Cost and Performance Summary Report
In Situ Biosolids and Lime Addition at the California Gulch Superfund Site, OU 11
Leadville, Colorado
February 2005

Summary Information [1, 2, 3, 4, 5, 6, 7, 8, 9]

The California Gulch Superfund Site, located in Leadville, Colorado, includes 16.5 square miles of land contaminated by metals from historic mining operations. Mining operations, dating back to 1859, included metals mining for lead carbonate, zinc, copper, silver, and iron-manganese ore; smelting operations; a cyanide mill, a molybdenum mill, and zinc concentrating mills. These operations resulted in large volumes of mine waste and acid mine drainage from mine workings. California Gulch was placed on the National Priorities List (NPL) in 1983 because of concerns about the impact of heavy metals on the Arkansas River and the impact of mine drainage on the surface waters of California Gulch. The primary contaminants of concern (COCs) at this site are cadmium, copper, lead, manganese, and zinc.

The site is divided into 12 operable units (OUs). Since the mid-1980s, there have been several EPA and state actions at the site, including removal actions, Records of Decision (RODs), Consent Decrees, Administrative Orders, and remedial investigations and feasibility studies. RODs have been signed for the majority of the OUs, and two Five-Year Reviews (1996 and 2001) have been performed for the site. EPA, the State of Colorado, and the potentially responsible parties (PRPs) are working as part of a cooperative agreement to clean up the site. EPA conducted the two five-year reviews of the site. The remediation of OU 11 was not underway at the time of these reviews.

This report focuses on a field demonstration conducted at OU 11, the Arkansas Floodplain, where tailings have been deposited into and along the banks of the Upper Arkansas River. Because of the acidic nature of the tailings, the deposits are devoid of vegetation, resulting in streambank instability and an increased risk to wildlife of exposure to contaminated metals. In 1998, as part of a program conducted by EPA Region 8 and the EPA Environmental Response Team Center (ERTC) to address these conditions and to evaluate the reduction in the bioavailability of metals to the biota in the area, tailing deposits in selected locations were treated with biosolids and agricultural lime. This report presents the results of a one-year study of this emerging in situ technology to reduce metals bioavailability, increase the pH of the tailings, and promote vegetation at OU 11. A ROD had not been issued for OU 11at the time of this report.

Additional studies are being performed to evaluate alternatives for restoring the Upper Arkansas River, including the use of various lime and organic amendments, including biosolids compost and/or biosolids pellets. Results of these studies are expected in the near future.

EPA ID Number:	COD980717938
Type of Action:	Remedial
Lead:	Fund Lead
Oversight:	EPA and State

Timeline [1]

Date(s)	Activity
June 17, 1998	Samples collected prior to application of soil amendments
July-August 1998	Biosolids and lime added to tailings and areas seeded with ryegrass
Early September 1998	Additional samples collected for soil microbial community analysis
Mid-March 1999	Samples collected and analyzed for metals
June-July 1999	Tailings reseeded and irrigated
August 19-20, 1999	Second phase of sample collection and analysis

Factors that Affected Technology Cost or Performance [1]

Listed below are the key matrix characteristics for this technology and the values measured for each during site characterization.

Matrix Characteristics [1]

Parameter	Value
Soil Classification	Mining tailings; high mineral content
Clay Content/Particle Size Distribution	Sand (63 - 83%), Silt (15 - 30%), Clay (5 -7%)
Total Organic Carbon	1.7 to 2.6%
pH and Acidity	2.4 to 4.5; 10.2 to 29.7 meq/100g soil
Specific gravity	2.30 to 2.47

Treatment Technology Description [1, 3, 9]

The application of biosolids and lime to acidic mine tailings is expected to reduce metals bioavailability because (1) the biosolids increase the carbon content and cation exchange capacity of the soils, thereby decreasing the mobility of the metals, and (2) the lime increases the pH of the soil, thereby decreasing the availability of most metals.

The demonstration of biosolids and lime amendments was performed from 1998 to 1999. Several tailing locations (identified using a two-letter designation) were selected for treatment, including areas with relatively high (CL/CO), intermediate (MB/ME and MP/MQ), and low metals concentrations (RA/RB). The locations are characterized by white crystals coating the soil surface, high mineralization, and the absence of vegetation. They each cover an area of 2,400 m^2 to 11,400 m^2. Information about contaminant concentrations was not provided, nor was a site map showing tailings locations.

Biosolids used in the study were EPA Class B anaerobically digested cake from the Denver wastewater treatment plant with a solids content of about 17%. Tailings were treated at a rate of 100 dry tons per acre of biosolids cake and 100 tons per acre of 3/8" agricultural grade lime. The biosolids and limestone were mixed on a volume basis using a front-end loader, applied to the tailings, and mixed with tailings using an industrial disk, a plow, and/or an excavator to a depth of up to 12 inches. Two months later, each location was seeded with ryegrass and native species. In June/July 1999, the areas were reseeded with Jose tall wheatgrass, Canadian wild rye, Canadian bluegrass, alkali grass, and red top and irrigated.

In order to evaluate treatment effectiveness, tailings samples were collected before, during, and after treatment. For comparison purposes, sample locations included the untreated tailings, treated tailings, and control (reference) samples from vegetated areas located upstream (from near the Leadville Mine Drainage Treatment Plant) and on-site (near the location of the A tailings). The first phase of sampling was conducted on June 17, 1998, prior to treatment, with surface soil samples collected for agronomic, physical, and metals analyses. Post-treatment samples were collected in early September 1998 for soil microbial community analysis and in mid-March 1999 for metals analyses. The second phase of post-treatment sampling was conducted on August 19-20, 1999 with samples collected for physical, chemical, toxicological, and biological characterization. Statistical analyses, including paired t-tests and Wilcoxon signed rank tests, were performed on the study results.

EPA noted that a large number of samples is generally needed to effectively evaluate a large site. However, given time and budget constraints, this study was designed to compare tailings before and after treatment using a limited number of samples. Samples collected from each of the tailing locations were composited such that four data points were available for comparison.

Operating Parameters [3, 9]

Operating Parameter	Value
Biosolids Application Rate	100 dry tons/acre
Lime Application Rate	3/8" agricultural lime at 100 tons/acre
Incorporation Depth	4 to 12 inches

Performance Information [1, 7, 9]

The following characteristics were used to determine if the addition of biosolids and lime had or had not improved the soil and habitat conditions of the study area, one year after application. These characteristics were compared in tailings before and after treatment:

- Target analyte list (TAL) total metals concentrations in soils, including the COCs - cadmium, copper, lead, manganese, and zinc.

- Contaminant availability, as measured by water leachable, exchangeable and weak acid extractable metals, Toxicity Characteristic Leaching Procedure (TCLP) metals, and Multiple Extraction Procedure (MEP) metals.
- Soil physical characteristics, including grain size, percent moisture, water holding capacity, and specific gravity.
- Soil chemical characteristics, including pH, acidity, limestone requirement, available nutrients, total organic carbon (TOC), cation exchange capacity, and salinity.
- Toxicity of tailings to plants or invertebrates.
- Community structure and function.

Detailed performance data are available for this study and are included in Reference 1, *Final Assessment Report, Effectiveness of Biosolids and Lime Treatment as Soil Amendments for Fluvial Tailings Along the Upper Arkansas River*. While statistical analyses were performed on the data, EPA indicated that the findings were statistically insignificant. EPA attributed this to the relatively small sample size and high variability in results between samples. EPA noted that sample locations were specifically selected to include a wide range of metal concentrations, and that no replicate samples were collected.

While the results of the comparisons were not statistically significant, EPA observed trends in the data and made inferences about the effectiveness of the treatment based on the observations. These trends and observations about the application of biosolids and lime to tailings are summarized below.

Overall Performance

The following inferences were made by EPA about treatment performance, based on the one year study (1998-1999). The application of biosolids and lime:

- Did not appear to dilute the COC concentrations in the tailings; no consistent trend in COC concentrations was observed before and after treatment.
- Appeared to reduce the availability of COCs, based on a decrease in extractable metals in treated tailings, including water leachable, exchangeable, weak acid extractable, TCLP, and MEP metals in treated tailings.
- Appeared to improve soil quality, based on an increase in pH, TOC, water holding capacity, total nitrogen, phosphorous, and chloride, as well as percent saturation in cation exchange capacity by potassium and sodium after treatment. In addition, in the treated tailings, there was a decrease in salinity, calcitic limestone requirement, and available metal nutrients.
- Increased plant and soil microbial activity. A plant community was established one year after treatment; however, the soil microbial community was still recovering. While data from the fungal, bacterial, and protozoan communities in treated tailings indicated that these communities were not balanced, the high biogeochemical activity of the soil was an indicator of active recovery of the soil microbial community.
- Reduced soil toxicity, based on the results of plant and earthworm assays, with the exception of tailings RA/RB. However, all treated tailings showed significant sub-lethal effects on plant root biomass, and COC concentrations in plants and earthworms in these tailings were higher than those found in the reference soils.
- Reduced the dietary exposure risk for higher trophic organisms, based on the results of several preliminary dietary exposure models; however, it was determined that there may be a risk to the mammal and avian communities from specific metals.

Vegetation was established at all of the sites treated with lime and biosolids. Vegetation was more vigorous at sites located near available water than those at elevations higher from the river and groundwater. Some bare areas were noted and "touch up" treatments (including addition of sugar beet lime and wood chips) were added in subsequent years. In addition to soil conditions, vegetation success was impacted by high elevation, recent drought conditions, and a short growing season.

EPA indicated that further investigation of biosolids and lime addition to tailings is needed to evaluate the long-term effectiveness of this treatment, including effects on the plant community and to qualify dietary exposure risk.

Summary of Performance

The following is a summary of the performance of the biosolids and lime treatment during 1998-1999. As noted above, detailed results are provided in Reference 1.

<u>TAL Metals Concentrations in Soil</u>

The concentrations of the COCs in the tailings did not show a statistically significant change after treatment, and there was wide variation in the results. For example, the concentrations of cadmium, copper, lead, and zinc in untreated and treated tailings were higher than the concentrations of these metals in the upstream reference soil, while the concentrations of cadmium, manganese, and zinc in treated tailings were lower than those in the on-site reference soil. According to EPA, these results suggest that the application of biosolids and lime did not dilute the total concentration of metals in soil. In addition, the results indicate that the spatial variability of metals concentrations in soil was high and that contamination at the site may be ubiquitous, given the elevated level of metals in the on-site soil reference.

Water Leachable Metals in Soil

There was a consistent reduction in water leachable metals concentrations in the treated tailings; however, the changes were not statistically significant because of the small sample size and high variability between samples. Concentrations of water leachable metals in treated tailings compared to untreated tailings decreased by 30 to more than 800 times for cadmium; 6 to 150 times for copper; 2 to 15 times for lead; 14 to 87 times for manganese; and 50 to 1,400 times for zinc. There was variation in concentrations of water leachable metals compared to the reference samples. According to EPA, the consistent reduction in concentrations of leachable metals in treated tailings indicates that the application of biosolids and lime reduced the bioavailability of the COCs in the tailings.

Exchangeable Metals in Soil

Concentrations of exchangeable metals decreased in the treated tailings, though the changes were not statistically significant because of the small sample size and high variability between samples. Concentrations of exchangeable metals in treated tailings compared to untreated tailings decreased by 2 to 30 times for cadmium; and 2 to 22 times for copper. According to EPA, the reduction in concentrations of exchangeable metals in treated tailings indicates that the application of biosolids and lime reduced the bioavailability of the COCs in the tailings.

Weak Acid Extractable Metals in Soil

Generally there was a reduction in weak acid extractable metals in treated tailings; however, weak acid extractable lead concentrations increased in treated tailings CL and CO, and weak acid extractable cadmium concentrations increased in treated tailing CL, though concentrations in the untreated tailings were very low. Concentrations of weak acid extractable metals were greater in on-site reference soil than in upstream reference soil, indicating elevated levels throughout the site. According to EPA, the reduction in concentrations of weak acid extractable metals in treated tailings indicates that the application of biosolids and lime may have improved soil conditions because the bioavailability of the COCs in the tailings was reduced.

TCLP

The TCLP concentrations of COCs in untreated soils were below the regulatory limit for all metals at all locations. TCLP concentrations of COCs decreased after treatment, with cadmium and zinc concentrations decreasing significantly. TCLP concentrations of cadmium, lead, and zinc in treated tailings were lower than in the on-site reference soil but higher than in the upstream reference soil.

Multiple Extraction Procedure (MEP) Metals

Untreated and treated tailings CO and CL were analyzed for metals by MEP, with treated tailings analyzed eight and 14 months after treatment. In the CO and CL tailings, MEP zinc and copper concentrations decreased significantly. Significant decreases in MEP cadmium concentrations were observed for the CO tailings eight and 14 months after treatment; and significant decreases in MEP manganese concentrations were observed in the CO tailings 14 months after treatment. For those metals with significant decreases in MEP metal concentrations after treatment, decreases were greatest in the initial availability of the metal, indicating that the application of biosolids and lime decreases the immediate bioavailability of metals.

Soil Physical Characteristics

Soils were analyzed for physical characteristics (pH, acidity, calcitic limestone requirement, grain size, distribution, specific gravity, texture class, and water holding capacity) before and after treatment. The following compares the soil characteristics before and after treatment.

- pH - Increased from a range of 2.4 to 4.5 in untreated tailings to 6.6 to 6.9 in treated tailings.

- Soil Acidity - Decreased from 10.2 to 29.7 meq/100 g of soil and a limestone requirement of 7.9 to 23.1 tons/acre in untreated tailings to a range of 0.0 to 2.5 meq/100 g of soil and a limestone requirement of 0.0 to 0.3 tons/acre in treated tailings.
- Grain Size and Specific Gravity - No significant change in grain size or specific gravity before and after treatment.
  - Sand: 63 - 80% untreated; 66 - 80% treated
  - Silt: 15 - 30% untreated; 15 - 29% treated.
  - Clay: 5 - 7% untreated; 5 - 6% treated
  - Specific gravity: 2.30 - 2.47 untreated; 1.32 - 2.62 treated
- Water Holding Capacity - Increased from a range of 11.9 - 24.5% in untreated tailings to 43.1 - 73.3% in treated tailings

Soil Nutrients

Soils were analyzed for micro- and macronutrients, including total organic carbon (TOC), nitrogen (total Kjeldahl nitrogen [TKN], nitrate nitrogen, nitrite nitrogen, and ammonium nitrogen), phosphate, sulfate, potassium, magnesium, calcium, molybdenum, boron, copper, manganese, zinc, chloride ion, total soluble salts, and cation exchange capacity. The results were compared with optimum ranges (A&L Eastern 1998), with some nutrients lower and some higher than these ranges, as noted below.

Macronutrients:

- TOC increased from 1.7 - 2.6% in untreated tailings to 4.2 - 7.6% in treated tailings
- TKN increased from 1,000 - 1,600 mg/kg in untreated tailings to 4,600 - 8,920 mg/kg in treated tailings; increase expected due to high nitrogen concentrations in biosolids
- Phosphorous increased from 1 - 12 mg/kg in untreated tailings to 333 - 433 mg/kg in treated tailings. The increase was expected due to high phosphorus concentrations in biosolids. Phosphorous concentrations in treated tailings were considered excessively high.
- Sulfate did not change significantly. Sulfate concentrations ranged from 396 - 9,900 mg/kg in untreated tailings and from 1,330 - 2,900 mg/kg in treated tailings. The sulfate concentrations were considered very high.
- Boron concentrations did not change significantly (0.7 - 1.5 mg/kg in untreated tailings and 1.1 - 2.5 mg/kg in treated tailings). Boron concentrations were considered intermediate to high.
- Chloride concentrations increased from 3 - 62 mg/kg in untreated tailings to 164 - 332 mg/kg in treated tailings. Chloride concentrations were considered to be high, but not at a level of concern.
- Weak acid extractable iron concentrations were 30 to 200 times lower after treatment, decreasing from as high as 1,190 mg/kg in untreated tailings to 6.5 mg/kg in treated tailings, and was considered to be low to intermediate.
- Available molybdenum concentrations ranged from 0.2 (exchangeable) to 0.6 (weak acid extractable) mg/kg in untreated tailings to below the method detection limit (exchangeable) to 0.52 (weak acid extractable) mg/kg in treated soil. There was wide variation in concentrations, with molybdenum considered to be low, intermediate, high, and very high depending on sample location.
- Total Soluble Salts ranged from 0.5 - 4.9 mmhos/cm in untreated tailings (1:2 soil:water ratio) to 2.5 - 3.5 mmhos/cm in treated tailings. These results indicated that vegetation at the site was apparently tolerant of higher soil salinities, as a level of 1.2 mmhos/cm is generally toxic to most plants.
- Cation Exchange Capacity (CEC) did not change significantly. CEC ranged from 16.5 - 43.5 meq/100g of soil in untreated tailings and 12.4 - 24.7 meq/100g of soil in treated tailings.

Toxicity Data

Plant and earthworm assays were performed, including 28-day plant growth assays and a 28-day earthworm bioaccumulation assay. For plant toxicity, no seeds germinated in the untreated tailings; however, 71.4% of the seeds germinated in the treated tailings, though all tailing samples had lower root biomass compared to reference samples. Manganese had the highest potential to accumulate in plant tissue from treated tailings, with cadmium, copper, and zinc having less potential to accumulate in treated tailings compared to the upstream reference. EPA noted that the bioaccumulation factors may be influenced by metabolic processes and by toxicity.

The earthworm study indicated that treating the tailings with biosolids and lime significantly reduced soil toxicity to soil invertebrates. Survival rates of earthworms exposed to tailings improved significantly after the tailings were treated, with the exception of tailings RA/RB; the lethal effect of treated tailings RA/RB may have been caused by elevated ion concentrations in the soil.

Soil Community Analysis

The results of the soil community analysis, including comparing the 1998 soil community structure and the 1999 soil community structure and respiration, indicated that the site had the potential to support microbial growth and activity after treatment. Compared to the untreated tailings, the treated tailings had significantly higher heterotrophic and oxidizing activity; a significantly greater pool of inorganic nitrogen, likely resulting from the addition of the biosolids; generally a net loss of dissolved organic nitrogen (DON); and generally a net increase in mobial biomass nitrogen (MBN).

Additional Monitoring Data Through 2001

Several of the tailing locations included in the one-year study have been part of ongoing monitoring by EPA of multiple soil amendment/revegetation projects on tailings adjacent to the Upper Arkansas River.

For the six tailing locations included in the 1998-1999 study, an additional 20 tons/acre of sugar beet lime was added to all plots, except for the control plot and the biosolids only plots. Additional plant samples were collected in October 2000 and August 2001.

Cost Information [10]

The total cost for the one-year field demonstration was $3,477,697. This cost included $1,738,750 for investigation and characterization and $1,738,947 for construction and cleanup.

Observations and Lessons Learned [1, 3]

The results of the one-year study of the application of biosolids and lime to mining tailings contaminated with metals indicated that this treatment reduced the availability of metals in the tailings, reduced soil toxicity, and improved soil quality and fertility. In addition, vegetation was established at all of the sites treated with lime and biosolids. The results also showed that there is a potential for chronic effects on plant growth and for dietary exposure to metals by wildlife. EPA indicated that additional investigation of the long-term effects of this treatment will be needed to address these issues.

The results of the study were not statistically significant. EPA attributed this to the small sample size and wide variation in results.

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10. Email from Michael Zimmerman, EPA On-Scene Coordinator to Harry Compton, EPA ERTC regarding cost data for the project. October 10, 2004

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