Revegetation of High Zinc and Lead Tailings with Municipal Biosolids and Lime: Greenhouse Study

Alex Svendson Herrera Environmental Consultants
Chuck Henry and Sally Brown* University of Washington

Acidic (pH 4.1) and high Cd, Pb, and Zn mine tailings (mean ± SD: 17 ± 0.4, 3800 ± 100, and 3500 ± 100 mg kg−1, respectively) from an alluvial tailings deposit in Leadville, Colorado were amended with municipal biosolids (BS) (224 Mg ha−1) and different types of lime (calcium carbonate equivalent of 224 Mg ha−1 CaCO3) in a greenhouse column study to test the ability of the amendments to neutralize surface and subsoil acidity and restore plant growth. The types of lime included coarse, agricultural, and fine-textured lime (CL, AL, and FL), sugar beet lime (SBL), and lime kiln dust (LK). The FL was also added alone. All treatments increased bulk pH in the amended horizon in comparison to the control, with the most significant increases observed in the FL, SBL+BS, and LK+BS treatments (7.33, 7.34, and 7.63, respectively). All treatments, excluding the FL, increased the pH in the horizon directly below the amended layer, with the most significant increases observed in the SBL+BS and LK+BS treatments (6.01 and 5.41, respectively). Significant decreases in 0.01 M Ca(NO3)2-extractable Zn and Cd were observed in the subsoil for all treatments that included BS with plant Zn, Cd, and Pb concentrations reduced over the control.

COSYSTEM impacts from historical mining and ore processing activities in the USA are often severe, and effective remedial options are limited. In many cases, contaminants from mining can affect aquatic and terrestrial ecosystems. The Arkansas River in Leadville, Colorado is one example of ecosystem damage as a result of mining activities. Leadville is located on the western slope of the Mosquito Range in Lake County at an elevation of 3100 m (39°14′ 50″N, 106° 17′ 33″W) (Levy et al., 1992). Leadville was founded as part of a large mining boom that encompassed much of the eastern Rocky Mountain Range west of Denver beginning in 1859. Extensive mining and smelting throughout the Leadville area extracted Au, Zn, Pb, Ag, Fe, and Mn from the metal-rich sulfide deposits found in the area. The ore bodies were primarily sulfidic, and the tailings materials contain reduced, oxidized, and partially oxidized minerals (Ostergren et al., 1999). Lack of government regulation resulted in large quantities of the tailings eroding or being deposited into nearby streams (Ranville et al., 1998). The widespread dispersal of the mine tailings resulted in the contamination of several areas along an 18-km stretch of the Arkansas River, which runs through Leadville (URS Operating Services, Inc., 1997; USGS, 2000). The majority of tailings entered the Arkansas River from California Gulch, which was placed on the USEPA's National Priority List in 1983.

The contaminated tailings deposits vary in terms of purity and depth along the affected stretch of the Arkansas River (USGS, 2000). Most of the fluvial deposits range from 15 cm to 1 m in depth. The mine tailings consist primarily of pyrite, galena, sphalerite, and Mn minerals, all in various stages of oxidation (USGS, 2000). Over time, the high reduced sulfur content of the tailings has oxidized, resulting in highly acidic conditions and in the conversion of metals to more soluble forms (Brown et al., 2005a). For example, one study analyzed the mineralogy of two tailings deposits and found a range in pyrite from 5 to 70 and jarosite from 7 to 17 (Ostergren et al., 1999). The acidity and elevated metal concentrations of the tailings deposits create highly phytotoxic conditions (Fischer et al., 2000). These conditions are exacerbated by the climate in Leadville. Due to the high altitude, the growing season averages 79 d. Average rainfall is low (40 cm yr−1), and the summer months can be droughty (National Oceanic and Atmospheric Administration, 2001).

Copyright © 2007 by the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

doi:10.2134/jeq2006.0411
Received 28 Sept. 2006.
*Corresponding author (slb@u.washington.edu).
© ASA, CSSA, SSSA
677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: AL, agricultural lime; BS, biosolids; CCE, calcium carbonate equivalent; CL, coarse lime; EC, electrical conductivity; FL, fine-textured lime; LK, lime kiln dust; SBL, sugar beet lime.
Due to the proximity to the river, the local groundwater table is high. This combination often results in the wicking of moisture through the tailings to the surface during drier portions of the year. As the water evaporates, a metal-rich salt crust is left on the surface. This increases surface metal concentration and electrical conductivity, both of which inhibit plant establishment (Mike Zimmerman, USEPA Region 8, personal communication).

Portions of the site were amended with a mixture of municipal biosolids and limestone in remedial actions undertaken by the USEPA Superfund Program (Brown et al., 2005a). Application of high rates of biosolids (BS) and lime (224 Mg ha\(^{-1}\) of each amendment) have reduced metal toxicity and restored ecosystem function to the site. Ecosystem function was measured using a number of parameters, including \(\text{CO}_2\) evolution, nitrogen cycling, earthworm survivability and metal uptake, plant germination and metal uptake, plant species diversity, and small mammal body metal concentration. This type of amendment has been effectively used at other mining sites and offers a potential low-cost remedial option (Brown et al., 2003; Sopper, 1993; Stuczynski et al., 2000; Tian et al., 2006). Restoration after BS amendment has been significantly more effective than the use of fertilizers alone (Sopper, 1993).

At the Leadville site, the previous application of liming agents (agricultural limestone [AL] and coarse limestone [CL]) for the large-scale treated areas did not increase surface pH > 7 (Brown et al., 2005b). In addition, measuring changes in subsoil pH were not included in the monitoring effort. It is possible that the amendment mixture used at the site, although generally effective, is not the optimal combination. It is likely that a more soluble liming agent would provide additional alkalinity to neutralize the surface acidity and potentially ameliorate subsoil acidity. Several types of lime or materials with a high calcium carbonate equivalent (CCE) are locally available in the Leadville region and in other regions of the country that have sites requiring remediation. These include AL, fine-textured limestone (FL), lime kiln dust (LK), and sugar beet lime (SBL). Prior research on ameliorating subsoil acidity in agronomic systems can be applied to the Leadville site to improve the remedial mixture.

Subsoil acidity is a common problem for many agricultural areas, and a large body of research has been directed toward correcting this problem. In general, subsoil acidity poses many of the same growth-inhibiting responses in plants as surface soil acidity, the most common of which is decreased rooting into the subsoil zone (Foy, 1992; Toma et al., 1999). Doss et al. (1979) found highly restricted rooting depths in five types of acid soils compared with similar soils that were limed at different depths. The effects of decreased subsoil rooting and branching are commonly manifested in decreased drought tolerance. The neutralization of subsoil acidity is complicated by several factors. The effects of surface application of limestone are generally limited to the area of incorporation (Liu and Hue, 1996). Hydroxide ions are quickly neutralized with the released Ca ion sorbed to surface exchange sites (Hue and Licudine, 1999). For example, Mathews and Joost (1990) observed no significant increase in subsoil pH after surface lime amendment of an acidic Toulasilt loam (pH 4.9–5.1) with the equivalent of 1.79 Mg ha\(^{-1}\) langbeinite, Ca-silicate slag, and calcitic lime.

Combining lime with organic amendments has been demonstrated to move alkalinity more effectively through the soil profile. In a greenhouse study, Tan et al. (1985) demonstrated that combining 112 Mg ha\(^{-1}\) biosolids with 4.5 Mg ha\(^{-1}\) lime (CaCO\(_3\)) mobilized significant amounts of Ca below the 45 cm depth in an Ultisol characterized by acidic subsoils (pH 5.2–6.2) in comparison to the lime alone treatment. They attributed the improved Ca movement to fulvic acids generated by the biosolids that chelated Ca ions and facilitated the movement of Ca into the acidic subsoil. Wright et al. (1985) observed significant increases in the pH of an acidic subsoil (pH 4.95) with surface applications of 44.8 Mg ha\(^{-1}\) of cow manure in combination with 8.4 Mg ha\(^{-1}\) of dolomitic lime and 5.1 Mg ha\(^{-1}\) ethylenediamine tetraacetic acid in combination with dolomitic lime. Application of dolomitic lime alone had no effect on subsoil pH. Root growth was observed in the subsoil of the manure+lime treatment, whereas no roots were observed in the subsoil of the EDTA+lime or lime alone treatments. Brown et al. (1997) sampled long-term biosolids amended soils, and application of 224 Mg ha\(^{-1}\) lime stabilized biosolids to an ultisol was sufficient to increase pH > 7.0 to a 1 m depth.

The most common liming minerals used to neutralize acidic soils include agricultural limestone or calcite (CaCO\(_3\)) and dolomite (CaCO\(_3\)-MgCO\(_3\)). The inherent low solubility of these materials and their large particle size can slow reaction times. Fine-textured limestone normally has faster reaction times due to its higher surface area. Quick lime or burnt lime (CaO) or hydrated or slaked lime (Ca(OH)\(_2\)) are alkaline minerals that can be applied to neutralize acidic soils (Cregan et al., 1989). Due to higher solubility, these minerals are extremely fast reacting and can neutralize soil acidity much more quickly than limestone or dolomite.

Several industrial and agricultural residuals possess a high calcium carbonate equivalent and are regionally available. Sugar beet lime, a sugar beet processing byproduct, is used as a liming agent in many agricultural soils and has been used as an amendment to remediate metal contaminated soils (Perez de Mora et al., 2006; Vakalis et al., 2005). Kiln dusts, byproducts of lime and cement kilns, contain 15 to 30% CaO and 50 to 70% unreacted limestone (Skousen et al., 2000). Kiln dusts harden when wetted, absorb moisture quickly, and make excellent liming amendments for acidic mine tailings (Dollhofp, 1996).

A greenhouse study was conducted to test the ability of alternative liming agents in combination with municipal biosolids to neutralize surface and subsoil acidity on alluvial tailings deposits. The objective of this study was to determine the effects of different types of lime in combination with municipal biosolids on tailings pH, alkalinity movement, electrical conductivity (EC), 0.01 M Ca(NO\(_3\))\(_2\)-extractable metals, plant growth, and foliar metal concentration. Two complete replicates of some of the amendment combinations were included in the experimental design to test how different rates of irrigation could influence these parameters.

**Materials and Methods**

The greenhouse study was conducted at the University of Washington Center for Urban Horticulture Greenhouse in Seattle, Washington in 2000. The tailings used in the study were collected from a privately owned ranch during the fall of 1999. Tailings were
collected from a deposit immediately adjacent to the Arkansas River that had been devoid of vegetation for more than 70 yr (URS Operating Services, Inc., 1997). Tailings were collected from the 0- to 50-cm depth using a stainless steel shovel. The tailings were stored in plastic 5-gallon containers in the greenhouse before the experiment. The collected materials were partially air dried, passed through a 2-mm sieve, and homogenized in a cement mixer before use in the study. The biosolids used in the study were obtained from the Renton, Washington South Treatment Plant. The anaerobically digested biosolids consisted of 18% solids, 58% volatile solids, and a total N concentration of 68 g kg⁻¹ (King County Department of Natural Resources, 2000). No lime is added to the biosolids during the wastewater treatment process. The elemental composition, pH, and EC of the homogenized mine tailings and biosolids used in the greenhouse study are presented in Table 1. The wastewater entering the plant is primarily derived from private residences, and the treatment process is identical to that used by Denver Metro. Denver Metro provided anaerobically digested cake for a significant portion of the large-scale field operation in Leadville. The SBL was obtained from Western Sugar (Greeley, Colorado). The rest of the liming agents used in the study were obtained from Calco Limestone Products (Salida, Colorado). The CCE for each lime type was determined using the gravimetric method for loss of CO₂ (Loeppert and Suarez, 1996). The pH, CCE, calcium species, and expected solubility of each type of lime are presented in Table 2. A sieve analysis was also conducted on each of the liming materials. The liming materials were air-dried, crushed using a stainless steel rolling pin, and passed through seven sieves using a sieve shaker (Central Scientific, Chicago, IL). The sieve sizes were 8, 2, 1, 0.5, 0.25, 0.15, and 0.075 mm. Liming agents with small particle sizes can be inferred to have a higher solubility and reactivity due to the higher surface area of the material compared with liming agents with larger particle sizes (Barber, 1967). For example, although the pH of the CL and the FL were statistically similar, only 52% of the CL had particle size ≤1 mm, whereas 100% of the FL had particle size ≤0.15 mm. The results of the sieve analysis are shown in Table 2.

Ten treatments were tested in the greenhouse study. They included a control and a FL alone treatment. The experiment was structured as a randomized complete block with three replicates of each treatment. Biosolids were included with different types of lime, including FL+BS, AL+BS, CL+BS, SBL+BS, and LK+BS. Biosolids were added at a rate equivalent to 224 Mg ha⁻¹. The different types of lime were added at rates equivalent to 224 Mg ha⁻¹ CCE. Three of the biosolids + lime treatments were also included at two rates of water addition.

Polyacrylic columns (10.2 cm wide and 45.7 cm high) were filled with tailings in combination with amendment mixtures. The lime and biosolids were hand mixed on a per-column basis with the tailings. Sand was added to the bottom 7.5 cm of the control and FL alone treatments to compensate for the additional volume added with the BS+lime treatments. A 30-cm layer of homogenized tailings was placed on top of the sand layer. For the FL alone treatment, the lime was mixed with the tailings and placed in the top 15 cm of the column. All other treatments contained a 22.5-cm amended layer consisting of mine tailings, lime, and BS above a 15-cm tailings layer. Two layers of 500-μm polyester mesh were placed at the bottom of each column to prevent soil loss. Diagrams of the different columns are shown in Fig. 1.

All of the BS treatments were amended with BS at a rate equivalent to 224 Mg ha⁻¹ dry weight. Several studies reclaiming acidic, heavy metal–contaminated soils have used similar reclamation rates of BS (Brown et al., 2005b; Pistelok, 2000). Liming rates for the tailings had been determined on samples collected from each of the tailings deposits in 1998. The liming rates to neutralize the existing acidity and the acid potential of the tailings were determined as follows. The lime requirement for the existing acidity was determined by incubating the tailings with a 1 M KOH solution. Eight samples were taken from representative tailings deposits to a depth of 1 m and sectioned into 15-cm increments. Three-milliliter aliquots of 1 M KOH, representing the equivalent of 33.6 Mg ha⁻¹ CaCO₃, were added to each 15-cm increment and placed in a side-to-side shaker for 20 h. The total lime requirement of each depth was established when the slurry reached pH > 7.5. Lime

---

**Table 1. Elemental concentrations, pH, and electrical conductivity of the Renton, Washington biosolids and <2-mm sediment collected from homogenized fluvially deposited mine tailings in Leadville, Colorado. SD is presented with data.**

<table>
<thead>
<tr>
<th>Soil</th>
<th>Cd</th>
<th>P</th>
<th>Pb</th>
<th>Zn</th>
<th>pH</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tailings</td>
<td>17 ± 0.4</td>
<td>1000 ± 25</td>
<td>3800 ± 100</td>
<td>3500 ± 100</td>
<td>4.1</td>
<td>14.6</td>
</tr>
<tr>
<td>Biosolids†</td>
<td>5 ± 0.7</td>
<td>31 000 ± 3000</td>
<td>54 ± 11</td>
<td>681 ± 73</td>
<td>8.49</td>
<td>7.4</td>
</tr>
</tbody>
</table>

† King County Department of Natural Resources (2000).

---

**Table 2. pH, calcium carbonate equivalent (CCE), calcium species, percent of particles ≤0.15 mm, and expected solubility of the liming agents used in the greenhouse study.**

<table>
<thead>
<tr>
<th>Lime type</th>
<th>pH</th>
<th>CCE</th>
<th>Calcium species</th>
<th>Percent ≤1 mm</th>
<th>Percent ≤0.15 mm</th>
<th>Expected solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse-textured lime</td>
<td></td>
<td></td>
<td>CaCO₃</td>
<td>52</td>
<td>14</td>
<td>low</td>
</tr>
<tr>
<td>Agricultural lime</td>
<td>8.68</td>
<td>79 CaCO₃</td>
<td></td>
<td>95</td>
<td>54</td>
<td>medium</td>
</tr>
<tr>
<td>Fine-textured lime</td>
<td>8.70</td>
<td>93 CaCO₃</td>
<td></td>
<td>100</td>
<td>100</td>
<td>high</td>
</tr>
<tr>
<td>Sugar beet lime</td>
<td>8.23</td>
<td>63 CaCO₃</td>
<td></td>
<td>100</td>
<td>84</td>
<td>high</td>
</tr>
<tr>
<td>Lime kiln dust</td>
<td>12.50</td>
<td>47 CaO</td>
<td></td>
<td>67</td>
<td>31</td>
<td>very high</td>
</tr>
</tbody>
</table>
required to neutralize existing acidity was summed, and a total lime requirement was determined. Unoxidized S and equivalent lime requirement was determined. A 30% solution of H$_2$O$_2$ was added to ground sample, and the sample was boiled for at least 60 min. If excess H$_2$O$_2$ was present at the end of the boiling period, 1 mL of a 0.0157 M Cu solution (CuCl$\cdot$2H$_2$O) was added to decompose the excess H$_2$O$_2$. The sample was filtered with several rinses of a 1 M CaCl$_2$ solution to remove all acidity. The leachate was then titrated with NaOH to pH 7 to determine lime requirement. This work was done at the laboratory of W.L. Daniels, Virginia Polytechnic University (Daniels and Stewart, 2000; O’Shay et al., 1990; Sobek et al., 1978). Oxidized and unoxidized S requirements were summed and averaged for an average lime application rate of 224 Mg ha$^{-1}$. Similar liming rates were used for the large-scale work on alluvial tailings in Leadville and in other studies (Brown et al., 2005b; Fischer et al., 2000). Although this method was not used on the tailings collected specifically for the greenhouse study, it was used to determine lime requirements for six deposits in the general area from which the tailings used for this study were collected. Total lime required ranged from 180 to 240 Mg ha$^{-1}$. Of this total, the lime required to neutralize potential acidity ranged from 7 to 21 Mg ha$^{-1}$. Using the CCE of each liming agent, treatments received 195 g of fine lime, 229 g of AL, 233 g of CL, 330 g of SBL, or 383 g of LK per experimental unit.

During the first week of the study, the treatments were watered with 200 mL deionized (DI) water each day, with leachate collection occurring every 2 d. During the following 3 wk, treatments received 200 mL DI water aliquots on the second and third days after the previous leachate collections, with leachate collection occurring every 3 d. During the rest of the study period, treatments received 200 mL DI water aliquots on the third and seventh days after leachate collections, with leachate collection occurring every week. The leaching rate performed on these treatments is representative of what would be expected for field treatments with heavy irrigation. The second leaching rate was used on the replicated FL+BS, SBL+BS, and LK+BS treatments. All of these treatments received a total leaching of 1.2 L (equivalent to 14.8 cm) DI water. These treatments were leached every day with 200 mL DI water for the first 6 d. Leachate was not analyzed for these treatments. The three treatments were subsequently maintained at field capacity for the duration of the study. This leaching treatment would most closely approximate field conditions.

Leachate was collected by draining the bottom of the columns through the plastic tubing into plastic cups. The collected leachate was filtered through Whatman #42 filter paper to remove larger organic and inorganic colloids. The pH of the leachate was analyzed using a Benchtop pH/ISE meter (Model 250A; Orion, Waltham, MA). After pH measurement, 3 mL of concentrated HCl was added to each sample to acidify the solution and to prevent microbially mediated changes to the leachate solution. The leachate solution was analyzed for elemental concentrations using ICP spectrometry (ICAP-AES model 61E; Thermo Jarrel Ash, Franklin, MA). Potentially due to the presence of dissolved organic material and other particulates, the last three leachate collections on days 59, 65, and 79 could not be filtered through and were analyzed for pH only.

After the leaching phase of the study, the columns were seeded with annual rye grass (Lolium multiflorum L.) purchased from a nursery in Seattle, Washington. Ten seeds were planted in each column after the 48-d leaching period. All of the plants were grown for 42 d, except for the control treatment, which was harvested after 35 d. The early harvest was necessary because the plants in this treatment showed signs of phytotoxicity. After the aboveground plant tissue was harvested, the material was washed with a dilute sodium lauryl sulfate solution, rinsed with DI water, and oven dried at 70°C. The dried plant tissue was weighed and ashed at 480°C in a muffle furnace for 16 h. The samples were digested in concentrated HNO$_3$ and dissolved in 3 M HCl. The digested solution was diluted to 25 mL using 0.1 M HCl and analyzed by ICP spectrometry (ICAP-AES model 61E; Thermo Jarrel Ash) to determine elemental concentrations. Blanks, replicates, and National Institute of Standards and Technology standards were routinely used in plant analyses for calibration and quality control. National Institute of Standards and Technology standards “Orchard Leaves” and “Spinach Leaves” were used along with an internal standard.分别为 orchard leaves 0.89 Pb and 1.12 Zn; Spinach leaves 0.84 Cd, 100 Pb, 0.98 Zn; and internal solution standard 1.00 Cd, 0.99 Pb, and 1.06 Zn.

After plant harvest, the columns were broken down, and the cores were sectioned at 7.5-cm intervals. The control and FL alone treatments were sectioned into four depths for analysis. The total depth of all columns that were amended with BS was 37.5 cm. These were divided into 7.5-cm sections, and each section was analyzed separately. The extra volume in the treatments resulted from the high rates of biosolids and lime that were added to the columns. The samples were stored at 2°C in a cold room until drying. The tailings were air dried and passed through a 2-mm sieve before further analysis.

The pH of the tailings was determined using an Orion pH meter model 720A. All pH measurements were performed using a 1:1 soil to DI water ratio (Thomas, 1996). The tailings were analyzed for EC using an Orion Conductivity/Salinity model 140 m. All EC measurements were conducted using a 1:5 soil to DI water ratio (Rhoades, 1996).

A 0.01 M Ca(NO$_3$)$_2$ solution was used to estimate the plant availability of the trace elements in the material (McLaughlin et al., 2000). Five grams of air-dried tailings was mixed with 25 mL of 0.01 M Ca(NO$_3$)$_2$ solution, placed on a side to side shaker for 1 h, filtered through Whatman #40 filter paper, and analyzed by inductively coupled plasma spectrometry (ICAP-AES model 61E; Thermo Jarrel Ash) to determine the trace element concentrations. Total metal concentrations were determined for the <2 mm fractions by aqua regia digestion (McGrath and Cunliffe, 1985) followed by analysis by ICP spectrometry (Thermo Jarrel Ash ICAP-AES model 61E). Total metal concentrations for the tailings before the initiation of the greenhouse study are shown in Table 1.

**Statistical Analysis**

Statistical analysis was conducted using SPSS version 10.0.5 (SPSS, 1999). Aboveground plant tissue elemental concentrations, tailings pH, EC, leachate Zn and pH, and Ca(NO$_3$)$_2$-extractable metals were tested for treatment effect using ANOVA. The main effect of treatment and interactions were examined. When the F
value of treatment was significant \( (p < 0.05) \), means separation procedures were conducted. Means were separated using the Waller-Duncan \( t \) test with a significance level of \( p < 0.05 \). Extractable Cd and Zn and plant tissue Cd, Pb, and Zn were log transformed before statistical analysis to normalize the data. Means ± 1 SD are presented in the text. Differences between means are indicated by different letters to show significant differences.

**Results and Discussion**

**Leachate Zinc and pH**

Leachate Zn concentrations are shown in Fig. 2. Over all sampling periods, treatment significantly affected leachate Zn concentrations. Time was also highly significant \( (p < 0.001) \), with the highest overall Zn concentrations in the first sampling significantly decreasing until the sixth sampling, after which there were no changes in mean Zn across all treatments. This initial high Zn concentration may be the result of disruption associated with column assembly and amendment addition. Because the treatment × time interaction was also significant, the effect of treatment on leachate Zn was analyzed for each time period. Initially, leachate Zn was highest in all treatments that included BS in combination with lime, with the exception of the LK+BS treatment, which was similar to the Control and the FL alone treatment. At the same period of the sampling at which overall Zn concentration became stable (sixth sampling), clear differences between treatments also emerged. For the last four sampling events, the highest leachate Zn was in the control treatment, with the next highest concentration in the FL alone treatment. All treatments that included BS and lime had significantly lower leachate Zn concentrations. These results are in agreement with data collected from sampling wells on the large-scale treated tailings areas (Walton-Day, USGS, personal communication). The field wells showed decreasing concentrations of Zn over time after a surface application of biosolids and coarse limestone.

Changes in leachate pH did not mirror changes in Zn concentration. Although time and treatment were significant for leachate pH \( (p < 0.001) \), the pH of the leachate did not follow a pattern consistent with the trends observed in leachate Zn. The only sampling date for which pH differed from other sampling dates was the final sampling, where average leachate pH measured 3.72 across all treatments. For all other sampling times, pH was similar and ranged from 4.32 to 4.76. In addition, the differences in leachate pH are not in agreement with differences in leachate Zn concentrations. Across all sampling periods, leachate pH was highest in the Control and FL alone treatments and lowest in the AL+BS and FL+BS treatments (Fig. 3). These results are also similar to field data collected from sampling wells in adjoining tailings deposits (Walton-Day, USGS, personal communication). The pH from water collected at the 36-cm depth from lysimeters in the field decreased over time (1999–2004) from near 5.00 to less than 4.00.

**pH**

All amendments significantly increased tailings pH in the depth of incorporation (0- to 15-cm depth for the FL alone treatment and 0- to 22.5-cm depth for all of the BS+lime treatments) (Fig. 4 and Table 3). Of all of the treatments, SBL+BS and the LK+BS raised pH to >7.0 for all amended depths. This increase, in comparison to that observed in the FL+BS, CL+BS, and AL+BS treatments, is due to the highly reactive and soluble CaO species in the LK and may be due to the smaller particle size of the SBL. In addition, the organic matter and other constituents left after the sugar purification process that are found in SBL may improve the solubility of the liming residual (Perez de Mora et al., 2006). No difference in pH was observed between the FL+BS, CL+BS, and AL+BS treatments. These results were unexpected because particle size was expected to play an important role in the solubility and reactivity of limestone (Barber, 1967). The pH increase for the FL alone (7.33) was greater than that for the FL+BS treatment (6.6). This may be the result of decomposition of the BS added organic
matter. It suggests that when organic residuals are used in combination with a liming agent, accounting for the acidity that is generated by organic matter decomposition is necessary.

All treatments, except the FL alone and the FL+BS with limited leaching, increased tailings pH for the 0- to 7.5-cm depth immediately below the amended horizon compared with the control (pH 3.98). This increase was greatest for the SBL+BS treatment with high leaching (pH 6.01) (Table 3). Additional water increased the efficacy of this treatment with the pH in the same horizon almost a full log unit less than when less water was added to the columns (5.05). The additional moisture was effective at moving alkalinity through the profile. A similar trend was observed with the FL+BS treatment where pH in the horizon below incorporation was 4.75 with high water volume and 4.34 with the lower rate of water. These results confirm other studies that have shown alkalinity movement when biosolids and lime have been added to the surface soil horizon (Brown et al., 1997; Tan et al., 1985).

Diff erences in pH were much less pronounced at the last measured depth of the columns where only two treatments were significantly greater than the control. The pH in the SBL+BS (4.54) and the LK+BS (4.46) treatments, although higher than the control (4.05), were most likely not suffi ciently increased to reduce metal availability and allow rooting to this depth.

**0.01 M Ca(NO₃)₂ Extractions**

The Ca(NO₃)₂–extractable, or water-soluble Zn and Cd, by depth and treatment are shown in Fig. 5 and 6 and Table 3. For all treatments, the Ca(NO₃)₂–extractable Cd and Zn in the amended portion of the columns was significantly (p < 0.05) lower than in the control treatment. Similar results for extractable metals have been observed for a range of amendments where pH increased as a result of amendment addition (Brown et al., 2005a).

In the tailings below the amended horizon, differences in extractable metals between the different treatments were observed. The Ca(NO₃)₂–extractable Cd and Zn in the FL alone treatment increased to levels similar to control in both of the unamended depths. This observation is likely related to the lower soil pH at both of these depths, resulting in no alteration of contaminant extractability in the unamended horizons (Fig. 4). All treatments that included BS and high rates of leaching had significantly lower extractable Zn and
Cd concentrations than the control and lime alone treatments for both measured depths below the amended zone. These decreases were the most pronounced for the SBL+BS treatment for Cd and Zn. For the treatments that had limited leaching, the decrease in extractable metals was much less pronounced (Table 3). Although lower than the control, the extractable Zn and Cd in the 0- to 7.5-cm section immediately below the amended layer was about two to three times higher than the same treatment with additional water for the SBL+BS and LK+BS treatments. The extractable metals in the FL+BS with limited leaching were similar to the control for both depths. At the lower depth below the amended horizon, extractable Zn and Cd were similar to the control for all treatments that had limited leaching. These results suggest that combining BS with reactive forms of lime can be an effective tool for neutralizing subsoil acidity and simultaneously decreasing extractable concentrations of metals. They also demonstrate that having sufficient moisture to facilitate movement of alkalinity is essential to the efficacy of this approach.

Tailings Electrical Conductivity

The average EC by depth and treatment is shown in Table 4. The control, FL alone, and the limited leached biosolids + lime had the highest EC concentrations at the 0- to 15-cm depth. These concentrations were high enough to inhibit plant growth for most species, including salt-tolerant plants. The leached BS-lime treatments had significantly (p < 0.05) lower EC levels at the 0- to 7.5-cm and 7.5- to 15-cm depths. Conductivity increased with depth for the amended portion of the columns for the leached treatments that contained BS. In the lower third of the amended horizons, EC in these treatments increased and was similar to the control, lime only, and limited leaching treatments. The lower EC levels in the BS-lime treatments at the surface are likely the result of the water removing soluble salts from the amended depths. The elevated EC concentrations in the limited leached treatments suggest that leaching, in addition to moving alkalinity and decreasing soluble metal concentrations, may be important for reducing the elevated soil EC concentrations present in the mine tailings to allow plant growth.

Below the amended depths, the limited leached BS-lime treatments had EC concentrations that were significantly higher (p < 0.05) than the control and leached treatments. Potentially, the amount of water that was added to these columns was sufficient to move a portion of the added salts through the profile but insufficient to move salts entirely through the columns.

Plant Growth and Metal Levels

Plant growth in the control and FL alone treatments was reduced (visual observation) in comparison to the rest of the BS-lime treatments. Plants in the control treatment showed visual toxicity symptoms, including stunted growth, chlorosis, and brown tips. In the FL alone treatment, plants were more vigorous than the control but showed similar symptoms of phytotoxicity. In contrast, all plants grown in the treatments that included BS seemed to be healthy with no signs of chlorosis.

The aboveground plant tissue Cd, P, Pb, and Zn concentrations are shown in Table 5. All treatments that included BS significantly reduced plant Cd, Pb, and Zn and increased plant P in comparison to the control soil. In addition, for treatments that were replicated to include high and reduced irrigation, reducing the quantity of water for a treatment generally resulted in decreased plant metal concentrations. For Cd, the lowest plant concentrations were observed in all treatments that included limited water (ranging from 0.75 ± 0.2 to 1.0 ± 0.2 mg Cd kg⁻¹) and the LK+BS treatment with unrestricted water (1.1 ± 0.5 mg Cd kg⁻¹). The

---

**Table 4. Electrical conductivity (dS m⁻¹) for samples collected from greenhouse columns at the end of the experiment.** For the fine lime alone treatment, the amended portion of the tailings extended to the 15-cm depth. For all other treatments excluding the control, the amended portion of the soil extended to the 22.5-cm depth. Means within each depth followed by the same letter are not significantly different (p < 0.05).

<table>
<thead>
<tr>
<th>Treatments</th>
<th>0–7.5 cm</th>
<th>7.5–15 cm</th>
<th>15–22.5 cm</th>
<th>22.5–30 cm</th>
<th>30–37.5 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>11.1d</td>
<td>11.2d</td>
<td>11.6b</td>
<td>11.8ab</td>
<td>NA</td>
</tr>
<tr>
<td>Fine lime alone</td>
<td>11.1d</td>
<td>11.1d</td>
<td>11.5ab</td>
<td>11.6a</td>
<td>NA</td>
</tr>
<tr>
<td>Coarse lime + BS†</td>
<td>3.6ab</td>
<td>8.9c</td>
<td>11.3ab</td>
<td>12.2bc</td>
<td>13.3a</td>
</tr>
<tr>
<td>Ag lime + BS</td>
<td>2.6a</td>
<td>6.8a</td>
<td>11.2ab</td>
<td>12.1ab</td>
<td>12.9a</td>
</tr>
<tr>
<td>Fine lime + BS</td>
<td>3.5ab</td>
<td>7.6ab</td>
<td>11.4ab</td>
<td>12.0ab</td>
<td>12.8a</td>
</tr>
<tr>
<td>SBL + BS</td>
<td>5.0c</td>
<td>8.5bc</td>
<td>10.8a</td>
<td>12.8c</td>
<td>13.2a</td>
</tr>
<tr>
<td>LK + BS</td>
<td>4.0bc</td>
<td>7.8b</td>
<td>11.4ab</td>
<td>12.8c</td>
<td>13.2a</td>
</tr>
<tr>
<td>SBL + BS + LL</td>
<td>11.2d</td>
<td>11.0d</td>
<td>12.4c</td>
<td>14.7d</td>
<td>15.9b</td>
</tr>
<tr>
<td>LK + BS + LL</td>
<td>10.1d</td>
<td>11.7d</td>
<td>12.9c</td>
<td>15.0de</td>
<td>15.8b</td>
</tr>
<tr>
<td>FL + BS + LL</td>
<td>10.5d</td>
<td>11.5d</td>
<td>13.0c</td>
<td>15.6e</td>
<td>16.4b</td>
</tr>
</tbody>
</table>

† BS, biosolids; FL, fine-textured lime; LK, lime kiln dust; LL, limited leaching; SBL, sugar beet lime.
Table 5. Elemental concentration of aboveground annual rye (Lolium multiflorum) grown in the column study. Means followed by the same letter are not significantly different (p < 0.05). Means ± SD are shown.

<table>
<thead>
<tr>
<th>Treatment†</th>
<th>Cd</th>
<th>P</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>4.85 ± 0.3a</td>
<td>2650 ± 444a</td>
<td>25.0 ± 13.2a</td>
<td>546 ± 63a</td>
</tr>
<tr>
<td>Fine lime alone</td>
<td>3.0 ± 0.8b</td>
<td>1075 ± 122a</td>
<td>9.7 ± 6.0ab</td>
<td>350 ± 183a</td>
</tr>
<tr>
<td>Coarse lime + BS</td>
<td>1.85 ± 0.6c</td>
<td>4910 ± 483b</td>
<td>8.4 ± 2.5b</td>
<td>214 ± 38b</td>
</tr>
<tr>
<td>Agricultural lime + BS</td>
<td>1.9 ± 0.7c</td>
<td>6000 ± 405b</td>
<td>7.5 ± 2.6b</td>
<td>210 ± 51bc</td>
</tr>
<tr>
<td>Fine lime + BS</td>
<td>2.6 ± 0.3bc</td>
<td>5225 ± 396bc</td>
<td>11.4 ± 1.3b</td>
<td>259 ± 16b</td>
</tr>
<tr>
<td>SBL + BS</td>
<td>2.3 ± 0.1c</td>
<td>4560 ± 1100b</td>
<td>7.5 ± 2.4b</td>
<td>210 ± 38c</td>
</tr>
<tr>
<td>LK + BS</td>
<td>1.1 ± 0.5d</td>
<td>5023 ± 922c</td>
<td>3.6 ± 2.2c</td>
<td>114 ± 36d</td>
</tr>
<tr>
<td>SBL + BS + LL</td>
<td>0.9 ± 0.1d</td>
<td>6430 ± 1715c</td>
<td>1.4 ± 0.6d</td>
<td>115 ± 10d</td>
</tr>
<tr>
<td>LK + BS + LL</td>
<td>0.75 ± 0.2d</td>
<td>6250 ± 1530c</td>
<td>1.4 ± 0.9d</td>
<td>103 ± 4d</td>
</tr>
<tr>
<td>FL + BS + LL</td>
<td>1.0 ± 0.2d</td>
<td>8860 ± 1370d</td>
<td>2.2 ± 0.8c</td>
<td>184 ± 12c</td>
</tr>
</tbody>
</table>

† BS, biosolids; FL, fine-textured lime; LK, lime kiln dust; SBL, sugar beet lime.

highest plant Cd concentrations were observed in the grass growing in the control soil (4.85 ± 0.3 mg kg⁻¹). Increasing the amount of water that was added to the columns also increased plant metal concentration. For example, plant Cd in the SBL+BS treatment with limited leaching was 0.9 ± 0.1 mg kg⁻¹, whereas with additional water and the same soil amendment, plant Cd increased to 2.3 ± 0.1 mg kg⁻¹. For Pb, all amendments, including the FL alone, reduced plant Pb, with the lowest plant Pb concentrations being found in the three treatments that included limited leaching (ranging from 1.4 ± 0.6 to 2.2 ± 0.8 mg Pb kg⁻¹). As with Cd, despite similar soil pH in the surface horizons, limited water resulted in significantly lower plant Pb uptake for SBL+BS, LK+BS, and FL+BS. For Zn, the highest plant Zn concentrations were observed in the control and FL alone treatments (545 ± 63 and 530 ± 183 mg kg⁻¹, respectively). All amendments that included BS significantly reduced plant Zn concentrations, with the most dramatic reduction observed in the LK+BS treatment (114 ± 36 mg kg⁻¹). As with Pb and Cd, increasing the amount of water added to the columns also generally increased plant Zn concentrations. The exception here was the LK+BS treatment, where Zn concentrations were similar for the high and low water treatments. The higher metal concentration for plants grown in treatments with higher amounts of water added was counterintuitive. These treatments also had lower dilute salt extractable metal concentrations than the same amendments with less water. These extractions are generally thought to reflect phytoavailable or bioavailable concentrations of metals (Condor et al., 2001; McLaughlin et al., 2000; Brown et al., 2005a). It seems that in this study, the Ca(NO₃)₂-extractable fraction of total Cd, Pb, and Zn was not representative of the phytoavailable fraction. This discrepancy may be the result of the elevated EC in the treatments with limited water. At low soil Cd concentrations, high EC, in particular high Cl⁻ concentrations, have been linked to elevated plant Cd concentrations (Smolders et al., 1997; Wegger-Beaton et al., 2000). Cadmium preferentially associates with Cl ions in solution and is transported to plant roots. However, in the case of elevated metals and very high conductivity, there may be increased competition for uptake sites between different ions. In a high salt solution, the effective metal concentration is also reduced in comparison to similar concentrations in a low salt solution. The control treatment had the highest plant metal concentrations and the highest extractable metal concentrations. At the lower end of the spectrum in this study, dilute salt extractable metals were not representative of the phytoavailable fraction of total metals. Similar discrepancies have been found with this type of extraction for plant available Cu concentrations (Zhang et al., 2001). In addition to altering the plant available fraction of Cd, Pb, and Zn, soil amendments also affected the P content of plant tissue. Lime alone reduced plant P in comparison to the control (1075 ± 122 and 2650 ± 444 mg P kg⁻¹, respectively). In contrast, all amendments that included BS increased plant P in comparison to the control. The most significant increase was in the FL+BS treatment with limited leaching, where plant P averaged 8860 ± 1370 mg kg⁻¹. In cases of Pb- and Zn-contaminated soils, P is often limiting for plant growth because P can form precipitates with both metals (Brown et al., 2003; Brown et al., 2005a). These results suggest that the BS were able to supply sufficient P for plant growth. With a BS application of 224 Mg ha⁻¹, a total of 6.9 Mg ha⁻¹ P was added to the soil. The high rates of P added with the BS may be one of the factors responsible for the vigorous growth in these treatments.

Conclusions

The results from this study confirm findings from previous studies that have shown that combining some type of organic matter with lime facilitates movement of alkalinity to subsoil horizons. This study is the first example of a lime and BS amendment mixture to be used for direct remediation of subsoil acidity in mine wastes. Here, all amendments that included BS were able to increase the tailings pH in the horizon below the incorporated amendment. Potentially as a result of increased pH, decreases in extractable Zn and Cd were also observed in surface and subsurface tailings. Leachate Zn was also reduced in these treatments. As with agronomic crops, reclamation sites that use this combination of amendments have lower susceptibility from drought if plants can extend roots into the subsoil.

The most successful amendments tested in this study were BS in combination with SBL and LK. Both of these materials are residuals from other industries and therefore offer a low-cost alternative to commercial limestone. This is also noteworthy because the high existing and potential acidity of the Leadville tailings requires high rates of neutralizing amendments. Here the Leadville tailings are similar to other mine wastes that have high acid-generating potential, including coal wastes and other ores from pyritic rock. The ability of residuals to effectively neutralize subsoil acidity offers a cost-effective alternative for remediation.

An unexpected result of this study was the discrepancy in response between the low and high water replicates of the SBL+BS, LK+BS, and FL+BS treatments. The replicates that included a high rate of water movement saw greater movement in the subsoil acidity off ers a cost-eff ective alternative for remediation.
to those with higher water addition. Plant metal concentration was also generally lower in the treatments that included limited water. Because the limited water treatments are more closely reflective of field conditions at the Leadville site, the greenhouse results suggest that the most successful amendments tested in the greenhouse have a high potential of success in the field.

References
King County Department of Natural Resources. 2000. Biosolids quality summary. Wastewater Treatment Div., Seattle, WA.
SPSS. 1999. SPSS for windows, release 10.0.5. SPSS Inc., Chicago, IL.