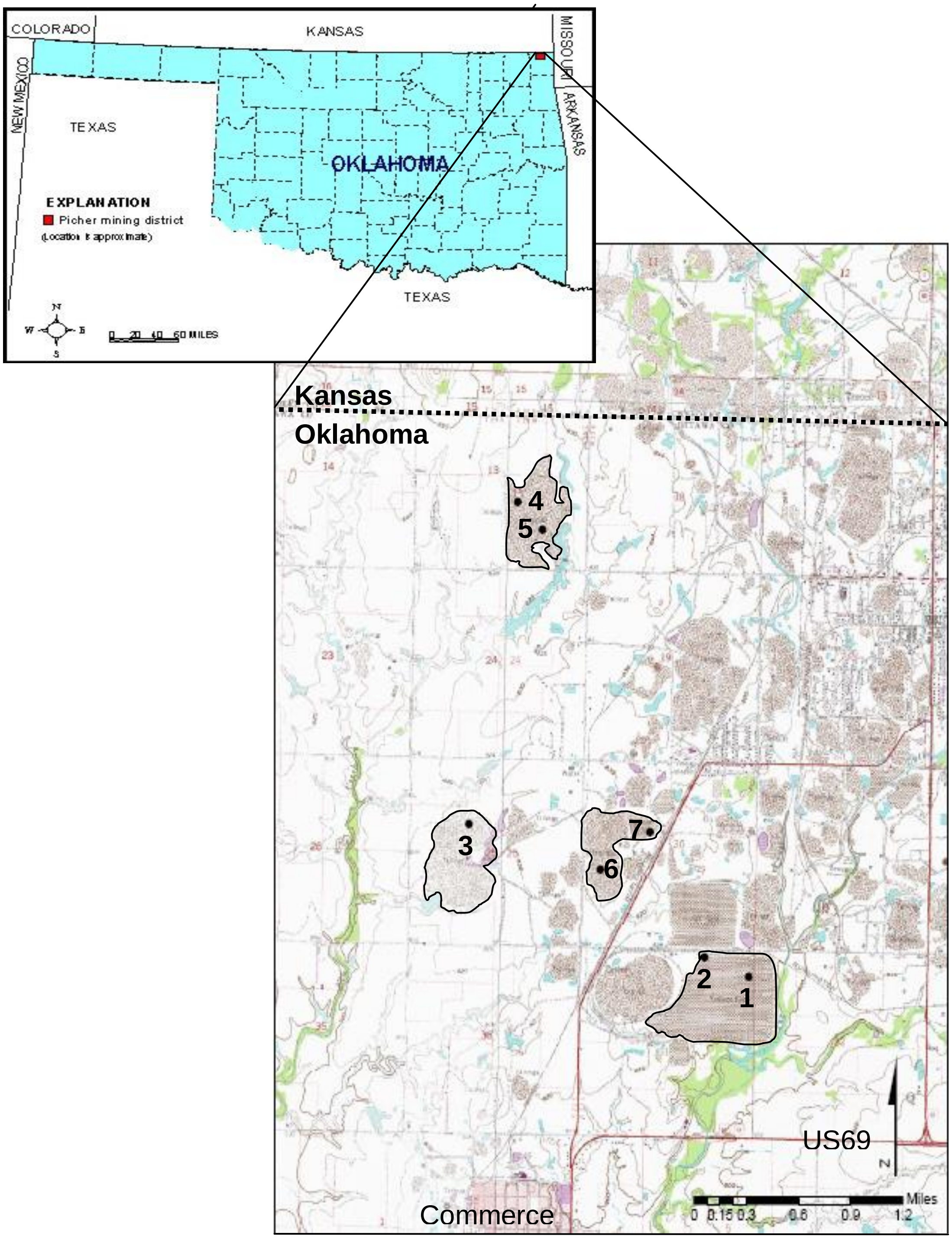

Figure 1. Location of sampled tailings impoundments; individual impoundments are numbered and their boundaries outlined. Base map is USGS 7.5-minute Picher Quadrangle. Smaller map shows location of the Picher Field of the Tri-State Mining District in Oklahoma (USGS 2006; NRCS Data Gateway, 2006).

Physical and Chemical Analyses

Texture of the floatation tailings was determined using the hydrometer method (ASTM, 1998). Air-dried tailings were ground using a soil grinder to break up any large clods, thus obtaining a sample representative of field conditions. Tailings were shaken using a hand operated soil shaker for two minutes and were passed through a series of six sieves (#10, #20, #60, #100, #270 and #325 representing material passing 2000, 850, 250, 150, 53 and 45 μm, respectively). Tailings mass retained on each sieve was recorded and a particle size distribution curve was generated. Bulk density, particle density, and porosity were determined according to standard methods (Tan, 1996).

Nine chemical properties, relevant to vegetation growth, were analyzed (Bradshaw and Chadwick, 1980). Moisture and organic matter content were determined immediately after collection according to Gardner (1996) and Nelson and Sommers, (1996) respectively. Tailings samples were allowed to air dry before further chemical analyses were performed. The pH was determined potentiometrically using a 1:1 (w/v; g/mL) ratio of tailings to deionized water (Thomas, 1996). Specific conductance was determined using a 1:2 (v/v; cm^3/mL) solution of tailings to deionized water (Soil and Plant Analysis Council, 1999). An Accumet AR60 dual-channel meter was used to measure both pH and specific conductance. Cation Exchange Capacity was determined using the ammonium acetate method at pH 7.0 (Tan, 1996).

Floatation tailing samples were also digested according to EPA Method 3050B (EPA, 1996) to obtain total Pb, Cd, Zn, and Fe concentrations and stored at 4°C until analysis. Bioavailable P, Pb, Cd, Zn, and Fe were extracted according to the Ammonium Bicarbonate-Diethylenetriamine pentaacetic acid (AB-DTPA) method and were stored at 4°C until analysis (Amacher, 1996; Kuo, 1996; Loeppert and Inskeep, 1996; Reed and Martens, 1996). Extracts were filtered through 0.45 µm pore size syringe-tip filters before analysis via inductively coupled plasma-optical emission spectroscopy (Varian Vista Pro simultaneous axial-viewed ICP-OES). Plant available NH_4^+ was extracted using the 2M KCl method, and extracts were stored at 4°C until analysis (Mulvaney, 1996) with a Spectronic Genesys spectrophotometer. Plant available NO_3^- was extracted using 0.01 M KCl, and sequentially analyzed with a MetroOhm 761 Ion Chromatograph (Mulvaney, 1996).

To ensure quality of data and reported results, quality assurance analyses were performed following standard methods (Csuros, 1994). Duplicate analyses were conducted on 10% of all samples for organic matter determination, pH, salinity, available nutrients, available metals, and total metals. In addition, blanks, reagent blanks, analytical duplicates, and standard checks were analyzed for 10% of all samples in the determination of CEC, total and available metals, and nutrients. Blanks, duplicates, and standard checks were within 10% of their expected values.

Statistical analyses were performed using Minitab 14 software. Pearson product moment correlation coefficients were determined and regressions were performed to analyze relationships between chemical and physical properties of the tailings impoundment materials.

Results

Physical Properties

The texture of tailings from sites 3, 4, 5, and 6 were all classified as silt loam. The tailings from sites 1 and 7 had the highest proportion of sand-sized particles and were both classified as loamy sand. Tailings from site 2 were classified as sandy loam. The particle size distribution curves of sites 1-7 are shown in Fig. 2.

The bulk densities of floatation tailings from sites 1-7 were all found to range between 1.00 g/cm^3 and 1.47 g/cm^3. These values fell within the range that is considered to be favorable for plant growth of 1.0-1.5 g/cm^3. Particle density ranged from 2.55 to 2.92 g/cm^3. Porosity ranged between approximately 48% and 64%, within the expected range for fine textured soils.

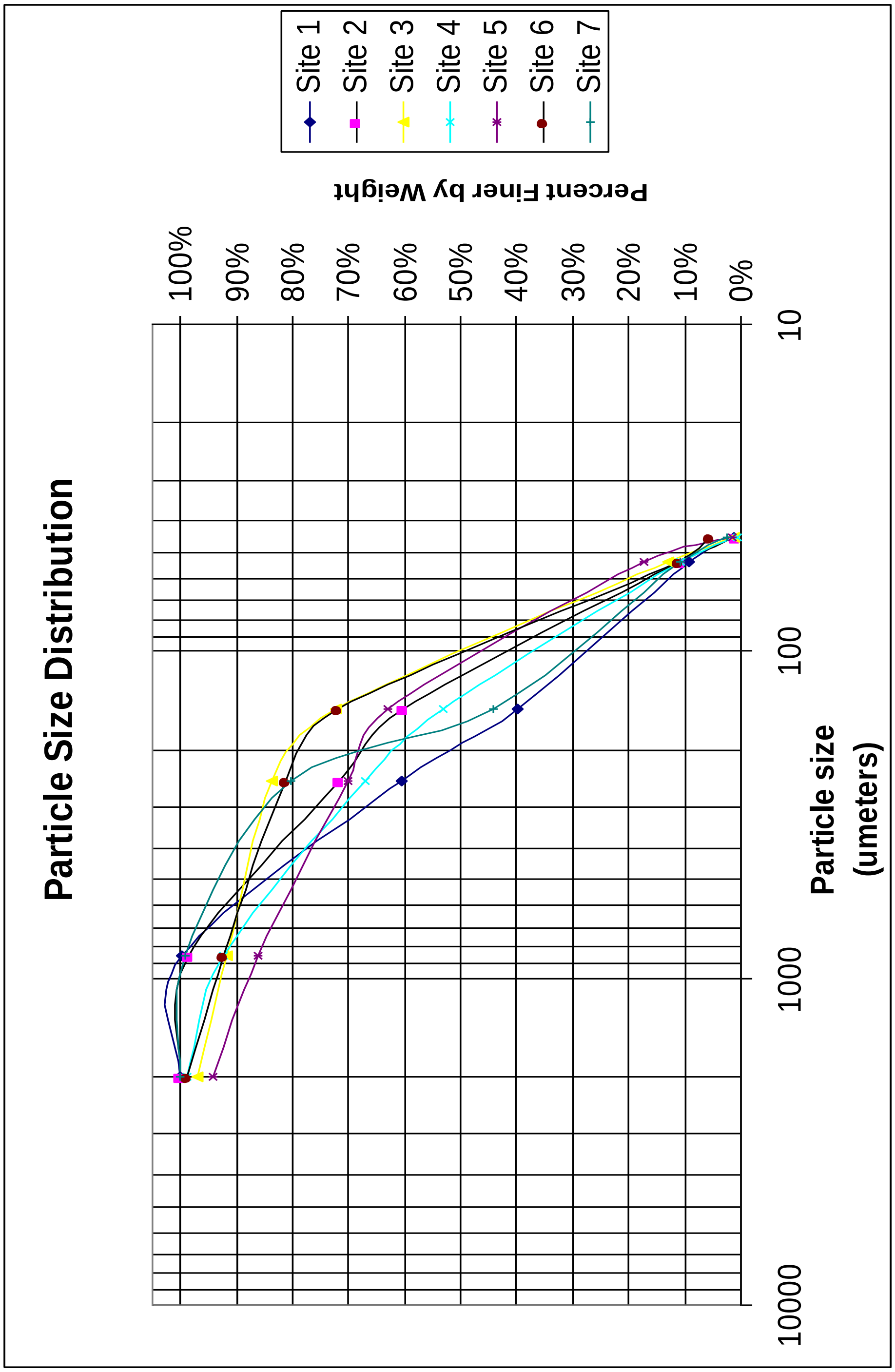

Figure 2. Particle size distribution curves for floatation tailings from Sites 1-7.

Chemical Properties

Table 1 summarizes chemical properties of tailings impoundment materials, showing means of all data (surface and subsurface samples combined). Mean pH values were neutral to slightly alkaline and considered not to be a factor limiting vegetation growth. Mean specific conductance ranged between 0.19 and 2.28 dS/m for surface samples and between 0.59 and 2.14 dS/m for subsurface samples, ranging from slightly to strongly saline. Mean CEC values ranged from 1.02 to 12.27 meq/100g in the surface tailings samples. These values generally fell below the range for normal plant growth of 10-30 meq/100g for naturally developed soils (Bradshaw and Chadwick, 1980). The CEC values, even though low in terms of soil fertility, can largely be attributed to exchangeable Ca^{2+} inherent of the limestone-rich parent material from which the floatation tailings were derived (Dames and Moore, 1993). Mean $\%O.M._{LOI}$ (percent organic matter as loss-on-ignition) values ranged between 0.64% and 2.82% in the surface tailings samples and between 0.61% and 2.50% in the subsurface tailings samples. In general, these values fall at or below the optimal range of 2% to 5% for normal soils (Shu et al., 2005). Even though there was no sign of vegetation growing on sites 3, 4, 5, 6, and 7, the mean $\%O.M._{LOI}$ values were comparable to sites 1 and 2, where some vegetation was present. This could be a result of the loss of materials other than organic matter on ignition, such as volatile salts, structural water within clay minerals and metal oxides, or inorganic carbon (Heiri et al., 2001).

Mean NO_3^- concentrations ranged between 6.08 and 54.77 mg/kg within the surface tailings samples and between 5.13 and 36.00 mg/kg in the subsurface samples. Mean NH_4^+ concentrations ranged between 46.48 and 94.01 mg/kg with the surface tailings samples and between 58.23 and 80.28 mg/kg within the subsurface tailings samples. Overall, mean NO_3^- and NH_4^+ concentrations fell within the range required for normal plant growth (2-20 mg/kg). The chemical additives used in the floatation process, as well as deposition from atmospheric inputs, could be a source of available nitrogen (Gibson 1972; Townsend et al., 1996; Keheley et al., 2003). One additive in particular, sodium aerofloat, contained ammonium, and residual amounts of the aerofloat compound may be adhering to the tailings, with NH_4^+ oxidizing to NO_3^-.

Mean concentrations of available P ranged between 0.14 and 4.57 mg/kg within the surface tailings samples and between 0.16 and 6.92 mg/kg within the subsurface tailings samples. Mean concentrations of available P at sites 3-7 fell below the range needed for normal plant growth (5-20 mg/kg).

Metal Concentrations

Mean concentrations of total and available Cd, Fe, Pb, and Zn in floatation tailings on Sites 1-7 were elevated compared to expected non-impacted soil values (Table 2). Mean total Cd ranged from 22.99 to 123.12 mg/kg, and available Cd ranged from 2.70 to 5.09 mg/kg. Mean total Fe ranged from 3970 to 18,246 mg/kg, and available Fe ranged between 0.49 to 3.87 mg/kg. Mean total Pb ranged from 628 to 13,556 mg/kg, and available Pb ranged from 8.18 to 35.86 mg/kg. Mean total Zn ranged from 4051 to 20,220 mg/kg, and available Zn ranged from 261.60 to 454.50 mg/kg.

Table 1. Chemical properties of floatation tailings; data are presented as mean ± standard deviation, n=6 except sites 1 and 2 where n=8.

	Site						
	1	2	3	4	5	6	7
pH	7.88 ± 0.49	8.23 ± 0.26	7.79 ± 0.09	7.83 ± 0.26	7.72 ± 0.12	7.79 ± 0.23	7.64 ± 0.10
Salinity (dS/m)	0.61 ± 0.58	0.60 ± 0.66	1.47 ± 0.19	1.80 ± 0.32	1.79 ± 0.37	2.21 ± 0.42	1.01 ± 0.21
%O.M. $_{LOI}$	2.64 ± 3.52	3.55 ± 7.01	1.60 ± 0.31	2.44 ± 1.10	2.60 ± 0.26	1.31 ± 0.48	0.80 ± 0.27
Moisture (%)	18.55 ± 11.79	13.33 ± 8.08	20.30 ± 11.79	19.82 ± 5.35	19.29 ± 4.27	15.52 ± 4.85	14.00 ± 5.19
CEC (meq/100g)	3.02 ± 2.99	3.84 ± 4.21	0.99 ± 0.27	1.58 ± 0.61	1.49 ± 0.25	10.50 ± 0.28	1.62 ± 1.20
Ca^{2+} (mg/kg)	2.78 ± 2.76	3.34 ± 3.66	1.39 ± 1.32	1.23 ± 0.34	1.08 ± 0.35	7.52 ± 11.91	3.53 ± 4.11
Mg^{2+} (mg/kg)	0.07 ± 0.08	0.21 ± 0.33	0.09 ± 0.12	0.13 ± 0.07	0.14 ± 0.08	0.20 ± 0.42	0.09 ± 0.15
Na^{+} (mg/kg)	0.15 ± 0.15	0.17 ± 0.17	0.24 ± 0.04	0.20 ± 0.16	0.14 ± 0.05	0.36 ± 0.36	0.19 ± 0.12
K^{+} (mg/kg)	0.03 ±0.03	0.05 ± 0.07	0.03 ± 0.02	0.03 ± 0.01	0.03 ± 0.02	0.02 ± 0.02	0.01 ± 0.01
NO_3^{-} (mg/kg)	10.07 ± 7.08	13.03 ± 8.58	8.46 ± 5.42	25.90 ± 4.14	45.39 ± 27.19	18.76 ± 22.87	6.94 ± 3.69
NH_4^{+} (mg/kg)	59.52 ± 12.35	103.5 ± 62.85	68.17 ± 19.08	64.01 ± 19.13	76.94 ± 42.30	54.80 ± 13.71	57.87 ± 13.96
Avail. P (mg/kg)	7.22 ± 5.14	3.89 ± 0.99	1.36 ± 0.52	1.13 ± 0.61	1.30 ± 0.78	0.66 ± 0.17	0.15 ± 0.13

In general, mean total Cd, Pb, and Fe concentrations were highest on sites 4 and 5. The mean total Zn concentrations were highest on sites 3, 4, and 5, exceeding 20,000 mg/kg. Mean total Cd, Pb, and Zn concentrations were found to be much lower on sites 1 and 2, where some vegetation was established. Mean total Fe concentrations at sites 1 and 2 were similar to those found on sites 6 and 7, indicating that vegetation has not decreased total Fe content of the floatation tailings. Mean total Cd, Fe, Pb, and Zn concentrations did not consistently increase or decrease depending on depth. In addition, the total metals concentrations found in the organic matter layers were similar to the concentrations found within the surface and subsurface samples at sites 1 and 2.

Available Cd, Fe, Pb, and Zn concentrations varied significantly according to site (Table 2). Available Fe and Pb concentrations were highest at sites 1 and 2; available Cd highest at sites 4 and 5; available Zn was highest at sites 6 and 7. The organic matter layers found at sites 1 and 2 appeared to affect the availability of the metals. Available Fe concentrations were much higher in the organic layers than in any of the other surface or subsurface samples on all of the sites. This suggests that organic matter renders Fe more available for biological uptake (e.g., Brady 1990). Concentrations of available Pb were lower in the organic layers than in the surface or subsurface tailings at sites 1 and 2. When compared to sites 3-6, sites 1 and 2 had the highest concentrations of available Pb despite the presence of organic matter and vegetation. Available Cd was highest and available Zn was lowest at sites 4 and 5, respectively. Concentrations of these metals were similar at sites 1, 2, 3, 6, and 7, despite the presence of organic matter and vegetation on sites 1 and 2.

<u>Relationships Between Factors Affecting Vegetation</u>

Significant relationships ($p<0.05$) were found between some of the eight chemical factors analyzed (Table 3). Positive statistically significant relationships ($p<0.05$) were found to exist between percent moisture and available P, percent moisture and $\%O.M._{LOI}$, and salinity and NO_3^-. Regression analyses revealed weak relationships between the chemical factors, and their r^2 values were 21.2%, 33.7%, and 27.1%, respectively. Negative statistically significant relationships ($p<0.05$) were found between pH and percent moisture, pH and salinity, and available P and salinity. Regression analyses also revealed weak relationships between these chemical factors, with r^2 values were 31.0%, 26.9%, and 23.9%, respectively. It is surprising that statistically significant relationships were not found to exist between $\%O.M._{LOI}$ and nutrients, and $\%O.M._{LOI}$ and CEC because organic matter is known to increase available nutrients and CEC within soils (Tordoff et al., 2000). Although a statistically relationship was found between $\%O.M._{LOI}$ and moisture content, regression analysis indicated that without the presence of outlying data points from the organic layers at sites 1 and 2, the relationship was weakened. Although the presence of organic matter is known to increase the moisture holding capacity of soils, moisture content within the non-organic tailings, as well as differences in mineralogy, may be contributing to the weakness of the relationship (Tordoff et al., 2000). A weak significant relationship ($p<0.05$) between pH and moisture was observed in the regression analysis. Although some of the relationships between the chemical factors were found to be statistically significant, none were strong.

Table 2. Total, available, and calculated percent available Cd, Fe, Pb, and Zn concentrations for floatation tailings; data are presented as mean ± standard deviation, n=6 except sites 1 and 2 where n=8.

	Site 1	2	3	4	5	6	7
Total Cd (mg/kg)	22.99 ±7.49	34.09 ±15.00	91.30 ±27.60	115.9 ±58.60	125.1 ±17.68	93.18 ±18.41	83.80 ±31.40
Avail. Cd (mg/kg)	2.70 ±0.75	2.83 ±1.28	2.98 ±0.74	4.78 ±1.86	5.09 ±2.50	2.88 ±1.47	3.89 ±0.98
Avail. Cd (%)	11.7	8.3	3.3	4.1	4.1	3.1	4.6
Total Fe (mg/kg)	4889 ±975	5850 ±872	7179 ±1126	15,849 ±5599	18,246 ±3034	3970 ±784	4469 ±1034
Avail. Fe (mg/kg)	3.87 ±2.69	1.97 ±0.73	1.50 ±0.81	0.71 ±0.31	0.88 ±0.88	0.49 ±0.11	0.74 ±0.24
Avail. Fe (%)	0.08	0.03	0.02	0.005	0.005	0.01	0.02
Total Pb (mg/kg)	870 ±517	628.4 ±121.6	4002 ±683	13,556 ±8872	13,413 ±4386	1726 ±402	1157 ±389
Avail. Pb (mg/kg)	34.22 ±11.69	35.86 ±19.38	17.01 ±5.24	16.59 ±19.10	15.37 ±15.26	8.18 ±4.03	9.57 ±3.78
Avail. Pb (%)	3.9	5.7	0.43	0.1	0.11	0.47	0.83
Total Zn (mg/kg)	4051 ±1093	4839 ±2090	20,059 ±5115	19,748 ±11,161	20,220 ±1326	18,459 ±4904	13,311 ±5873
Avail. Zn (mg/kg)	386.7 ±79.30	369.7 ±148.2	422.2 ±69.50	282.0 ±83.80	261.6 ±67.30	454.5 ±63.2	474.9 ±23.92
Avail. Zn (%)	9.6	7.6	2.1	1.4	1.3	2.5	3.6

Several significant ($p<0.05$) relationships were found between the chemical properties of floatation tailings and the total, available, and percent available Cd, Fe, Pb, and Zn. Table 4 summarizes the Pearson product moment correlation coefficients associated with these relationships. Salinity, nutrients, and pH appeared to have the strongest relationship with total and available metals. However, $\%O.M._{LOI}$, NH_4^+, and CEC did not significantly affect the concentrations of total, available, or percent available Cd, Fe, Pb, or Zn in the floatation tailings.

Table 3. Summary of Pearson Product Moment correlation coefficients between chemical properties of floatation tailings. † indicates significance at the $p<0.05$ level.

	pH	Salinity	Moisture	$\%O.M._{LOI}$	CEC	P	NO_3^-	NH_4^+
NH_4^+	0.19	-0.12	0.08	0.16	0.00	-0.01	0.08	1.0
NO_3^-	-0.16	0.52†	0.22	0.25	-0.08	-0.14	1.0	
P	0.12	-0.49†	0.46†	0.28	0.05	1.0		
CEC	-0.08	0.16	0.04	0.21	1.0			
$\%O.M._{LOI}$	-0.25	0.14	0.58†	1.0				
Moisture	-0.56†	0.24	1.0					
Salinity	-0.52†	1.0						
pH	1.0							

Table 4. Summary of Pearson Product Moment correlation coefficients between chemical properties of floatation tailings and total, available, and percent available Cd, Fe, Pb, and Zn concentrations. † indicates significance at the $p<0.05$ level.

	pH	Salinity	CEC	$\%O.M._{LOI}$	P	NO_3^-	NH_4^+
Total Cd	-0.40†	0.69†	-0.03	0.00	-0.55†	0.48†	-0.12
Total Fe	-0.21†	0.43†	-0.20	0.14	-0.24	0.61†	0.30
Total Pb	-0.27	0.48†	-0.16	0.08	-0.29	0.59†	0.02
Total Zn	-0.37†	0.71†	-0.00	-0.03	-0.53†	0.44†	-0.15
Avail. Cd	-0.15	0.09	-0.09	-0.00	-0.16	0.21	-0.07
Avail. Fe	0.10	-0.60†	0.02	0.37†	0.73†	-0.15	0.06
Avail. Pb	0.50†	-0.38†	-0.12	-0.17	0.55	-0.28	0.00
Avail. Zn	0.16	-0.52†	0.23	-0.53†	0.08†	-0.58†	-0.20
%Avail. Cd	0.43†	-0.68†	-0.01	-0.07	0.61†	-0.31†	0.11
% Avail. Fe	0.13	-0.74†	0.04	0.25	0.71†	-0.34	0.02
% Avail. Pb	0.62†	-0.72†	-0.03	-0.16	0.60†	-0.22†	0.10
% Avail. Zn	0.50†	-0.56†	-0.04	-0.24	0.59†	-0.42†	0.12

Significant correlations ($p<0.05$) were found between salinity and both the total and percent available concentrations of Cd, Fe, Pb, and Zn. Significant correlations ($p<0.05$) were also found between salinity and available Fe, Pb, and Zn, but not Cd. Regression analyses revealed that the total concentrations of metals increased with increasing salinity and that the percent available metals decreased. Although the percent available Fe decreased with increasing salinity, the amount of change was small, less than 0.2%. Pearson product moment correlation coefficients were greatest between salinity and percent available Cd and Zn. Percent available Cd and Zn responded similarly to increasing salinity. It is difficult to speculate if salinity directly results in a decrease in percent available metals. The decrease in the percent available metals may be a result of increased total and decreased available concentrations with increasing salinity. The negative significant correlation coefficients found between salinity and available Fe, Pb, and Zn indicate that increasing salinity may decrease the availability of these metals. These relationships indicate that by decreasing the salinity of floatation tailings, a larger amount of total Fe, Pb, and Zn may become available for biological uptake.

Correlation coefficients (Pearson product moments, $p < 0.05$) between pH and percent available Cd, Pb, and Zn, but not Fe, were significant. Regression analysis revealed a weak relationship between decreasing pH and decreasing percent of the total Cd, Pb, and Zn available for biological uptake. This relationship may be beneficial for initial plant growth and establishment because organic matter additions cause pH to decrease. Addition of organic amendments and vegetation may have the potential to decrease the proportion of total Cd, Pb, and Zn that are available for biological uptake (Ross, 1994; Tordoff et al., 2000).

Correlation coefficients were found to be statistically significant between available P and the percent available Cd, Fe, Pb, and Zn ($p<0.05$). Regression analyses revealed that increasing concentrations of available P significantly increased with the availability of the metals. These regression relationships were found to be weak overall, and were especially weak for percent available Cd, Pb, and Zn ($r^2 <35.2\%$). Although increasing concentrations of available P were not significantly correlated with either total or available Pb, they were significantly correlated with percent available Pb. This correlation is surprising because the formation of hydroxyapatite through additions of phosphate is a widely used method for remediation of Pb-contaminated soils (e.g., Mavropoulos et al., 2002). In this study, there may be a mechanism within the tailings that releases available P while at the same time increasing the availability of metals. Additional research is recommended to determine the specific metal-minerals and forms of P within the Tri-State floatation tailings to determine effects on one another.

Significant correlations ($p<0.05$) were found between NO_3^- concentrations and the total Cd, Fe, Pb, and Zn within the floatation tailings. The regression analyses showed that although there was a statistically significant relationship between NO_3^- and total metals, the relationships were not very strong ($r^2 <37.3\%$). It can be concluded that NO_3^- does not likely control the total concentrations of metals. Similarly, correlation coefficients relating NO_3^- to the percent available Cd, Pb, and Zn were significant but weak. Correlation coefficients were -0.31 and -0.22 for percent available Cd and Pb, respectively. Although the correlation coefficient was -0.42 for percent available Zn, the relationship may have been affected by both an increase in total Zn and decrease in available Zn with increasing NO_3^-. A weak significant relationship was found between NO_3^- and available Zn. As NO_3^- concentrations increased, the concentration of available Zn tended to decrease. Significant relationships were not found between NO_3^- and available Cd, Fe, or Pb.

Discussion

The results of this research study provide many insights into the potential for abandoned tailings impoundments to be revegetated. In general, the physical characteristics evaluated in this study were found to be satisfactory for plant growth and establishment and varied only slightly between sites 1-7. The particle size distributions, along with the textural classifications of the tailings, indicate that the particle sizes that make up the floatation tailings are not unfavorable for establishing vegetation. The texture at each of the sites varied between sandy loam, loamy sand, and silt loam. The presence of silt- and clay-sized particles in the floatation tailings may provide exchange sites for nutrients, increased water holding capacity, and aid in the formation of silt-humus complexes (Krazklewski and Pietrzykowski, 2002). Sites 2, 3, 4, 5, and 6 all contained over 50% silt- and clay-sized particles. This high proportion of small sized particles may make revegetation efforts easier on these sites, due to the ability of smaller sized particles to bind metals and provide exchange sites for plant essential nutrients (Bradshaw and Chadwick, 1980; Ripley et al., 1996; Tordoff et al., 2000).

Bulk density measurements at each of the sites fell within the range needed for normal plant growth without restricting root development, 1.0-1.5 g/cc. Porosity ranged between 48% and 64%. It is expected that due to this porosity, adequate drainage and aeration would occur within the top 40 cm of the floatation tailings (Bradshaw and Chadwick, 1980). Field observations noted that drainage is impeded and moisture is held within the tailings impoundments due largely to the presence of silt- and clay-sized particles and indicating possible stratification.

Of the properties analyzed, pH and moisture content would not likely inhibit growth and establishment of vegetation. Although mean pH values were slightly above the ideal for plant growth (5.0-7.5), they were not too acidic or too alkaline for establishment and growth of most plants (Bradshaw and Chadwick, 1980). The optimal range for pH is between 6 and 7; Table 1 suggests it is not a limiting factor for vegetation establishment and growth on the floatation tailings. Through the accumulation of organic matter and subsequent vegetation establishment, pH will possibly decrease over time As a result, the availability of some plant essential nutrients, such as potassium, will increase, while others may become more limited (Taiz and Zeiger, 1998).

Vegetation is more likely to be inhibited from establishment on tailings impoundments due to the pattern of moisture distribution than the moisture holding capacity. Although the percent moisture within the tailings ranges between 13.3% and 20.3%, the top surface (2 cm) of the tailings remains very dry. Although the data do not show this pattern (likely due to the depth partitioning of samples), it was observed in the field. This pattern of moisture distribution could prevent germination and inhibit natural plant establishment on impoundments without organic matter to increase water retention at the surface. Successful establishment of vegetation on the impoundments with adequate moisture available for germination and root uptake is possible.

Salinity may inhibit plant growth on some of the tailings impoundments. Salinity was much lower at sites 1 and 2, where vegetation was established, than on sites 3 -7. The unvegetated sites were classified as saline, moderately saline, and strongly saline. The presence of undesirable salts may require that salinity tolerant species be planted in vegetation efforts. Non-salinity tolerant deep rooting species may be restricted from growth if soluble salts are leached into the lower layers of the tailings impoundments (Bradshaw and Chadwick, 1980).

In general, the floatation tailings at sites 1-7 had low CEC values. With the exception of site 6, where mean CEC was found to be 10.50 meq/100g, CEC was below 4 meq/100g. The CEC of the floatation tailings fell far below the CEC of a typical prairie silt loam soil of 26 meq/100g (Bradshaw and Chadwick, 1980). The presence of Ca^{2+} from the limestone rich parent materials, rather than K^+ and Na^+, contributed largely to CEC (Table 1). K^+ and Na^+ concentrations were extremely low, and thus the fertility of the floatation tailings can be considered impaired in terms of cation exchange (Dames and Moore, 1993).

The percent organic matter calculated as loss-on-ignition for typical prairie silt loam soils is around 4%. The mean $\%O.M._{LOI}$ at sites 1-7 was 3.55% or lower, falling slightly below the average for soils of the prairie region (Bradshaw and Chadwick, 1980). The organic layers of sites 1 and 2 contained 7.95% and 12.30% organic matter, respectively, due to the presence of vegetation and litter. The lack of organic matter within the floatation tailings will inhibit plant growth because it is needed for healthy nutrient cycling within soils. Organic matter will need to be added to the impoundments in order to establish vegetation.

The concentrations of NO_3^- and NH_4^+ were elevated, given the lack of vegetation within the floatation tailings. Mean NO_3^- ranged between 6.94 and 45.39 mg/kg, and mean NH_4^+ ranged between 54.8 and 103.5 mg/kg. For normal plant growth to occur, both forms of nitrogen should be between 2 and 20 mg/kg. Chemical additives such as sodium aerofloat were used to extract metals from the ore before the floatation tailings were placed into the impoundments (Keheley et al., 2003). Ammonium-containing chemicals used during the milling process may remain bound to the tailings and thus provide the substrate with a supply of NH_4^+ and NO_3^-. Regardless of the source, the NO_3^- and NH_4^+ available within the tailings could be beneficial for plant growth, given that other conditions are not restricting the cycling of these nutrients.

Although levels of NH_4^+ and NO_3^- fell within the range for normal plant growth, available P levels were very low on the unvegetated tailings impoundments. Between 5 and 20 mg P/kg is desirable for normal plant growth (Bradshaw and Chadwick, 1980). Plant available P ranged between 0.15 and 1.36 mg/kg on the unvegetated impoundments and, at sites 1 and 2, mean available P was 7.22 and 3.89 mg/kg, respectively. The lack of available P on the unvegetated tailings impoundments will likely restrict plant growth and establishment.

Both total and available Cd, Fe, Pb, and Zn were elevated in the floatation tailings. Sites 4 and 5, particularly, contained the highest concentrations of these metals. Mean total Cd, Pb, and Zn were much lower on sites 1 and 2 where vegetation was present than on sites 3-7 which remained barren. Elevated concentrations of total and available Cd, Pb, and Zn are likely to inhibit vegetative growth on these sites because these metals interfere with normal plant physiological functions (Bradshaw and Chadwick, 1980; Krazklewski and Pietrzykowski, 2002; EPA, 2006). Although these sites contain elevated concentrations of heavy metals, successful revegetation at sites 1 and 2, which contain tailings of similar metals concentrations, holds promise for reclamation of sites 3-7. Plant growth and establishment may be successful on these tailings impoundments through the addition of organic matter and nutrients.

Although statistically significant relationships were found to exist between some of the eight chemical factors, regression analyses revealed that these relationships were weak. The presence of a statistically significant relationship between the chemical properties did not indicate a causal relationship. Further research into the behavior of the chemical properties of floatation tailings is suggested to more fully understand the effects on the growth of vegetation.

Overall, the relationship between the salinity of the floatation tailings and the concentrations of Cd, Fe, Pb, and Zn was the strongest. Although the total metals concentrations tended to increase with increasing salinity, the percent available tended to decrease. This may be an important relationship for reclamation managers to examine further to explore if a decrease in salinity of the tailings through revegetation or organic matter additions may actually increase the proportion of the total metals that become available for biological uptake. It can be speculated that by changing salinity, the mobility or availability of the metals may be altered.

The relationships between available metals and nutrients, though not very strong, are of interest. They suggest that there may be a link between the addition of nutrients and the concentrations of metals available for biological uptake. Although the addition of P seems to point to an increase in available Pb and Fe, there are many interaction effects within the tailings environment that may decrease the availability of these metals. The same is true for NO_3^-. Although additions of NO_3^- seem to reduce the amount of available Zn, the relationship is weak and therefore cannot soundly be used to predict metals behavior.

It is difficult to determine whether or not single factors can be used as predictors of mobility and availability of heavy metals in a complex substrate such as floatation tailings. It is likely that interactions between these chemical properties, along with soil processes such as weathering, are controlling the availability of Cd, Fe, Pb, and Zn rather than individual variables (Ross, 1994).

The results of this study revealed that tailings impoundments are heterogeneous entities that cannot be generically characterized in terms of chemical properties. The physical characteristics of the floatation tailings were consistent between sites 1-7. This trend may have been an artifact of the sampling procedure as only one composite sample was collected from each site for physical analysis. On the other hand, the chemical characteristics were quite variable between sites 1-7, and variability within each site was substantial. Tailings impoundments were used for several types of chat and tailings processing and were operated at different time periods (Keheley et al., 2003). These factors, coupled with the natural variability of the source geologic material, have contributed to the formation of heterogeneous site conditions.

This study reinforces the need for comprehensive research into the site specific properties of derelict land areas before revegetation efforts are implemented. To achieve maximum potential for successful reclamation, site specific conditions should be considered. More research is suggested to further evaluate these sites for their potential for revegetation. However, it can be concluded that given available nutrients and a source of organic matter, vegetation has the potential to successfully grow on tailings impoundments within the Tri-State Mining District.

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