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Soil health as a proxy for long-term reclamation success of metal-contaminated mine tailings using lime and biosolids

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Abstract

Mine lands games contaminted with heavy metals pose environmental risks, and thus reclamation is paramount for improving soil, plant, animal, and ecosystem health. A metal-contaminated alluvial mine tailing, devoid of vegetation, received 224 Mg ha^{-1} of both lime and biosolids in 1998, and long-term reclamation success was quantified in 2019 with respect to soils, plants, and linkages to animals. Reclamation success was quantified using the Soil Management Assessment Framework (SMAF), in conjunction with bioavailable (0.01 M $CaCl_2$ extractable) and plant-available (Mehlich-3 extractable) soil metal concentrations, X-ray absorption spectroscopy, plant metal concentrations, and plant quality characteristics. Results showed that all soil indicators were improved in successfully-reclaimed areas as compared to on-site degraded areas, including

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Appendix A. Supplementary data
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increases in soil aggregate stability, pH, plant-available P and K, soil organic C, potentially-mineralizable N, microbial biomass C and β-glucosidase activity and decreases in soil bulk density and electrical conductivity. Of indicators, unitless soil health scores were assigned based on the SMAF, with data suggesting that bulk density, wet aggregate stability, potentially-mineralizable N, microbial biomass C, pH, and electrical conductivity should be monitored in the future. The long-term effects of lime and biosolids application have improved soil physical, biological, and overall soil health. Plant metal concentrations have decreased by an order of magnitude since early reclamation, with most plant metal concentrations being tolerable for domestic livestock consumption. From an animal health perspective, feeding grasses from this site during latter parts of a growing season may need supplemental feed to provide greater protein and energy content, and to reduce potentially-harmful Cd concentrations from food chain bioaccumulation. However, a health concern exists based on soil bioavailable Cd and Zn concentrations that exceed ecological soil screening levels. Still, plants have stabilized the soil and acidity remains neutralized, leading to long-term improvements in soil health, with overall improved ecosystem health.

Graphical Abstract

Keywords

Soil management assessment framework; Ecological soil screening level; Plant and animal health; Potentially-mineralizable N; β-glucosidase activity; Plant-available metals; Microbial biomass C; Bioavailable metals; Soil reclamation; Aggregate stability

1. Introduction

Lands that have been degraded due to historic mining operations have led to serious soil, plant, animal, human, and environmental health threats. These threats are not inconsequential. There are as many as half a million abandoned mines documented across the United States alone (U.S. Department of Interior, Bureau of Land Management, 2023), and an estimated, undocumented 400,000 mining features yet to be accounted for on U.S. federal lands (United States Government Accountability Office (GAO); 2020). While a majority of these cases are characterized by soils that are incapable of supporting plant life, a subset poses additional concerns due to the presence of potentially toxic metals and/or acidity. The GAO (2020) has identified at least 140,000 abandoned hard rock mining features, with over 22,000 of these potentially posing risks to human and animal health from harmful substances exposure. Acidity, the result of oxidation of sulfur-bearing minerals, in combination with heavy metals are of greatest concern as acidic soil conditions increases the solubility of most metals.

In addition to toxic metal concentrations, these mine-affected sites threaten plant health via soils that are acidic to the point where plants cannot adequately thrive. Subsequently, these mine-affected sites often contain soils that are low in organic carbon (C), the energy source for microorganisms, thus limiting their activity that should effectively force nutrient cycling, turnover, and ultimately support below- and above-ground community structure and function. Without proper soil functionality, plants do not thrive, leaving the soil bare, allowing for further environmental degradation such as erosional losses into sensitive water bodies and the subsequent degradation of aquatic habitats and species therein. For example, Brown et al. (2005) amended acidic (pH 3.5) alluvial mine tailings with 224 Mg ha^{-1} of lime and 224 Mg ha^{-1} of biosolids and studied reclamation success on plant, earthworm, microbial function, small mammal, and fish survivability. Amended tailings led to 71–88% survivability of perennial ryegrass, a 10–100% survivability of earthworms, and >90% survivability of fathead minnow; in unamended tailings, survivability of plants, earthworms, and fish were 0 to <10%. Other recent studies, whereby acidic mine soils have been amended with lime and organic amendments, have shown similar results (e.g., Brown et al., 2007, 2014; Fernández-Caliani et al., 2021; Trippe et al., 2021; Lwin et al., 2018; Asensio et al., 2013). It is of paramount importance in these degraded ecosystems that future environmental degradation be avoided by 1) reducing soil heavy metal bioavailability and acidity, 2) increasing soil organic C via amendment application, and 3) monitoring long-term reclamation success.

Through a combination of points one through three above, a means by which long-term reclamation success can be quantified is through the use of soil health metrics that measure alterations in soil physical, chemical, and biological characteristics. Stutler et al. (2022) used the U.S. Natural Resources Conservation Service's Soil Quality Test Kit to quantify coal mine land reclamation success 2–32 years since reclamation. The authors found that bulk density (Bd) was lower, and infiltration, wet aggregate stability, and soil respiration were greater, in older versus younger reclaimed sites. Adeli et al. (2013) also looked at alterations in soil health parameters as a function of time since coal mine land reclamation (0, 2, 7, or 12 years since reclamation). Similar to Stutler et al. (2022), Bd decreased and wet aggregate stability, microbial biomass C, and organic C increased with time since reclamation. Adeli et al. (2013) noted that soil health indicators reached levels like those found in undisturbed soils within 7–12 years following reclamation. Fernández-Caliani et al. (2021) focused on a heavy metal-affected (total Pb, Cu, and Zn concentrations ranged from 2160 to 4080, 298 to 632, and 174–1040 mg kg^{-1}, respectively) mine land site that, prior to reclamation, did not support vegetation due to excess acidity (pH 2.6). Fifteen years post reclamation (with composted biosolids), soil structural stability, soil organic C, nutrient status, and microbial growth were all significantly improved, and plant communities thrived. Mukhopadhyay et al. (2014) evaluated coal mine land reclamation success at 2-, 5-, 7-, and 17-years post-reclamation. Soil Bd decreased and soil organic carbon (C), available N and

P, cation concentrations, dehydrogenase activity, microbial biomass C, and soil respiration increased over time. In addition, reclamation supported plant communities. Brown et al. (2014) focused on heavy metal affected (total Cd, Pb, and Zn concentrations ranged from 43 to 53, 1100 to 3400, and 9700–10000 mg kg^{-1}, respectively) mine land reclamation success between 10- and 14-years post reclamation, comparing 112 Mg ha^{-1} biosolids + 24 Mg ha^{-1} lime or 336 Mg ha^{-1} biosolids + 48 Mg ha^{-1} lime to a control. The authors found significant decreases in Bd, and increases in water held in soil and total C and N concentrations with the greatest in both biosolids + lime treatments as compared to the control.

Others have combined soil health metrics into scoring functions and subsequent frameworks that quantify soil health using "the greater an index value, the healthier the soil" approach. For example, in the Mukhopadhyay et al. (2014) study, the authors placed soil metrics data into a self-developed mine soil quality index tool (on a scale from 0 to 1), showing the 2-year-old reclaimed site had a lower index value as compared to the 17-year-old reclaimed site (0.22 versus 0.67, respectively). In a subsequent study, Mukhopadhyay et al. (2016) developed a soil health index (on a scale from 0 to 1) based on a principal components analysis approach, showing that soil health was greater in soil surface (~0.53) as compared to the subsurface (~0.50), and that reclaimed sites had between 52 and 93% greater soil health index values as compared to non-reclaimed sites. Asensio et al. (2013) developed a soil health index (on a scale from 0 to 100), also based on principal components analyses, showing that the soil health index improved from untreated mine tailings (0.0) to mine tailings treated with a combination of biosolids and papermill sludge (52.6). All of these works utilized soil health indices developed specifically for particular studies. However, it might be useful to utilize pre-existing soil health frameworks to quantify soil health for mine land reclamation success.

Of the major pre-existing soil health frameworks utilized in the U.S. (Haney Soil Health Test (Haney et al., 2008, 2012); Cornell Assessment of Soil Health (Cornell College of Agriculture and Life Sciences, 2024); Soil Management Assessment Framework (SMAF; Andrews et al., 2004)), to our knowledge only the SMAF has been used, and once only, to quantify soil health changes for mine land reclamation. SMAF considers soil quality, not soil health, but the two can be considered interchangeable for our purposes. Ruiz et al. (2020) utilized the SMAF to determine reclamation success in an open-pit limestone mine, with reclamation occurring via the use of backfilling with overburden. Comparing 3 to 7–20 years since reclamation occurred, the SMAF showed that the soil health index score significantly changed from 0.70 to 0.67 to 0.88, respectively, with the 20-year location having a greater soil health index score compared to native soil (0.69; all on a scale from 0 to 1). It may prove useful to quantify long-term reclamation success, and thus provide continued assurance against environmental degradation, in heavy metal contaminated mine soils using the SMAF. This first attempt to use the SMAF for such a purpose helps lay the foundation for including soil aspects currently not included in the SMAF, including heavy metal bioavailability and/or plant availability. Ultimately, this could lead to a universal program used for mine land reclamation that is built upon the backbone of the SMAF, thus reducing the need for individuals to create their own soil health protocols. The objective of the current study was to quantify long-term (>20 years) alluvial mine tailing reclamation success using a combination of the SMAF, bioavailable (i.e., 0.01 M $CaCl_2$

extractable) and plant-available (i.e., Mehlich-3 extractable) soil heavy metal concentrations, plant heavy metal concentrations, and measures of forage quality. We hypothesized that long-term alluvial mine tailing reclamation success can be directly tied to improvements in soil physical, chemical, and biological properties, and that reclaimed soils will have greater soil health index scores as compared to degraded soils.

2. Materials and methods

An alluvial mine tailings deposit (sandy loam soil texture) near Leadville, Colorado, USA (latitude 39.204347 N longitude −106.352753W; elevation of 2940 m; 31 cm of annual precipitation; annual temperatures can range from −39 to 30 °C), under the U.S. Superfund National Priorities List (NPL), was amended in 1998 to a depth of 20 cm with 224 Mg ha^{-1} of agricultural lime (Calco, Salida, Colorado, USA) and 224 Mg ha^{-1} anaerobically digested biosolids (Denver, Colorado, USA wastewater treatment facility). The original tailings had a pH of 3.4, had an organic C content ranging from 17 to 26 g kg^{-1}, contained total Cd, Pb and Zn concentrations of 16, 3170, and 1730 mg kg^{-1}, respectively, and contained varying extractable Cd (~1–10 mg kg^{-1}), Pb (1–100 mg kg^{-1}), and Zn (90–900 mg kg^{-1}) concentrations (Brown et al., 2005). Additional site characterization and amendment addition information can be found in Brown et al. (2005). This approach was used to restore all of the alluvial tailings within the designated NPL site.

The site was revisited in mid-August 2019. The 2019 study area (Fig. 1) was approximately 1 ha in size. Based on grid sampling and kriging, utilizing techniques performed by Freeman et al. (2008) and Freeman (2008), four 20-m transects were chosen to represent the entire area that contained approximately equal soil pH values yet varying extractable metal concentrations. The site was dominated by slender wheatgrass (*Elymus trachycaulus*), western wheatgrass (*Pascopyrum smithii*), and tufted hairgrass (*Deschampsia cespitosa*).

2.1. Plant sampling and analysis

At 5 m intervals along each 20-m transect, above-ground biomass was collected at a height of 5 cm above the soil surface within a 0.5 m^2 quadrat. Twenty total plant samples were collected across the site. Plant samples were placed in paper bags, returned to the laboratory, dried at 60 °C for at least 72 h, and then weighed. Plant samples were then ground, digested using concentrated HNO_3 and 30% H_2O_2 (Huang and Schulte, 1985), and analyzed for metal concentrations using inductively coupled plasma-optical emission spectroscopy (ICP-OES; Optima 8300, PerkinElmer, Inc., Waltham, MA, USA). Plants were also analyzed for crude protein, acid detergent fiber, and neutral detergent fiber using near-infrared spectroscopy (NIRS) analyses (SpectraStar 2600 XT, Unity Scientific/KPM Analytics, Westborough, MA, USA). Relative feed value, an index to compare forage quality to that of alfalfa, was determined based on calculations presented by McFarland et al. (2007), and rearranged for simplicity as:

$$\text{Relative Feed Value (unitless)} = ((88.9 - (0.779 \times \%\ \text{Acid Detergent Fiber})) * (120 / \%\ \text{Neutral Detergent Fiber}))/1.29$$

[Equation 1]

where 88.9, 0.779, and 120 are empirical constants.

2.2. Soil sampling and analysis

At 5 m intervals along each 20-m transect, one soil sample for Bd and gravimetric moisture content was collected using a 0.9 cm diameter push probe to a depth of 15 cm. Twenty soil samples were collected, five per transect. Soil was placed into a tin can, immediately weighed, then oven-dried at 105 °C for 24 h and weighed again. At each sampling point, a 0–15 cm depth soil sample was obtained with a tile spade, with approximately 2 kg of soil collected. Soils were placed in a 3.78 L Ziploc bags (SC Johnson & Son, Inc., Racine, Wisconsin, USA) and returned to the laboratory. Five seeps were located on site, which were considered a representation of site conditions prior to reclamation, because finding true background conditions in this area was not an option. Seep areas, where groundwater had found its way to the soil surface, were void of plants and appeared to be either wet and/or showed signs of salt precipitates on the soil surface. All seep soils were collected in the same fashion as those along the transects. A total of twenty-five soil samples were collected across the site.

Once returned to the laboratory, soils were entirely passed through an 8-mm sieve, and then a 150 g subsample of field-moist soil was placed into a separate Ziploc bag and stored at 4 °C. Approximately 300 g of the field-moist 8-mm sieved soil was passed through a 2-mm sieve and then air-dried. Once air-dried, approximately 10 g of the 2-mm sieved soil was powder ground. The remaining 8-mm field-moist soils were allowed to air dry.

Soil metal bioavailability (Ippolito et al., 2017; Pueyo et al., 2004) was determined by weighing 3.00 g of 2-mm air-dried soil into a 50 mL centrifuge tube, adding 30 mL of 0.01 M $CaCl_2$, shaking at 120 rpm for 2 h, centrifuged at 500×g, filtered through a 0.45 μm membrane filter, and then analyzing the filtrate for Cd, Cu, Fe, Mn, Pb, and Zn determined via ICP-OES. In agroecosystems, plant-available metal concentrations are often determined using a Mehlich-3 extraction (Mehlich, 1984). In the case of the current study, the Mehlich-3 extraction procedure was also followed, with Cd, Cu, Fe, Mn, Pb, Zn, and S concentrations determined via ICP-OES. For comparison sake, the 0.01 M $CaCl_2$ and the Mehlich-3 extraction procedures were both utilized, so as to ultimately choose which extractant might be utilized for developing a future SMAF for mine land soils. Lastly, both Mehlich-3 and 0.01 M $CaCl_2$ concentrations were compared to US EPA ecological soil screening levels (Eco-SSLs; US EPA, 2003, 2005a,b, 2007a,b,c) which are US EPA defined metal concentrations that are protective of birds and mammals that may come in contact with or consume biota that live in or on this soil.

Various sieved soil fractions were subjected to soil characterization following steps outlined for the SMAF by Andrews et al. (2004). Briefly, SMAF development essentially utilized a decision support system to evaluate and reduce a plethora of soil indicators into a minimum dataset for soil quality quantification (Andrews et al., 2004). We consider the soil quality quantification of Andrews et al. (2004) to be the same as soil health quantification, and subsequently will use the term “soil health” instead of “soil quality” when referred to SMAF. Specifically within SMAF, eleven soil characteristics are quantified, including Bd and wet aggregate stability (physical soil health indicators), pH and electrical conductivity (EC; chemical soil health indicators), plant-available P and K (nutrient soil health indicators), Potentially-mineralizable N (PMN), Microbial biomass C (MBC), β-glucosidase activity (BG), and SOC (biological soil health indicators), and clay content as a dependent variable that influences soil physical, chemical, and biological characteristics. Once collected, each indicator is scored on a scale from 0.00 to 1.00, with 0.00 being “worst” and 1.00 being “best”, with indicator scores based on either a “more is better” (e.g., SOC), “less is better” (e.g., Bd), or “somewhere in the middle is better (e.g., plant-available P) approach. Indicator scores are weighted for soil physical, chemical, nutrient, biological, and overall soil health scores, again on a scale from 0.00 to 1.00. More detailed information can be found in Andrews et al. (2004), while a detailed description of soil indicator analysis is provided in Supplemental Table S1.

2.3. X-ray absorption spectroscopy (XAS) measurement and analysis

Zinc XAS was collected at the Materials Research Collaborative Access Team beam line 10-BM for Zn (Kropf et al., 2010), Advanced Photon Source (Argonne National Laboratory; Cd and Pb XAS were not collected as their concentrations were below XAS detection limits). The storage ring operated at 7 GeV and in top-up mode and on both 10-BM and 10-ID, a liquid N2-cooled double crystal Si(111) monochromator was tuned to select incident photon energies and a platinum-coated mirror was used for harmonic rejection. Samples were prepared for XAS by grinding in agate mortar and pestle, mixed with polyvinylpyrrolidone as a binder, hand-pressed into a 1-cm pellet, and mounted on Kapton tape for measurement.

Zinc XAS data collection at 10-BM was measured at the Zn K-edge (9659 eV) using a 4-element Vortex fluorescence detector with several layers of aluminum foil shield to suppress fluorescence from other elements (i.e., Fe) in the samples. For each sample, three to five scans were collected in both transmission and fluorescence with simultaneous measurement of Zn metal foil down beam from sample in transmission. Energy was calibrated by shifting spectra eV to match first derivative inflection point of Zn foil to be 9659 eV (Beak et al., 2009).

The spectra were analyzed by linear combination fits with Zn standard spectra (Manceau et al., 2002). Spectra were fit in 1st derivative XANES LCF over an energy range −20 to 30 eV from e0, constraints of all weights between 0 and 100% and force weights to sum to 100%. Zinc standards were collected at sector 10-BM during the same or previous visits and included: Zn adsorbed (ads.) ferrihydrite, Zn ads. goethite, Zn ads. hematite, Zn ads. humic acid, Zn ads. montmorillonite, $ZnSO_4$, and Zn–Al layered double hydroxide (Zn–Al LDH). All standard spectra can be found in the supplemental information Figure S2.

2.4. Study design and statistical analysis

Each point along one of the four individual transects was considered a replicate, and the area represented by the transect was considered a treatment. This was based on data from Freeman et al. (2008) and Freeman (2008) who showed that soil pH was approximately the same across the entire site yet soil heavy metal concentrations varied across the site. The transects were placed to represent varying heavy metal conditions on-site (e.g., Fig. 1, upper right inset picture, with areas labeled as 1 through 4 in Fig. 1; further information can be found in Freeman, 2008). Based on Freeman et al. (2008) and Freeman (2008): Southeast Area 1 represented neutral pH yet with the greatest Mehlich-3 metal concentrations; Southwest Area 2 represented neutral pH yet with the second greatest Mehlich-3 metal concentrations; Northwest Area 3 represented neutral pH yet with the third greatest Mehlich-3 metal concentrations; and Northeast Area 4 represented neutral pH yet with the lowest Mehlich-3 metal concentrations. All five seep sampling points on-site were considered as a separate treatment and were used to represent pre-reclamation site characteristics as, again, finding true background conditions in this area was not an option. Data were analyzed using the Proc GLM in SAS version 9.4 (SAS Institute, 2016) at a $p < 0.05$. When significance was present, a Tukey adjusted pairwise comparison was used to identify differences across the reclaimed site. When required to meet the conditions of both normality and homoscedasticity for constant variance, data were transformed. However, all presented data are untransformed.

3. Results and discussion

3.1. Soil health

Soil physical, chemical, nutrient, and biological indicator concentrations are presented in Table 1. Significant differences existed for every soil indicator, with seeps having the least favorable characteristics. For example, field locations 1 through 4 had lower Bd and electrical conductivity, and greater aggregate stability, pH, plant-available P and K, SOC, PMN, MBC, and BG activity as compared to seep areas. If seep areas represent pre-reclamation conditions, then reclamation of this alluvial mine tailing with lime and biosolids is successful solely on soil health indicators alone. Previously studied mine land reclamation success, as a function of similar or identical soil indicators, has been documented by a number of scientists (Stutler et al., 2022; Fernández-Caliani et al., 2021; Mukhopadhyay et al., 2014; Adeli et al., 2013). From a long-term mine land reclamation success point of view, the single-most important soil indicator might be SOC, as SOC feeds microorganisms that force nutrient cycling and turnover (e.g., likely expressed as increases in PMN, MBC, and BG activity). Mukhopadhyay et al. (2014) observed a similar response, noting that long-term SOC increases were due to leaf litter accumulation, decomposition, and the formation of humus. In the current study, biosolids borne-C likely provided the initial organic C stock to begin nutrient cycling and turnover, and in conjunction with lime to raise pH, supported above-ground plant growth (described below) that contributed long-term litter accumulation and decomposition, and ultimately long-term increases in on-site SOC.

The SMAF utilizes scoring functions to convert soil health indicator data into unitless scores from 0.00 to 1.00, with 0.00 and 1.00 being considered “worst” and “best”, respectively; SMAF indicator scores are presented in Table 1. Based on indicator concentrations and SMAF algorithms, significant differences existed between field locations for Bd, wet aggregate stability, EC, plant-available K, PMN, and MBC. Reclamation success appears to be driven by these six indicators, as field locations 1 through 4 tended to have significantly greater (i.e., better) indicator scores as compared to seep areas. Asensio et al. (2013) focused attention on developing a soil health index for mine tailings, showing that among other indicators, Bd, wet aggregate stability, MBC were also important for describing soil health. Mukhopadhyay et al. (2014) developed a scoring function to quantify mine land reclamation success. Their important indicators included SOC, CO_2 respiration, dehydrogenase enzyme activity, the percent of coarse soil fraction, moisture content, and base saturation. Mukhopadhyay et al. (2016) also developed a mine land soil quality index, showing that pH, EC, SOC, plant-available P, Ca, S, dehydrogenase enzyme activity, and the coarse soil fraction were key indicators for quantifying soil health in relation to improvements in above-ground plant biomass.

Within SMAF, the indicator scores are weighted into soil physical, chemical, nutrient, biological, and an overall soil health score. Fig. 2 shows that lime and biosolids application to this heavy metal containing alluvial mine tailing has been successful in the long-term (>20 years) with respect to improving soil: 1) physical health (driven by improvements in Bd and wet aggregate stability; $p < 0.001$); 2) biological health (driving by improvements in PMN and MBC; $p = 0.033$); and thus 3) overall soil health ($p < 0.001$). Importantly, these data suggest that of the set of soil health indicators monitored, focusing at the very least on Bd, wet aggregate stability, PMN, and MBC into the future could be followed to reduce overall monitoring costs while maintaining assurance of long-term reclamation success. It is equally important to note that soil chemical health was not significantly different across on-site locations due to the combined pH and EC indicator scores negating each other within the SMAF. Yet, because this site was originally acidic and that salt precipitates can occur within on-site seeps over time, soil pH and EC should also be used as indicators of soil health and reclamation success. Moreover, the approach of using the SMAF in terms of quantifying mine land reclamation success, based solely on indicators currently within SMAF, can be compared to past observations from other researchers who developed their own soil health framework approach. Instead of deriving specific frameworks for a specific mine land location, the SMAF may be used across mine land locations in the future. This could potentially reduce the time necessary to derive reclamation solutions.

3.2. Soil 0.01 M $CaCl_2$, Mehlich-3 extractable elements, and XAS

The major impetus for quantifying soil health, using the SMAF or other soil health protocols, works well for agroecosystems. However, these soil health protocols lack heavy metal bioavailability or plant availability components necessary for quantifying reclamation success in heavy metal contaminated lands. Heavy metal scoring functions should eventually be built into the SMAF in order to use this framework for heavy metal contaminated land reclamation purposes. Regardless, understanding how these components act in systems such as that studied here may eventually lead to the addition of this information into the SMAF for mine land reclamation. Bioavailable and plant available heavy metals, as a function of 0.01 M $CaCl_2$ or Mehlich-3 extractions, respectively, are presented in Table 2. When significance was present, successfully reclaimed areas (e.g., field locations 1 through 4) always had lower 0.01 M $CaCl_2$ and Mehlich-3 metal concentrations, as compared to seeps, likely due to long-term effectiveness of lime and biosolids application. An identical response was noted by Brown et al. (2005) for this site only one to two years following reclamation activities. Reductions in bioavailable heavy metal concentrations with remedial actions have been equated to conversion of metal speciation to less soluble phases (e.g., the formation of metal-carbonate or metal-oxyhydroxide phases, or reactions with surface functional groups

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(e.g., Yuan et al., 2011; Ippolito et al., 2012)). Regardless, bioavailable and plant-available heavy metal reductions, over time, could be equated to improvements in overall soil health and thus should be taken into account in soil health quantification protocols. Indeed, Asensio et al. (2013) proved that, in addition to other biogeochemical parameters, 0.01 M $CaCl_2$ extractable Mn and Zn were key metal parameters needed to assess soil health in mine impacted soils. Furthermore, understanding the forms in which metals accumulate in mine impacted soils may shed light on their environmental impact.

Thus, XAS was performed on soils to identify and quantify the relative abundances of Zn species, with results summarized in Fig. 3 (linear combination fitting analyses is presented in Table S2, and Zn K-edge XANES spectra are presented in Figure S1). Again, XAS was only performed on Zn as the other metals present were below the limit of detection using XAS. Zinc in soils is preferentially bound to mineral surfaces rather than to organic matter as observed in our XAS results. All samples contained a combination of Zn either adsorbed to iron oxides (Zn ads ferrihydrite, Zn ads goethite), to clay minerals (Zn-montmorillonite), or a precipitated Zn–Al layered double hydroxide (LDH). Under certain conditions, Zn can form a Zn–Al LDH precipitate by reacting with aluminum minerals in the soil, yet this requires a neutral pH. Given this field site's low initial pH prior to reclamation, this presence of this phase was likely a result of lime amendment. Zn–Al LDHs is highly insoluble and highly stable at surface environmental conditions once they are formed, and thus its presence suggests great long-term sequestration and remediation success. Iron oxides are preferential adsorption surfaces for Zn in soils, with the formation of Fe–Zn mineral phases common. Several field locations had Zn adsorbed to montmorillonite clay; this phase may be considered exchangeable and thus plant available as compared to Zn bound to Fe oxides and precipitated as Zn–Al LDH, both of which bind Zn via inner sphere complexation (i.e., relatively strong bonding as compared to Zn in the exchangeable phase). Plant-available Zn concentration is not a part of SMAF, and thus in heavy metal contaminated systems it is important to fully quantify metal presence and forms to assess soil health (e.g., Asensio et al., 2013). On average, seep field locations (i.e., 5A-E) contained 10% more Zn–Al LDH than other field locations. Two seep locations contained Zn adsorbed to montmorillonite (i.e., exchangeable Zn), while seep location 5E contained $ZnSO_4$. The presence of $ZnSO_4$ in location 5E was potentially a function of relatively low soil pH (5.17; data not shown) and the increased presence of S; Mehlich-3 extractable S concentrations in seeps were significantly greater than all other sampling locations (Table 2). The greater exchangeable Zn found in seep areas could have increased Zn salt and LDH precipitation. Furthermore, seeps were more acidic and contained higher EC values than all other sampling locations (Table 1). A lower pH and higher total salinity could promote increased exchange of Zn, the formation of Zn salts (i.e., $ZnSO_4$), and result in greater 0.01 M $CaCl_2$ and Mehlich-3 extractable Zn (Table 2). Reductions in these "negative" effects, due to successful mine land reclamation, should lead to improved soil health as supported by findings presented in Fig. 2.

Regardless of the decreases in heavy metal bioavailability, extractability, or mineral forms present, some of these metal concentrations may be of concern from a soil health standpoint if birds or mammals were to consume biota that live in or on this soil. Although studies focused on biota have been performed on this site (e.g., Brown et al., 2005) and similar

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sites (e.g., Brown et al., 2014) and have shown no excessive body burdens, it is still wise to follow such an approach over the long-term. The Mehlich-3 Cd and Zn concentrations all exceeded Eco-SSLs, while Mehlich-3 extractable Cu in seep areas and several in-field Mehlich-3 extractable Pb concentrations also exceeded Eco-SSL concentrations (Table 2). Although Mehlich-3 data are presented, it is important to note that this extractant is typically used for determining nutrient and metal plant-availability (in, for example, agroecosystems), and in comparison to a more commonly used extractant such as 0.01 M $CaCl_2$ (or 0.01 M $CaNO_3$; Brown et al., 2014), is likely too aggressive of an extractant for heavy metal bioavailability in reclaimed heavy metal mine land soils. Although total metal concentrations were not determined in this study, if the somewhat aggressive Mehlich-3 extraction were considered as a proxy for total metal concentrations, further investigation due to exceeding Eco-SSLs would be warranted. That further investigation would utilize bioavailable metal concentrations as a function of a 0.01 M $CaCl_2$ extraction. Findings showed that the 0.01 M $CaCl_2$ Cd and Zn concentrations in seep areas exceeded critical Eco-SSLs for birds and mammals, respectively (Table 2). This is concerning as Eco-SSLs are based on total metal concentrations, not bioavailable metal concentrations as determined by a 0.01 M $CaCl_2$ extraction. Regardless, although current soil health metrics support long-term reclamation success, some soil metal concentrations may be of concern from an environmental health standpoint, especially with respect to consumption by birds and mammals.

3.3. Plant metal concentrations and plant quality

Plant heavy metal concentrations and quality characteristics are presented in Table 3. All plant metal concentrations were similar across the reclaimed site except for Mn, which was greater in field location 1 as compared to other locations (for reasons unknown). These plant metal concentrations are about an order of magnitude lower than those first reported by Brown et al. (2005) for this site, supporting the contention of Brown et al. (1998) that plant metal concentrations decrease as a function of time since biosolids application. In addition, all plant metal concentrations were below those set forth as maximum tolerable levels in domestic livestock feed for animals such as horses or cattle (Table 3; National Research Council, 2005), both of which are raised in this area of Colorado.

From an overall environmental health perspective, there are several other important points to make with regards to the observed plant metal concentrations. First, Kabata-Pendias (2011) reported that Cd in grasses typically ranges from 0.07 to 0.27 mg kg^{-1}, well below Cd concentrations within on-site plants. And although the National Research Council (2005) suggested greater limits for animal tolerance, they also suggested that lower plant Cd concentrations are necessary to avoid accumulation in edible animal tissue. Second, healthy plants typically have Fe:Mn ratios between 1.5 and 2.5, and below this range Mn toxicities and Fe deficiencies may occur (Kabata-Pendias, 2011). The on-site Fe:Mn plant ratios ranged from 0.2 to 1.1, well below the critical range, yet visual signs of either Mn toxicity or Fe deficiency were not observed. In general, grasses tend to contain Fe and Mn concentrations ranging between 43 to 376 and 17–334 mg kg^{-1}, respectively (Kabata-Pendias, 2011), and on-site plant Fe and Mn concentrations mostly fell within these ranges. Last, although plant Zn concentrations were not toxic (i.e., no visual toxicities present), Zn concentrations were up to 6 times greater than commonly found in grasses (12–80 mg kg^{-1}; Kabata-Pendias, 2011); some plants are Zn sensitive at concentrations between 100 and 500 mg kg^{-1} (Macnicol and Beckett, 1985), yet plants on-site were tolerant of greater Zn concentrations. An identical observation for Zn (and Pb) was made by Brown et al. (2005) when ryegrass was grown in these alluvial mine tailings.

Above-ground plant quality data are presented in Table 3. When above-ground plant tissue is used for animal feed, >7% crude protein is required for maximum growth and activity of ruminal microorganisms (Cappellozza, 2013). Crude protein content was mostly <7% across the site, but protein content declines as the growing season progresses (Joe Brummer, personal communication; Trlica, 2013). Based on crude protein content at the time of plant collection (mid-August), animals might require supplemental dietary protein feed sources to meet their minimum nutritional requirements. As grasses mature, plant structural components in the cell wall (i.e., more indigestible plant portions) also increase, as measured by acid- and neutral-detergent fiber contents (Jeranyama and Garcia, 2004). Neutral-detergent fiber measures the total structural plant components of cellulose, hemicellulose, and lignin, which correspond to an animal's voluntary intake, while acid-detergent fiber measures just the cellulose and lignin content which is directly related to the less or indigestible plant components and provides an indirect measure of digestible dry matter or energy (Schick, 2023). The acid-detergent fiber content ranged between 33 and 35%, in-line with that found in early bloom alfalfa and late vegetation grasses (Schick, 2023; Jeranyama and Garcia, 2004). The neutral-detergent fiber content ranged between 56 and 63%, similar to late vegetation grasses but greater than early bloom alfalfa (Schick, 2023; Jeranyama and Garcia, 2004). Neutral-detergent fiber values at ~40–55% allow for more intake of forage, thus are favorable for providing more energy to animals. The % acid- and neutral-detergent fiber contents were used to determine relative feed value compared to full-bloom alfalfa using equation (1). Relative feed values ranged from 93 to 104 (overall site average = 97; data not shown), suggesting that these plants might act similarly in terms of feed to that of full-bloom alfalfa. However, from an animal health perspective, if cattle or horses grazed on this site later in the season, supplemental feed that provides greater protein and energy content may be warranted. And, of course, a producer should be concerned with plant Cd concentrations as well as soil metal concentrations that exceed Eco-SSLs for mammals.

4. Conclusions

Reclamation success of acidic mine tailings is often driven by lime and organic amendment additions. In 1998, an acidic, alluvial mine tailing received 224 Mg ha^{-1} of both lime and biosolids, and reclamation success was quantified in 2019 using a soil health approach, in combination with plant characteristics and connections to domestic livestock. Twenty-one years following reclamation: 1) soil physical health has improved as driven by decreases in bulk density and increases in wet aggregate stability; 2) soil biological health has improved as driven by increases in potentially mineralizable nitrogen and microbial biomass carbon; and 3) overall soil health has improved by a combination of these four soil characteristics as determined using the Soil Management Assessment Framework. Soil health improvements were also observed via decreases in bioavailable soil metal concentrations as compared to early reclamation observations; above-ground plant metal concentrations have also decreased as compared to earlier findings. All plant metal concentrations were below those determined as maximum tolerable levels for horses and cattle. Some soil metal concentrations (e.g., Cd and Zn) may be of concern from an environmental health standpoint as they exceed US Environmental Protection Agency ecological soil screening levels, especially with respect to consumption by birds and mammals. Fortunately, this site is relatively small and grazing here is limited to a small portion of the year due to snow cover and freezing temperatures. Most importantly, on-site acidity has remained neutralized, bioavailable soil and plant metal concentrations have decreased over time, plants are well-established, and soil health has improved. Soils on this site are likely stabilized, leading to a reduction in off-site erosional losses into nearby waters. Thus, long-term reclamation success can be quantified via a soil health approach, leading to improvements in plant, animal, and ecosystem health in heavy metal contaminated lands. However, one of the major shortcomings of the Soil Management Assessment Framework is that it does not include scoring functions for heavy metals. In the future, soil bioavailable heavy metal scoring functions should be created and included in the Soil Management Assessment Framework in order to better quantify long-term reclamation success. Ultimately, findings from this and past work, in conjunction with soil health frameworks such as the Soil Management Assessment Framework, may eventually lead to the creation of an international approach for assessing soil health and reclamation success for heavy metal contaminated mine lands.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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HIGHLIGHTS

- Soil health was a proxy for reclamation success of alluvial mine tailings contaminated with heavy metals.
- Improvements in soil health led to improvements in plant health.
- Bioavailable Cd and Zn in seeps exceeded ecological soil screening levels.
- Highly insoluble Zn–Al compounds indicated long-term Zn stabilization.

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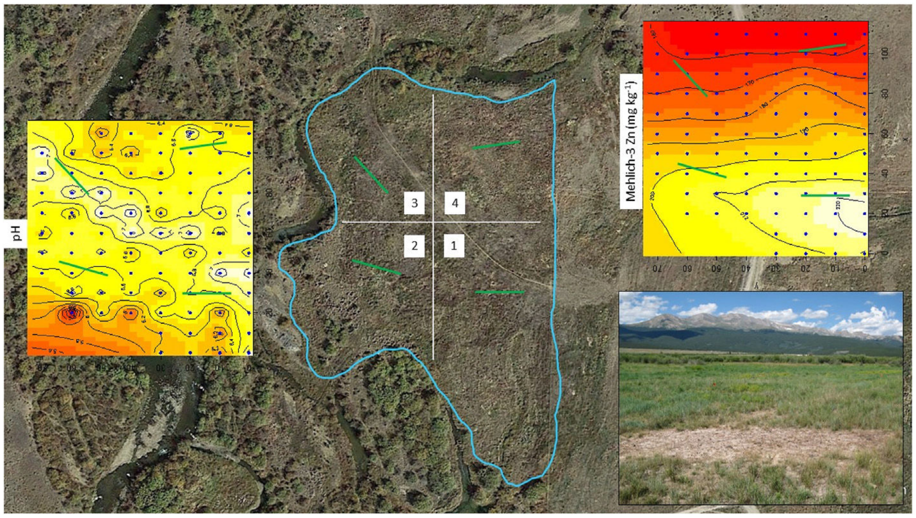

Fig. 1.

Leadville, Colorado USA, 2019 soil health sampling approach. Approximate study area (blue line) of an alluvial mine tailings deposit amended with 224 Mg ha^{-1} of lime and 224 Mg ha^{-1} of anaerobic biosolids in 1998. The site was separated into four areas (labeled 1 to 4) based on relatively uniform pH (left inset picture; lightest yellow colors = pH 6.8 to 7.0) yet varying metal concentrations (e.g., Mehlich-3 extractable Zn, upper right inset picture; dark red = 160 and light yellow = 220 mg kg^{-1}) as determined by Freeman et al. (2008) and Freeman (2008) using a 10 m by 10 m grid approach followed by kriging. Green lines inside blue area (and colored maps) represent 20 m transects for soil (0–15 cm depth) and total above-ground biomass plant sampling (0.5 m^2 quadrat), with both obtained at 5 m intervals along the transect. Bottom right inset photo shows the site (in 2019) looking from the area's east edge towards the west. Most of the site is dominated by grass species, yet seep areas exist where metal concentrations were elevated and plants have died. Seep areas were used to represent original background conditions.

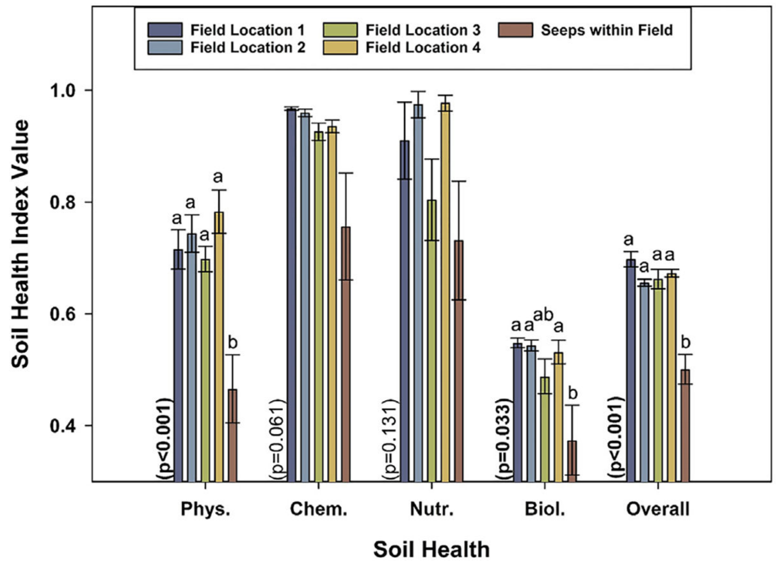

Fig. 2.

Leadville, Colorado USA, 2019 soil physical, chemical, nutrient, biological, and overall soil health index values as a function of field location (see Fig. 1).

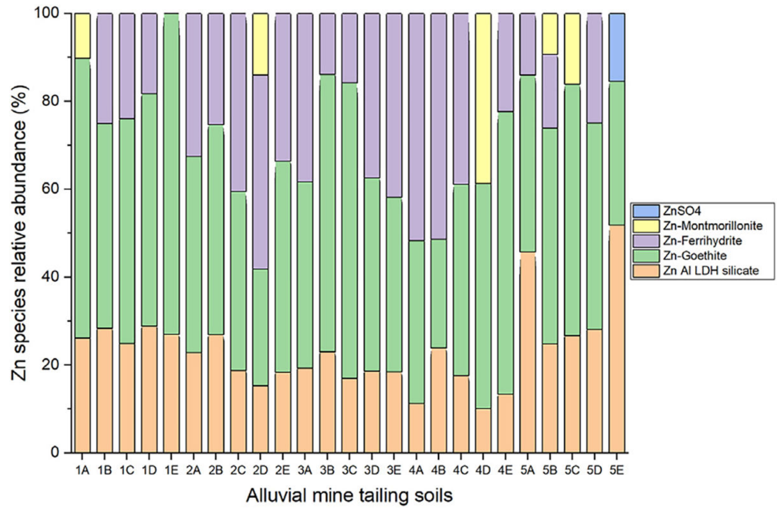

Fig. 3.

Zinc K-edge XANES analysis for speciation and relative abundance in alluvial mine tailing soils. Standard error 5%. LDH = layered double hydroxides. On the x-axis, 1, 2, 3, and 4 A through E represent the five soil samples obtained along transects 1 through 4 (Fig. 1), while 5 A through E were obtained within in-field seep locations where no plants were present (i.e., areas too small to be represented within Fig. 1).

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Table 1

Mean Soil Management Assessment Framework (SMAF) physical [bulk density (Bd) and wet aggregate stability (WAS)], chemical [pH and electrical conductivity (EC)], nutrient [Mehlich-3 extractable P and K], and biological [soil organic C (SOC), potentially mineralizable N (PMN), microbial biomass C (MBC), and β-glucosidase activity] indicators and SMAF indicator scores as a function of alluvial mine tailing reclamation location (field locations 1 through 4 were sites with plant growth, seeps were sites where metal salts have accumulated and with no plant growth; see Fig. 1). Values inside parenthesis represent the standard error of the mean (n = 5). Different lowercase letters after an individual indicator or a SMAF indicator score indicate a significant difference as determined by a Tukey adjusted pairwise comparison.

Field Location	**Physical Indicators**		**Chemical Indicators**		**Nutrient Indicators**		**Biological Indicators**			
	Bd (g cm^{-1})	**WAS (%)**	**pH**	**EC (dS m^{-1})**	**M - 3 P(mg kg^{-1})**	**M - 3 K(mg kg^{-1})**	**SOC (%)**	**PMN (mg kg^{-1})**	**MBC (mg kg^{-1})**	**β-glucosidase (mg pnp[a] kg^{-1} soil h^{-1})**
1	1.24(0.04)b	14.0(2.6)ab	7.2(0.0)a	2.66(0.42)b	259(43)ab	400(86)ab	3.64(0.40)ab	38.3(12.2)ab	51.6(2.8)a	99(86)ab
2	1.12(0.06)b	16.3(2.9)ab	7.3(0.1)a	2.86(0.07)b	322(14)a	336(49)ab	4.93(0.23)a	72.1(10.1)ab	37.3(4.6)ab	93(49)ab
3	1.11(0.04)b	12.2(1.7)ab	7.5(0.1)a	3.35(0.09)b	231(33)ab	327(62)ab	3.55(0.41)ab	40.8(13.9)ab	38.2(2.6)ab	87(62)ab
4	1.25(0.07)b	21.0(3.1)a	7.4(0.1)a	3.06(0.14)b	333(44)a	474(84)a	3.95(0.54)ab	79.2(15.2)a	32.3(2.6)bc	115(84)a
Seeps	1.50(0.07)a	8.4(1.6)b	6.3(0.4)b	5.24(0.23)a	117(40)b	162(52)b	2.68 (0.22)b	19.6(12.8)b	19.6(4.5)c	18(52)b
ANOVA										
p-value	***0.001***	***0.014***	***0.004***	***<0.001***	***0.006***	***0.009***	***0.017***	***0.036***	***<0.001***	***0.034***
SMAF Indicator Scores (scale of 0.00–1.00)										
1	0.98(0.01)a	0.45(0.07)ab	0.93(0.01)	1.00(0.00)a	0.43(0.21)ab	0.99(0.01)a	0.97(0.02)	0.98(0.01)ab	0.10(0.01)a	0.14(0.06)
2	0.99(0.01)a	0.50(0.06)ab	0.92(0.01)	1.00(0.00)a	0.00(0.00)b	0.97(0.02)a	1.00(0.00)	1.00(0.00)a	0.07(0.01)b	0.11(0.03)
3	0.99(0.00)a	0.40(0.06)ab	0.88(0.02)	0.97(0.02)a	0.46(0.17)ab	0.96(0.03)a	0.96(0.02)	0.83(0.13)ab	0.07(0.00)b	0.09(0.03)
4	0.96(0.02)a	0.61(0.06)a	0.88(0.02)	0.99(0.01)a	0.18(0.18)ab	0.99(0.01)a	0.94(0.06)	1.00(0.00)a	0.06(0.00)b	0.13(0.01)
Seeps	0.63(0.12)b	0.30(0.05)b	0.92(0.04)	0.20(0.08)b	0.73(0.14)a	0.73(0.11)b	0.90(0.04)	0.52(0.21)b	0.04(0.01)c	0.03(0.11)
ANOVA										
p-value	***<0.001***	***0.012***	*0.193*	***<0.001***	*0.071*	***0.009***	*0.418*	***0.034***	***<0.001***	*0.128*

[a] pnp = *p*-nitrophenol.

Table 2

Mean soil 0.01 M $CaCl_2$, soil Mehlich-3, and above-ground plant Cd, Cu, Fe, Mn, Pb, Zn, and S concentrations as a function of alluvial mine tailing reclamation location (field locations 1 through 4 were sites with plant growth, seeps were sites where metal salts have accumulated and with no plant growth; see Fig. 1). Values inside parenthesis represent the standard error of the mean (n = 5). Different lowercase letters after an individual element for a particular extraction indicates a significant difference as determined by a Tukey adjusted pairwise comparison. Eco-SSLs are presented for consideration and protection of birds and mammals that may consume biota living in or on this soil.

Field Location	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**	**S**
			0.01 M $CaCl_2$ Extractable (mg kg^{-1})				
1	0.19(0.06)b	0.16(0.03)	1.63(0.30)	6.62(3.44)b	0.04(0.02)	1.17(0.47)b	ND[a]
2	0.30(0.12)b	0.19(0.02)	1.68(0.26)	3.15(0.84)b	0.03(0.02)	3.21(1.64)b	ND
3	0.28(0.11)b	0.16(0.04)	2.45(0.70)	2.03(0.49)b	0.24(0.14)	1.06(0.36)b	ND
4	0.19(0.04)b	0.14(0.02)	2.82(1.30)	1.60(0.71)b	0.19(0.13)	0.26(0.20)b	ND
Seeps	9.02(4.74)a	0.12(0.05)	1.04(0.49)	124(51)a	0.02(0.02)	72.9(29.0)a	ND
ANOVA							
p-value	***0.043***	*0.762*	*0.276*	***0.002***	*0.082*	***0.004***	
			Mehlich-3 Extractable (mg kg^{-1})				
1	10.3(2.6)ab	28.2(8.8)b	46.8(6.6)	99.6(29.9)b	101(28.3)a	840(200)b	3700(240)b
2	9.5(2.1)ab	27.2(5.0)b	40.4(2.0)	56.7(9.4)b	35.6(5.6)ab	1070(290)b	3780(730)b
3	11.6(3.3)ab	24.9(8.4)b	47.6(5.4)	64.6(14.4)b	49.5(12.7)ab	740(140)b	4490(450)b
4	3.5(1.4)b	19.6(2.7)b	70.3(7.8)	27.7(8.3)b	82.5(14.3)ab	270(90)b	3530(640)b
Seeps	30.8(10.5)a	105(31)a	46.1(19.5)	255(68.5)a	22.2(5.5)b	2310(440)a	8400(760)a
ANOVA							
p-value	***0.027***	***0.008***	*0.114*	***0.001***	***0.015***	***0.001***	***<0.001***
			Eco-SSLs[b] (mg kg^{-1})				
Birds	0.77	28	None	4300	11	46	None
Mammals	0.36	49	None	4000	56	79	None

[a] ND = Not Determined.

[b] Eco-SSLs = Ecological Soil Screening Levels, or soil concentrations that are protective of birds and mammals that can come in contact with or consume biota that live in or on soil. Cd (US EPA, 2005), Cu (US EPA, 2007a), Fe (US EPA), Mn (US EPA, 2007b), Pb (US EPA, 2005b), and Zn (US EPA, 2007c).

Table 3

Mean above-ground plant Cd, Cu, Fe, Mn, Pb, Zn, and S concentrations, and plant biomass, and plant crude protein, acid detergent fiber, neutral detergent fiber, and relative feed value as a function of alluvial mine tailing reclamation location (field locations 1 through 4 were sites with plant growth, seeps were sites where metal salts have accumulated and with no plant growth; see Fig. 1). Values inside parenthesis represent the standard error of the mean (n = 5). Different lowercase letters after an individual element for a particular extraction indicate a significant difference as determined by a Tukey adjusted pairwise comparison.

Field Location	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**	**S**
Above-ground Plant Metal Concentrations (mg kg^{-1})							
1	0.76(0.14)	5.48(0.70)	40.4(4.4)	169(28.8)a	1.22(0.44)	180(36.2)	ND
2	0.49(0.13)	5.93(0.93)	38.0(1.8)	34.3(5.6)b	1.04(0.32)	188(43.5)	ND
3	0.74(0.24)	4.53(0.40)	41.1(1.4)	70.6(7.3)b	1.29(0.27)	94.1(16.8)	ND
4	0.77(0.10)	5.56(0.44)	40.3(2.8)	77.9(14.5)b	0.74(0.16)	105(14.7)	ND
Seeps	NP[a]	NP	NP	NP	NP	NP	NP
ANOVA							
p-value	*0.474*	*0.351*	*0.775*	***0.001***	*0.665*	*0.176*	
NRC Mineral Tolerance Levels[b]	10	40–250	500	400–2000	10–100	500	
	Biomass	Crude Protein	Acid Detergent Fiber	Neutral Detergent Fiber	Relative Feed Value		
	(g m^{-2})		(%)		(unitless)		
1	275(36)	6.0(0.4)b	33.6(0.9)	60.4(1.4)ab	96.8(2.9)ab		
2	327(71)	6.6(0.3)b	34.9(1.2)	62.2(2.1)a	92.8(3.7)b		
3	204(48)	6.2(0.8)b	33.0(1.0)	56.2(0.4)b	104.5(2.0)b		
4	265(40)	10.0(1.0)a	33.2(0.7)	63.3(2.0)a	93.0(3.5)b		
Seeps	NP[a]	NP	NP	NP			
ANOVA							
p-value	*0.602*	***0.008***	*0.369*	***<0.001***	***0.0003***		

[a]ND = Not Determined; NP ▫ No Plants.

[b]National Research Council (2005) mineral tolerance concentrations for horses and cattle.