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Using municipal biosolids in combination with other residuals to restore metal-contaminated mining areas

Sally L. Brown[1,3], Charles L. Henry[1], Rufus Chaney[2], Harry Compton[3] & Pam S. DeVolder[1]
[1] *Ecosystem Sciences, College of Forest Resources, University of Washington, Seattle, WA 98195, USA.* [2] *USDA Agricultural Research Service, Beltsville, MD, USA.* [3]*US Environmental ProtectionAgency, Environmental Response Team, Edison, NJ, USA.* [3]*Corresponding author**

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Abstract

High metal waste materials from historic mining at the Bunker Hill, Idaho (ID) Superfund site was amended with a range of materials including municipal biosolids, woody debris, wood ash, pulp and paper sludge, and compost. The existing soil or waste material has elevated metal concentrations with total Zn, Pb and Cd ranging from 6000 to 14 700, 2100 to 27 000 and 9 to 28 mg kg^{-1}, respectively. Surface application of certain amendments including biosolids mixed with wood ash resulted in significant decreases in subsoil acidity as well as subsoil extractable metals. This mixture was sufficient to restore a plant cover to the contaminated areas. At the Bunker Hill site, a surface application of high N biosolids (44 or 66 tons ha^{-1}) in combination with wood ash (220 tons ha^{-1}) with or without log yard debris (20% by volume) or pulp and paper sludge (44 tons ha^{-1}) was able to restore a vegetative cover to the metal contaminated materials for 2 years following amendment application. Plant biomass in 1999 was 0.01 mg ha^{-1} in the control versus a mean of 3.4 tons ha^{-1} in the residual amended plots. Metal concentrations of the vegetation indicated that plants were within normal concentrations for the 2 years that data were collected. Surface application of amendments was also able to reduce $Ca(NO_3)_2$ extractable Zn in the subsoil from about 50 mg kg^{-1}in the control to less than 4 mg kg^{-1}in two of the treatments. Use of conventional amendments including lime alone and microbial stimulants were not sufficient to support plant growth. These results indicate that surface application of biosolids in combination with other residuals is sufficient to restore a vegetative cover to high metal mine wastes.

Introduction

Bunker Hill, ID is included on US EPA Superfund's National Priorities List (NPL) of highly contaminated sites. Mining and smelting of Zn and Pb ores for much of the 20th century has resulted in extensive metal contamination of the hillsides and waterways in the vicinity of the operation. The area that falls under the Superfund designation is well over 600 ha. As part of their clean-up efforts, EPA has been depositing contaminated tailings and dredged materials in a Central Impoundment Area (CIA). This area is over 100 ha (US Army Corp of Engineers). These materials generally contain high concentrations of potentially phytotoxic metals, little to no organic matter, are moderately to severely acidic, and are deficient in essential macro- and micro-nutrients. Conventional restoration technologies involve covering tailings with an impermeable plastic material (such as linear low density polyethelene) and then importing topsoil to establish a plant cover over the barrier. The plastic barrier is installed to prevent water flow through the contaminated material and into groundwater. The lifespan of these plastic barriers is not known and failures have occurred in liners installed at the Bunker Hill Site (Scott Peterson, Idaho Department of Environmental Quality, personal communication). In addition, importing topsoil is not always cost effective and has a negative environmental impact in the area that the topsoil is mined. For example, at the Bunker Hill

* E-mail: slb@u.washington.edu.

site, sourcing replacement topsoil involved excavating 66 cm of topsoil from a 50 ha (Silverman, 2001). The negative environmental impacts associated with this removal resulted in an attempt by the state to block the topsoil removal. With the use of blended residuals to create a manufactured topsoil, it may be possible to restore a vegetative cover directly on mine tailings, providing an alternative to current accepted technologies within the Superfund program (such as conventional capping).

The use of residuals, primarily municipal biosolids, for mine land restoration is a long-standing practice with many sites having been successfully restored for 25 years or more (Haering et al., 2000; Sopper, 1993). Biosolids have been effectively used on strip mines, coal refuse piles, and other disturbed soils. Although less common, other residual materials such as pulp sludge and fly ash have also been used as soil amendments for restoration (Gorman et al., 2000; Li and Daniels, 1997). Amendment mixtures have also been used to achieve specific soil chemical objectives (Brown et al., 2000). It is possible to use combinations of materials to correct specific problems in an affected ecosystem. For example, woody material was added to fly ash to reduce erosion potential on abandoned coal mines (Gorman et al., 2000). Where concerns over excess nitrates exist, biosolids have been combined with high carbon materials to reduce the potential for nitrate leaching (Haering et al., 2000; Sabey et al., 1975).

In recent years, there has been a growing recognition that biosolids may also be used to restore metal-affected ecosystems. Initial concerns about potential negative effects to plant and human health as a consequence of application of high metal biosolids to agricultural lands prompted a great deal of research on the behavior of metals in biosolids amended soils. Scientists have consistently demonstrated that metals in biosolids are much less available than equivalent metals added to soils as salts (Brown et al, 1998). In addition, use of high quality biosolids generally results in no observable increase in plant metals (Brown et al, 1998). It should be noted that many of the historical biosolids restoration projects used material that would not be acceptable for beneficial use under current regulations (Haering et al., 2000). Metal concentrations in these biosolids were significantly higher than is currently allowed under Code of Federal Regulations (CFR) Part 503. In fact, the metals in historic biosolids used were as high as soil metal concentrations in some of the mining affected sites that are on US EPA Superfund's NPL. Despite this fact, the sites that were restored using these materials have been able to maintain healthy plant cover with plant metal concentrations within an acceptable range (Sopper, 1993). From these observations as well as research on the phytoavailability of metals in biosolids/soil systems came the notion that high quality biosolids could be used to limit metal toxicity in metal contaminated soils. As a quantitative understanding of the metal binding properties of biosolids is developed, it may be possible to tailor biosolids application rates to correspond with metal concentrations in the affected soil (Li et al., 2000).

At the present time, for use on metal contaminated sites, biosolids must be combined with either conventional limestone or high calcium carbonate equivalent (CCE) residuals to be fully effective for restoration. Research at Palmerton, Pennsylvania and Katowice, Poland demonstrated that application of biosolids in combination with high calcium carbonate equivalent residuals to highly metal contaminated soils was sufficient to restore a vegetative cover (Sopper, 1993; Stuczynski et al., 1997). Laboratory studies have also indicated that addition of alkaline biosolids to mine tailings was sufficient to permit earthworm (*Eisenia fetida*) survival (Conder et al., 2001).

The current research was undertaken to determine if similar remediation mixtures would be effective at restoring a self-sustaining vegetative cover at the Bunker Hill Superfund sites. By using residuals, the negative environmental impacts associated with mining large quantities of topsoil for replacement material can be avoided. To test the potential for residuals to serve as a topsoil replacement, a wide range of materials were used in the present study. These focused on locally available residuals and included municipal biosolids, wood ash, primary pulp and paper sludge, biosolids compost, and log yard debris (high carbon woody materials remaining after log processing). Establishing a vegetative cover directly over these materials will reduce the potential for erosion and contaminant transfer. In addition, a plant cover may reduce the volume of water percolating through the contaminated soils by creating a transpiration demand (Vangronsveld et al., 1995; Zhu et al., 1999). There is some evidence that surface application of amendments may reduce the concentration of contaminants in leachate (Abbott et al., 2001;Vangronsveld et al., 1995). In the case of amendment incorporation, this may occur if the amendment provides binding sites for the contaminants. For surface applied materials, this

Table 1. Amendment mixtures used in small scale field plots to determine the ability of a surface application of residual mixtures to restore a vegetative cover on metal mine tailings. Low N and High N refer to biosolids with low and high concentrations of nitrogen. Log yard refers to woody waste material from wood processing. Ash refers to wood ash and pulp and paper refers to primary pulp and paper sludge

Treatments	Biosolids	Ash	Log yard	Pulp fines	N
	(dry tons ha^{-1})				(kg ha^{-1})
Control					
Low N66/ash	66	155			
Low N66/ash/log yard 66	155	55			
Low N99/ash	99	155			
Low N99/ash/log yard	99	155	55		
High N44/ low ash	44	175			
High N44/ash	44	155			
High N44/ash/log yard	44	155	55		
High N66/ash	66	155			
High N66/ash/log yard	66	155	55		
High N44/pulp and paper	44	155		44	
High N66/ash/pulp and paper	66			44	
Compost low	10				
Compost high/ash	165	155			
Logyard/ash/N (inorganic)		155	110		200
High N3 (H-N3+Ly)	50	155	55		
Biosol®(approx. 1500 kg ha^{-1})					
Kiwi Power™ (approx. 50 l ha^{-1})					

may also occur if the amendment alters the chemistry of the tailings (Svendsen et al, 2001).

This study was conducted to ascertain whether surface application of residual mixtures directly on metal mine tailings was sufficient to restore a vegetative cover on the wastes. In addition, the effect of application of a surface amendment on the subsurface materials was examined. Research was conducted by the University of Washington in cooperation with the USDA-Agricultural Research Service and US-EPA-Environmental Response Team.

Materials and methods

Amendments

Field plots were installed in October, 1997 and consisted of small-scale treatment plots (1 × 4 m) in a randomized block design with three replicates. The surface materials in the field plot area consist of heterogeneous Pb and Zn mining wastes with little to no organic matter (total C = 4.2 g kg^{-1}) and low nutrient status (i.e., total N below detection P$\simeq$530 mg kg^{-1}). Total metal concentrations ranged from 2500 to 19 100 mg kg^{-1} Zn , 1100 to 8700 mg kg^{-1} Pb, and 13 to 82 mg kg^{-1} Cd. Copper concentrations were not significantly elevated. Soil pH ranged from 4.8 to 8.0. All amendments were surface applied. Amendments for this study included high N (4.4–5.3%) and low N (2.8%) biosolids applied at a range of rates (Table 1). The high N biosolids were produced through anaerobic digestion. The low N biosolids were stabilized in a lagoon with stabilization involving a lengthy retention time and increased decomposition of organic matter. All of the biosolids used met US EPA CFR Part 503 requirements for Class B pathogen reduction. A previous study at the Bunker Hill site indicated that more of the low N material was required to achieve a homogeneous mixture with the wood ash, probably due to its lower moisture content. Because of this, the low N materials were applied at consistently higher rates in the current study than the high N biosolids (Brown et al., 2000). In addition to the biosolids, log yard debris was included in several of the amendment mixtures. Log yard debris consists of the woody material that accumulates in wood processing facilities

Table 2. Total trace metal concentrations (mg kg^{-1}) in materials and treatments used in small scale field plots. Means ± standard deviation (n=3) are shown for the amendment mixtures. Means alone are shown for the components of the mixtures

	Cadmium	Lead	Zinc
Materials			
High N biosolids	3.0	170	820
Low N biosolids	23.1	400	1960
Biosolids compost	0.7	42	330
Low ash	2.6	34	600
Ash	3.0	79	390
Treatments			
Low N66/ash	5.9 ± 2.9	200 ± 50	2400 ± 300
Low N66/ash/log yard	5.5 ± 0.6	340 ± 20	5300 ± 200
Low N99/ash	5.9 ± 0.9	310 ± 90	5200 ± 900
Low N99/ash/log yard	8.5 ± 4.6	380 ± 90	7100 ± 1200
High N44/ low ash	6.2 ± 0.8	440 ± 200	3300 ± 600
High N44/ash	6.1 ± 3.7	180 ± 30	5400 ± 700
High N44/ash/log yard	7.0 ± 0.9	450 ± 20	7500 ± 200
High N66/ash	9.6 ± 8.0	350 ± 140	8100 ± 4000
High N66/ash/log yard	6.2 ± 1.1	280 ± 90	10200 ± 300
High N44/pulp and paper	5.5 ± 0.8	320 ± 100	5200 ± 2400
High N66/ash/pulp and paper	3.7 ± 0.8	100 ± 70	1600 ± 1400
Compost high/ash	6.1 ± 1.8	280 ± 80	9800 ± 2900
Logyard/ash/N	4.2 ± 1.2	220 ± 100	5700 ± 1200

(tree bark and branches) along with a small amount of soil. The material used for this study contained 88 g kg^{-1} C and 2 g kg^{-1} N. Wood ash was used as a high CCE material. The $CaCO_3$ content of the ash varies depending on burn temperature. At higher burn temperatures, more CO_2 will volatilize, resulting in more caustic ash materials. As the ash ages, the CaO will interact with atmospheric CO_2 causing the pH of the material to decrease (Campbell, 1990; Ohno, 1992). Both fresh and aged ash were used in the current study. The fresh ash was obtained from a wood burning power plant and had a pH of 12.8 and total C equal to 230 ± 10 g kg^{-1}. The calcium carbonate equivalent (CCE) of this ash was equal to 38%. The less reactive ash was generated by burning log yard debris (90%) and paper sludge (10%). The pH of this ash was initially 12 and total C was equal to 330 ± 110 g kg^{-1}. The CCE of this ash was 11± 1.6%. Primary pulp and paper sludge is a carbon rich waste material that results from paper manufacturing. It has been used as a source of organic matter for manufactured topsoils (Carpenter and Fernandez, 2000). At a certain moisture content, it can also be highly adhesive and may have potential for use as a surface amendment on hillsides.

In addition to the primary goal of assessing the ability of surface applied soil amendments to sustain a vegetative cover on the tailings, materials were mixed to answer some additional questions. Biosolids and caustic ash (155 tonnes ha^{-1}) were tested at two application rates (66 and 99 tonnes ha^{-1} for the low N and 44 and 66 tonnes ha^{-1} for the high N biosolids) ± log yard debris (55 tonnes ha^{-1}) to test the importance of log yard debris in this mixture. The high N biosolids (44 tonnes ha^{-1}) was applied with both types of wood ash to test if the more caustic ash was a more effective liming material. Log yard debris (110 tonnes ha^{-1}) was used in combination with wood ash and inorganic nitrogen fertilizer to evaluate the performance of this source of organic matter in comparison to municipal biosolids. Pulp and paper sludge (44 tonnes ha^{-1}) was used with high N biosolids (66 tonnes ha^{-1}) with and without ash to test the performance of this carbon-rich residual (C:N ratio = 200:1). Two rates of biosolids compost were compared: 10 and 165 tonnes ha^{-1}. Compost had previously been tested at the Bunker Hill site for suitability as a soil restoration amendment. Compost had been applied at 10 tonnes ha^{-1} and had not performed differently from unamended soil. The low rate of compost had been tested without any type of limestone. In our study, a 'reclamation rate' of the compost with wood ash was used in addition to the low rate. Finally, two commercially available soil restoration products, Biosol® and Kiwi Power™ were included in the trial. Biosol® claims to be an organic fertilizer. Kiwi Power™ includes microorganisms, enzymes, and growth hormones. Both products have been used extensively for soil restoration projects. For this study, the Kiwi Power™ and Biosol® amendments are referred to as 'conventional' treatments.

Amendments were placed on the plots, then mixed by hand before application. This resulted in incorporation of some of the surface material into the amendment mixtures. The high metal concentrations in the surface soils elevated metal concentrations in the amendments. Mixtures were sampled on a per plot basis immediately after surface application of the treatments. Total metals were determined using the Aqua Regia procedure followed by flame atomic adsorption analysis (McGrath and Cunliffe, 1985). Metal concentrations of the amendments are reported in Table 2. Plots were hand seeded with a mixture

Table 3. Germination seedlings in small scale plots by day of seeding. Treatments are grouped as containing high nitrogen biosolids, low N biosolids, compost, or conventional mixtures. Conventional includes the control, Kiwi Power™ and Biosol® amendments

	Treatments				
	Overall (%)	Low N (%)	High N (%)	Composts (%)	Conventional (%)
Day 1	82	100	71	89	100
Day 2	81	100	67	78	89
Day 7	39	50	29	22	67
Day 14	0	0	0	0	0

of a western wheat grass (*Pascopyrum smithii*) and vetch (*Vicia sativa* L.) on days 1, 3, 7, and 14 after amendment application. The purpose of different seeding dates was to investigate an earlier problem encountered; when research began at this site, germination was inhibited by high ammonium concentrations when seeds were mixed directly into the amendment mixture just prior to application (Brown et al., 2000). Germination results indicate that the 24-h waiting period was sufficient to permit germination. Seedings done at 7 and 14 days were less effective, most likely due to low air temperatures. A hard frost after the day 14 seeding prevented any germination. Germination results are presented by time as well as by amendment in Table 3. Results indicate that initial germination was best in the conventional treatments (Biosol®, KiwiPower™, and low compost) and in the low N biosolids treatments.

Sampling

Plant samples for elemental analysis were collected in July 1998 and June 1999. In each case, a composite sample, consisting of a minimum of three subsamples, was collected from each plot for elemental analysis. For this purpose, only grass samples were collected. The samples were washed and rinsed in deionized or distilled water. Samples were ashed at 480 °C, digested with concentrated HNO_3, and analyzed using a flame atomic adsorption spectrometer or an inductively coupled argon plasma spectroscopy (ICP: Thermo Jarrel Ash ICAP 61E). Values were corrected for background variation through the use of blanks and the inclusion of replicate subsamples. NIST tomato leaf standards were routinely included in the digests. Recovery on the standards ranged from 125% for Pb, 90% for Cd and P, and 100% for Zn. Harvestable biomass was measured in 1998 and 1999. Samples for biomass measurements were collected from three areas of each plot using a circular measure that was 615 cm^2. All plants within the circular measure were included in the biomass measurements.

In addition to plant samples, soil samples were collected in the amended layer as well as in the 0–15-cm horizon directly below the amendment in 1998 and 1999. Three subsamples from each sampling horizon were composited per plot. These samples were analyzed for pH and $Ca(NO_3)_2$ extractable metals. For pH, air-dried soils were mixed with deionized water at a 1:2 volume ratio and allowed to equilibrate for 1 h before measuring. For extractable metals, 25 ml of 0.01 M $Ca(NO_3)_2$ solution was added to 5 g of air-dried soil. Samples were shaken on a side to side shaker for 1 h and filtered through Whatman # 40 filter paper. Filtrate was analyzed using an ICP. Samples from the amended horizon were collected in all years and analyzed for carbon and nitrogen concentrations by dry combustion using a Perkin-Elmer CHN analyzer. It has been suggested that the C:N ratio of the soil over time will give an indication of the amount of microbial decomposition, and therefore nutrient cycling, in a soil system (Steve McGrath, IACR, Rothamstead, UK, personal communication). Data was analyzed by analysis of variance using a SAS statistical analysis program (SAS Institute, 1990). Means were separated using the Duncan Waller procedure with $P<0.05$ used as the level of significance. In addition, contrast statements were used to compare specific types of amendments.

Results and discussion

Soils

There were significant differences between treatments in both the amended and subsoil horizons in both pH and extractable Zn (Table 4). The pH of the amendments ranged from 7.1 to 8.2. All of the amendments that contained the more reactive wood ash had pH $\approx$ 8.0 with the exception of the High N66/ash/pulp and paper treatment (pH of 7.8). The biosolids treatment containing the less reactive wood ash had pH of 7.8. For all of the conventional treatments (including the low rate of compost addition), surface or amendment pH was measured in the upper 15 cm of the soil. For these treatments, pH ranged from 5.6 to 7.0. This is

Table 4. Soil pH in the amendment, and pH and extractable zinc (mg kg^{-1}) in the 0–15-cm depth of tailings directly below the amendment. Means within columns followed by the same letter are not significantly different

Treatment	pH		Zn
	Amendment	Subsoil	
Control		6.8 e	48 b
Low N66/ash	8.1 abc	7.6 abcde	7.7 defgh
Low N66/ash/log yard	8.0 abc	8.0 abc	3.2 hi
Low N99/ash	8.2 a	7.0 de	11 cde
Low N99/ash/log yard	8.1 a	8.1 ab	10 defg
High N44/ low ash	7.9 bc	7.6 abcde	13 cd
High N44/ash	8.1 a	8.1 ab	3.9 ghi
High N44/ash/log yard	8.2 a	8.2 a	4.5 efghi
High N66/ash	8.2 a	8.2 a	4.0 fghi
High N66/ash/log yard	8.1 abc	8.2 ab	4.9 efghi
High N44/pulp and paper	7.1 d	7.2 bcde	36 b
High N66/ash/pulp and paper	7.8 c	8.0 abc	4.8 efghi
Compost low		7.0 cde	59 ab
Compost high/ash	8.1 ab	7.93 abcd	7.0 defgh
Logyard/ash/N	8.1 ab	7.37 abcde	10 def
Biosol®		5.6 f	148 a
Kiwi Power™		7.4 abcde	28 bc

within the range of pH values observed for the unamended soils, indicating that these amendments had no effect on soil pH. For many treatments, surface application of the amendment was sufficient to increase subsoil pH over the conventional treatments and the control. The most effective treatments for increasing subsoil pH included the high rate of compost + ash as well as the high N biosolids + ash amendments. Contrast statements were used to directly compare different amendments. These indicated that, among all of the application rates tested, the high N biosolids+ ash treatments were more effective than the low N biosolids + ash treatments at increasing subsoil pH. In addition, inclusion of log yard debris in the high N biosolids treatments resulted in a small, but significant, increase in subsoil pH. Finally, the more reactive ash was more effective at neutralizing subsoil pH than the less reactive ash. This may be the result of the increased reactivity, however, it is more likely a function of the higher CCE of the reactive ash.

Increases in pH were generally accompanied by decreases in the $Ca(NO_3)_2$ extractable Zn in the subsoil horizons (Table 4). For all residuals amendments excluding the High N 66 + pulp and paper, $Ca(NO_3)_2$ extractable Zn was close to detection limits in the amended horizon (results not shown). In the subsoil, the high N biosolids + ash amendments were the most effective at increasing subsoil pH and reducing extractable Zn concentrations. The high rate of compost + ash amendment also decreased subsoil Zn. Specific contrasts between the high N and low N materials indicate that the high N treatments were more effective. In addition, including log yard debris in the amendment mixtures made both the high and low N biosolids treatments more effective at reducing extractable Zn in the subsoil. As above, the higher CCE ash was more effective than the less reactive material.

The reduction in $Ca(NO_3)_2$ extractable Zn along with increased soil pH that was observed in the subsoil under several treatments suggests that some of the alkalinity added with the surface amendment moved downward in the soil. Reduced concentrations of Zn in the soil solution indicate a reduction in phytotoxicity. The proliferation of roots into the subsoil in the plots (visual observation) may be the result of the amendment's ability to reduce bioavailable metal concentrations in the subsoil. Such visual observations also suggest that the higher N biosolids which are less stable and decompose more readily than the low N biosolids, are more effective at translocating alkalinity to the untreated subsoil. The subsoil extractable Zn was significantly lower than control and conventional treatments in the range of residuals treatments that included wood ash and biosolids or biosolids compost (excluding the low rate of compost). These results suggest that the surface application of residuals amendments have the ability to reduce the phytoavailability of metals under the amendments.

C:N Ratio

Changes in the C:N ratio of the amendment horizon over the 3-year period of the study are presented in Figure 1. A stable C:N ratio of approximately 12:1 is indicative of a well functioning soil system. The maintenance of a specific C:N ratio suggests that the vegetative cover is self sustaining. For this study, the C:N ratio of the amendment horizon did not change significantly for the 2 years following amendment addition. Both the initial C:N ratio of the amendments and the average C:N ratio from the second and third

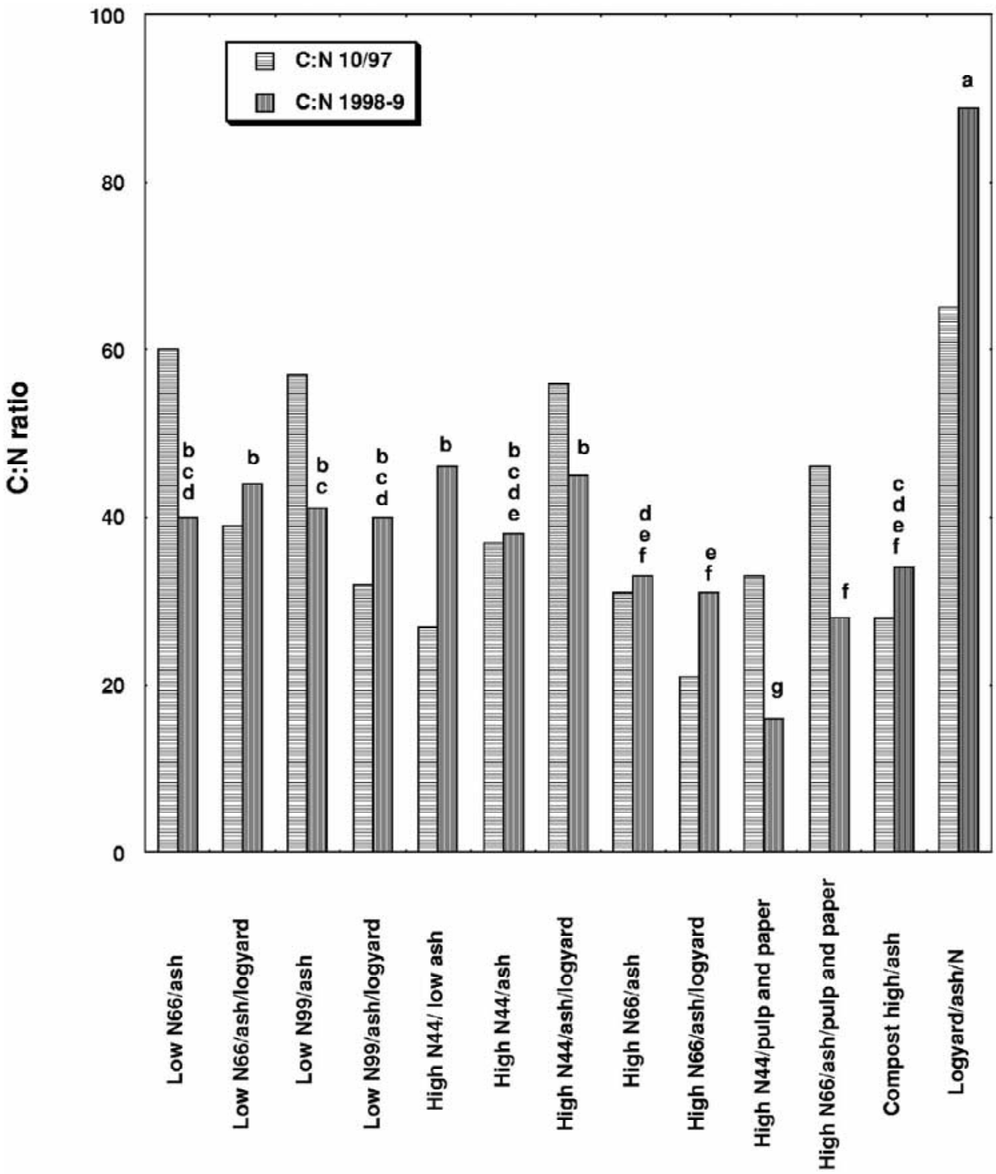

Figure 1. Carbon:nitrogen (C:N) ratios for residual amendments surface applied to Pb and Zn mine wastes. The first value for each treatment represents the C:N ratio of the original amendment mixture. The second value is the mean C:N ratio of samples collected from the mixtures during the 1998 and 1999 seasons. Means labeled with the same letter are not significantly different ($P<0.05$) using the Duncan Waller procedure.

year after application are shown in Figure 1. Initially, all of the low application rate treatments of the low N biosolids had C:N ratios $\geq$40:1. The high N biosolids treatments generally had lower initial C:N ratios. Including log yard debris in the mixtures did not consistently increase the C:N ratio as would have been expected. This is likely due to variations caused by the large particle size of some of the material (2 cm). In the 2 years after application, the lowest ratios were generally found in the amendments that included a high application rate of high N biosolids as well as the high compost treatment. Both treatments that included pulp and paper solids had the ratios closest to 20:1. These treatments also showed the largest consistent decrease in C:N ratio after application. This may be related to the ease of decomposition of the pulp and paper sludge and may also indicate that this residual is an important addition to an amendment mixture for

Table 5. Plant Zn and P concentrations (mg kg^{-1}). Results are presented for two harvests. Means of three replicates for each year followed by the same letter are not significantly different

	Zinc		Phosphorus	
	1998	1999	1998	1999
Control	–	239 a	–	630 f
Biosol®	302 a	133 abc	581 ef	950 ef
Kiwi Power™	268 ab	175 ab	530 gf	1213 def
Low N66/ash	218 abc	53 c	875 def	1606 bcde
Low N66/ash/log yard	117 cd	59 bc	862 def	1735 abcde
Low N99/ash	130 cd	48 c	959 def	1930 abcd
Low N99/ash/log yard	126 cd	53 c	976 cde	1533 cde
High N44/ low ash	193 abcd	74 bc	1410 ab	2043 abcd
High N44/ash	134 cd	45 c	1508 a	1965 abcd
High N44/ash/log yard	118 cd	50 c	1217 abcd	2073 abcd
High N66/ash	122 cd	61 bc	1398 abc	2442 ab
High N66/ash/log yard	118 cd	54 c	1506 a	2052 abcd
High N44/pulp and paper	276 a	156 abc	1017 bcde	2484 a
High N66/ash/pulp and paper	105 cd	59 bc	1529 a	2129 abc
Compost low	297 a	143 abc	868 def	1673 abcde
Compost high/ash	90 cd	63 bc	1190 abcd	1556 cde
Logyard/ash/N	141 bcd	66 bc	890 def	1524 cde

this type of restoration. The highest ratios were observed in the log yard and ash treatment (89:1). This was also the amendment mixture that initially had the highest C:N ratio. The observed increase in the ratio over time indicates that this amendment may not be self-sustaining. In addition, the lower application rates of the high N biosolids and all rates of the low N material maintained high ratios. Additional data over time would be required to show clearer trends in organic matter decomposition and to indicate whether the vegetative cover on these treatments would be self sustaining.

Plant biomass

For biomass, both year and treatment were significant factors. Plant yield for 1998 and 1999 are presented in Figure 2. For both years, biomass in all of the amendment treatments (excluding the log yard and ash and low N 66/ash treatments) was consistently higher than in the conventional and control treatments. In addition, yield increased in the second season for all amendment treatments, excluding the High N44/pulp and paper treatment. Contrast statements showed that the high N biosolids amendments supported higher yield than the low N treatments. Contrast statements were also used to test the addition of log yard debris on yield. These indicated no effect on yield resulting from the inclusion of log yard debris in the amendments. In addition, the higher rate of each amendment did not support higher biomass than the lower application rates. Yield was highest in the High N44/low ash and the HighN66/ash/pulp and paper treatments, with biomass during the second season equal to 5.8 and 6.1 tons ha^{-1}, respectively. In comparison, yield in the control treatment varied from 0.01 to 0.07 tons ha^{-1} for 1998 and 1999, respectively.

Plant metal and nutrient status

Elemental content of above ground biomass was measured for grass species collected in both 1998 and 1999. Average plant concentrations of Zn and P are presented in Table 5. For both Zn and P, the effects of both

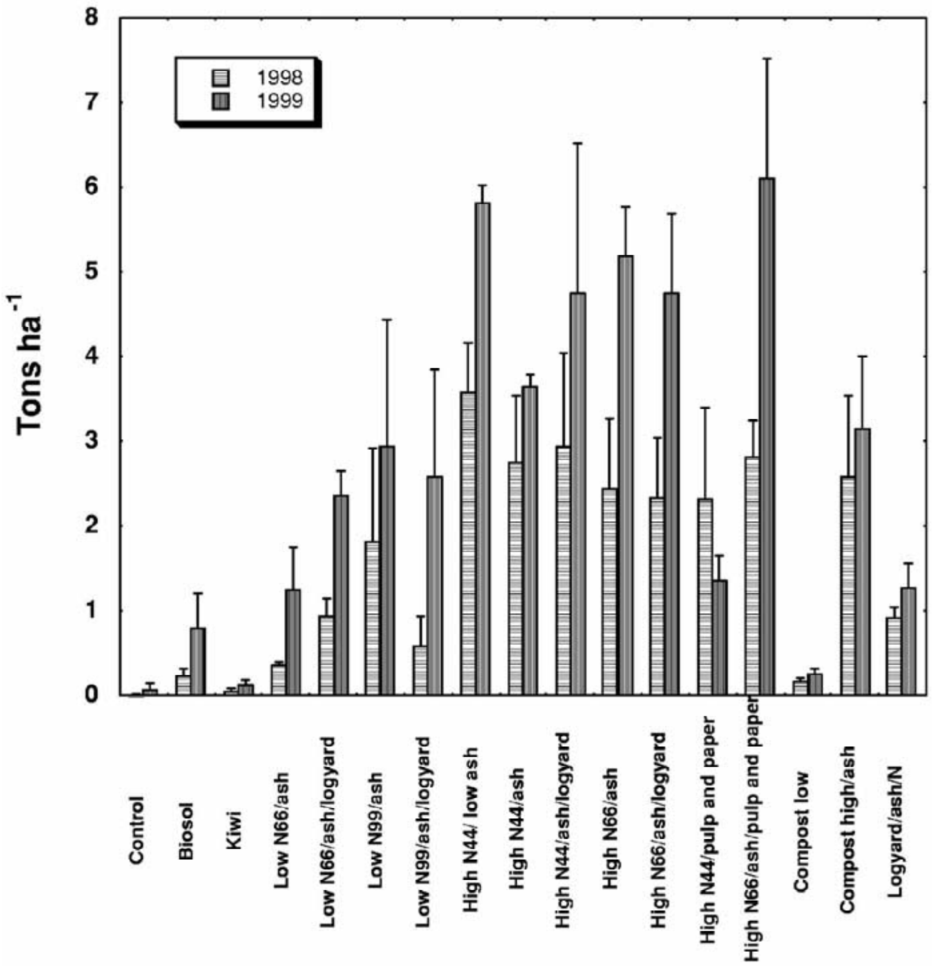

Figure 2. Biomass (tons ha^{-1}) for 1998 and 1999 for plots established on Pb and Zn mine wastes that had been treated with a surface application of different residual mixtures. Bars represent standard errors of the mean.

treatment and year were significant. Overall, plant Zn concentrations decreased dramatically from 1998 to 1999. Average Zn concentration across all treatments was 162 mg kg^{-1} in 1998, and decreased to 81 mg kg^{-1} the following year. The observed decrease in plant Zn concentrations is potentially the result of the stabilization of organic matter in the biosolids fraction of the amendments. Metal uptake by plants in biosolids amended soils is generally highest in the first year following application (Logan and Chaney, 1983). This may also be the case when these residuals are used for restoration of metal contaminated soils. In 1999, Zn concentrations in plants grown most of the biosolids treatments were similar to those expected for plants grown on uncontaminated soils. It is important to note that, despite high total soil Zn, plant Zn concentrations in all treatments that included wood ash were below levels associated with Zn toxicity (Chaney, 1993).

For this study, all plant tissue collected from the conventional (1998+1999) and low N biosolids treatments (1998 only) indicated P deficiency. Phosphorus deficiencies have been observed for plants growing in Zn and Pb contaminated soils (Christensen et al., 2001; Svendsen et al., 2001). This type of deficiency may be common for plants growing on high Zn and Pb soils. Phosphorus tends to form insoluble complexes with these metals and is generally limiting for plant growth. All of the amendments contained excess P for plant growth. Phosphorus concentrations in the low N and high N biosolids were 9000–10 000 mg kg^{-1} and 27 000 – 30 000 mg kg^{-1}. The low application

Table 6. Plant Cd and Pb concentrations (mg kg^{-1}) for plants grown on surface amended Zn and Pb mine tailings. Results are presented for two harvests. Means of three replicates for each year followed by the same letter are not significantly different

	Cadmium		Lead	
	1998	1999	1998	1999
Control	–	0.1 c	–	9.7 ab
Biosol®	2.9 a	1.1 ab	26.5 ab	5.8 bc
Kiwi Power™	1.5 abc	1.1 ab	30.8 ab	14.2 a
Low N66/ash	1.16 abc	1.14 ab	45.3 a	1.37 c
Low N66/ash/log yard	1.05 c	0.39 bc	38.2 ab	1.97 c
Low N99/ash	1.2 bc	0.23 bc	31.9 ab	1.23 c
Low N99/ash/log yard	1.32 bc	0.51 bc	30 ab	1.47 c
High N44/ low ash	1.82 abc	0.63 abc	36.3 ab	1.67 c
High N44/ash	0.58 c	0.31 bc	28.3 ab	1.4 c
High N44/ash/log yard	1.25 bc	0.35 bc	31.5 ab	1.73 c
High N66/ash	0.7 c	0.4 bc	34 ab	2.1 c
High N66/ash/log yard	0.97 c	0.36 bc	34.5 ab	2.33 c
High N44/pulp and paper	1.83 abc	1.17 ab	32.8 ab	4.07 bc
High N66/ash/pulp and paper	1.0 c	1.53 a	32.1 ab	1.5 c
Compost low	2.56 ab	1.14 ab	22 b	6.6 bc
Compost high/ash	0.73 c	0.47 bc	24.1 b	3.87 c
Logyard/ash/N	0.95 c	0.37 bc	38.3 ab	4.73 bc

rate of the biosolids was equivalent to a P application of 660 kg ha^{-1} for the low N and 1300 kg ha^{-1} for the high N. In both cases, this is well above fertilizer requirements. The observed deficiencies in the low N biosolids amendments suggest that an insufficient fraction of the total P in the low N material is plant available. There was an increase in plant P in the 1999 growing season. The reason for this increase is not clear. However, the increase was observed in all treatments. This suggests that it may be related to climatic conditions as opposed to particular characteristics of individual treatments. This increase in plant available P may also have some relationship to the observed decrease in plant Pb and Zn from 1998 to 1999. When plants are severely deficient in P or another essential nutrient, it is difficult to look at concentrations of other elements in a quantitative way. Deficiencies result in the break down of plant metabolic processes and in the integrity of root uptake mechanisms. It is possible that observed concentrations of both nutrient and unessential elements in plants in the control treatment as well as in some of the conventional and low N biosolids treatments have been influenced by deficient levels of P in plant tissue.

Cadmium and Pb concentrations in plant tissue are presented in Table 6. For both metals, year was the most important factor with plant concentrations decreasing for all treatments from 1998 to 1999. In 1998, the highest Cd concentrations were observed in plants grown on the conventional treatments (low compost, Kiwi Power™ and Biosol®), the low rates of the low N biosolids and the high N biosolids treatments that included the less reactive wood ash or did not include wood ash. The lowest values were recorded on the high rates of the high N treatments, the high rate of compost and the log yard waste and ash amendments. For the second year, the highest Cd concentrations were found in plants grown in the conventional treatments, the low rates of the low N biosolids and the high N/ash/pulp and paper treatment. For Pb, average plant Pb across all treatments was 32 mg kg^{-1} in 1998 and 6.6 mg kg^{-1} in 1999. Decreases in total plant Pb concentration may be related to increases in plant P concentrations. In 1998 the lowest plant Pb concentra-

Table 7. Plant Ca, K, and Mg concentrations (mg kg^{-1}) for select treatments. Means ± standard deviation (n=3) for each year are presented

Treatment	Year	Ca	K	Mg
Control	1998	–	–	
	1999	2700 ± 1900	6700 ± 1800	560 ± 220
Low N66/ash	1998	2500 ± 1800	13500 ± 800	2060 ± 320
	1999	1500 ± 1100	12100 ± 800	680 ± 55
Low N66/ash/log yard	1998	2700 ± 1900	13300 ± 1700	1920 ± 240
	1999	1900 ± 1300	13300 ± 1500	810 ± 27
Low N99/ash	1998	2500 ± 1700	14900 ± 3600	1680 ± 500
	1999	1600 ± 1100	13600 ± 800	710 ± 75
Low N99/ash/log yard	1998	2900 ± 2100	13800 ± 700	1840 ± 320
	1999	1700 ± 1200	10800 ± 1300	580 ± 100
High N44/ash	1998	1900 ± 1400	15900 ± 3400	2580 ± 310
	1999	1400 ± 1000	11300 ± 1200	810 ± 38
High N44/ash/log yard	1998	2500 ± 1800	15600 ± 200	2970 ± 800
	1999	1700 ± 1200	13300 ± 900	870 ± 62
High N66/ash	1998	2700 ± 1900	20500 ± 1700	3660 ± 710
	1999	1500 ± 1100	14800 ± 1400	1000 ± 38
High N66/ash/log yard	1998	3100 ± 2200	17200 ± 1500	3230 ± 650
	1999	1500 ± 1100	12100 ± 1200	810 ± 140
High N44/ P & P	1998	6300 ± 4500	5500 ± 600	2780 ± 650
	1999	3900 ± 2700	9100 ± 1000	1270 ± 74
High N66/ash/ P and P	1998	2300 ± 1600	19700 ± 3300	2020 ± 170
	1999	1600 ± 1100	12800 ± 900	700 ± 38
Compost high/ash	1998	1700 ± 1200	12600 ± 2700	1400 ± 15
	1999	1900 ± 1400	12300 ± 800	810 ± 13
Logyard/ash/N	1998	1700 ± 1200	14100 ± 1400	1630 ± 380
	1999	2100 ± 1500	13800 ± 1100	1060 ± 6

tions (22 mg kg^{-1}) were recorded in the low compost treatment with the highest value (45.3 mg kg^{-1}) in the low N/ash treatment. In 1999, the highest Pb values were recorded in the conventional treatments and the high N44/pulp and paper treatment. Plant Pb concentrations were significantly lower in all of the biosolids and ash treatments.

For the range of macro- and micronutrients examined, the effects of both treatment and year varied (Table 7). In general, year was the most important factor with the total concentration of a range of nutrients decreasing from 1998 to 1999. For certain elements in certain treatments, total concentrations were close to or below deficiency levels (Marschner, 1995). Calcium concentration across all treatments in 1998 averaged 3100 mg kg^{-1}. In 1999, the average Ca concentration decreased to 2030 Mg kg^{-1}. Similar trends were observed for Cu (5.2 mg kg^{-1} in 1998 and 4.1 mg kg^{-1} in 1999), Mn (69 mg kg^{-1} in 1998, 32 mg kg^{-1} in 1999), and Mg (2095 mg kg^{-1} 1998 versus 781 mg kg^{-1} 1999). There is no clear explanation for this observed decrease in plant nutrient concentration. The amendment mixtures generally had very high concentrations of all of the elements listed above. Wood ash can be used as a K fertilizer (Ohno, 1992). In addition, its CCE is very high. The high application rates of ash used as components of the amendment mixtures would suggest that sufficient quantities of these elements had been included with the mixture. There may have been some interaction with the amendments and the tailings that were incorporated into the surface amendment mixtures that resulted in the decreased phytoavailability of these elements. For future projects, it may be important to increase the application rates of certain of the amendments to insure that macro and micro-nutrient deficiencies do not occur over time.

The High N 44/pulp and paper treatment supported the highest plant concentrations of Ca. The High

N 66/low ash and two of the conventional treatments were also higher than the other treatments. Considering that none of these treatments included the high CCE wood ash, these results are somewhat anomalous. For Mg, the highest concentrations were observed in the High N biosolids treatments, including the high N 44/pulp and paper treatment. The lowest concentrations were observed in the conventional treatments. The highest plant K concentrations were found primarily in the higher application rates of the High N biosolids/ ash treatments. The lowest values for K were observed in the High N/pulp and paper treatment as well as the conventional treatments.

Conclusions

A general conclusion of the current study is that a surface application of high N biosolids in combination with a high CCE residual such as wood ash is effective in establishing a vigorous plant cover directly on metal mine tailings for at least two growing seasons after amendment application. More specific conclusions are difficult to formulate. The different indices used to quantify the success of the amendments gave somewhat unclear results. This illustrates the complexities involved in attempting to restore a vegetative cover through the use of surface applied amendments. If biomass alone is considered, it seems that plant establishment was more successful during the second growing season of the study. This increase in biomass was most pronounced for the amendments that contained high N biosolids and wood ash. It also appears that the higher application rates promoted better growth than the lower application rates. While the yield increase in and of itself is encouraging, it is important to try to relate this increase to some of the other parameters measured in the study to both predict the longevity of the vegetative cover as well as to develop an understanding of the basis for the observed increase.

For the high N treatments that included the more reactive wood ash, the subsoil pH was amongst the highest observed in the study. In addition, subsoil extractable Zn was lowest in these treatments. However, both the high rate of compost + ash and the high rate of low N biosolids + ash and log yard waste amendments showed similar increases in pH and decreases in subsoil Zn as the high N/ash amendments. Despite this, biomass for these treatments was lower than in the high N amendments. This may be related to P deficiencies for these treatments. Although the clearest indications of P deficiency were seen in the control and conventional amendments, reduced plant P may have resulted in decreased yields for the low N treatments during the first growing season. For all low N amendments as well as the log yard/ash amendment plant P was less than 1000 mg kg^{-1} in 1998. Plant P increased to greater than 1500 mg kg^{-1} in these treatments in 1999 and yield also increased in the low N treatments. In the high compost treatment, plant P was greater than1100 mg kg^{-1} for both harvests. This treatment also maintained consistent yield for both harvests. Plants in the high N amendments contained higher P concentrations for both sampling times than plants in the low N and high compost treatments and yield was higher than the low N or log yard/ash treatments for both years of the study. It may be that the elevated Pb concentrations in plant tissue observed during the first growing season were also related to P deficiency. While this connection is plausible for treatments with low plant P, it is not likely the basis for elevated Pb uptake observed in the high N treatments. The reasons for increased Pb in plant tissue during the first year of the study for these amendments are not obvious. There was also a marked decrease in plant Zn concentrations for the 1999 harvest. Additional monitoring would be required to determine if the results from the first or second year of the study for plant P, Zn, and Pb uptake reflect long-term patterns.

Another problematic observation was the general decrease in plant Ca, K, and Mg concentrations over the two years of the study. It is not clear if this decrease is the result of a decrease in phytoavailability of the added nutrients. Loading rates of each of these amendments should have been sufficient to satisfy plant demand. It may be that the mineral composition of the mine tailings is sufficiently different in concentrations of essential plant nutrients that higher amendment loading rates are required to provide a self-sustaining plant cover.

Despite these complicating factors, biosolids in combination with reactive high CCE materials such as wood ash appears to offer a viable alternative for restoration of metal-affected ecosystems at least in the short term. Additional research should enable scientists to more specifically determine appropriate amendment mixtures to address the specific characteristics of each site. Long-term monitoring will also enable an evaluation of this type of in situ remediation technology.

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