

Accelerated Weathering of Biosolid-Amended Copper Mine Tailings

Andrew P. Pond, Scott A. White, Michael Milczarek, and Thomas L. Thompson*

ABSTRACT

Application of municipal biosolids to mine tailings can enhance revegetation success, but may cause adverse environmental impacts, such as increased leaching of NO_3^- and metals to ground water. Kinetic weathering cells were used to simulate geochemical weathering to determine the effects of biosolid amendment on (i) pH of leachate and tailings, (ii) leaching of NO_3^- and SO_4^{2-} , (iii) leaching and bioavailability (DTPA-extractable) of selected metals, and (iv) changes in tailing mineralogy. Four Cu mine tailings from southern Arizona differing in initial pH (3.3–7.3) and degree of weathering were packed into triplicate weathering cells and were unamended and amended with two rates (equivalent to 134 and 200 Mg dry matter ha^{-1}) of biosolids. Biosolid application to acid (pH 3.3) tailings resulted in pH values as high as 6.3 and leachate pH as high as 5.7, and biosolids applied to circumneutral tailings resulted in no change in tailing or leachate pH. Concentrations of NO_3^- -N of up to 23 mg L^{-1} occurred in leachates from circumneutral tailings. The low pH of the acidic tailing apparently inhibited nitrification, resulting in leachate NO_3^- -N of <5 mg L^{-1} . Less SO_4^{2-} -S was leached in biosolid-amended versus unamended acid tailings (final rate of 0.04 compared with 0.11 g SO_4^{2-} -S wk^{-1}). Copper concentrations in leachates from acidic tailings were reduced from 53 to 27 mg L^{-1} with biosolid amendment. Copper and As concentrations increased slightly in leachates from biosolid-amended circumneutral tailings. Small increases in DTPA-extractable Cu, Ni, and Zn occurred in all tailings with increased biosolid rate. Overall, there was little evidence of potential for adverse environmental impacts resulting from biosolid application to these Cu mine tailings.

REMOVAL OF LARGE quantities of material from mining sites and deposition of waste can drastically alter the physical characteristics of the area, including topography, hydrology, vegetative cover, wildlife habitat, and susceptibility to erosion. In addition, as mine wastes weather, they may release acid rock drainage into ground and surface waters, polluting them through increases in acidity, toxic elements, and salinity (Bell, 1999; Ernst, 1988; Pentreath, 1994).

The goals of mine tailing reclamation are to establish a self-sustaining plant community on tailings impoundments (Bradshaw, 1999), to stabilize the tailing surface, and to minimize wind and water erosion. Common chemical limitations to plant growth on mine tailings include low pH, high salt content, lack of required nutrients, and metal toxicities. Physical limitations include high bulk

density, lack of structure, slow water infiltration, low water retention, and low air permeability (Harris, 2001).

To overcome these limitations, amendments may be added. One amendment that shows promise is municipal biosolids (sewage sludge). Biosolid application to tailings can have several benefits, including neutralization of acidity, metal sorption, and addition of organic matter; however, these effects may be short lived (Pietz et al., 1989a). Several researchers have found that biosolids are an effective amendment for preventing erosion and establishing a sustainable plant community (Abbott et al., 2001; Harris, 2001; Cravotta, 1998). Although biosolid application may aid in the reclamation of mine tailings, it may also result in pollution. Due to the high biosolid application rates needed for reclamation, NO_3^- pollution of ground and surface water is a concern (Cravotta, 1998).

Field experiments provide a short-term evaluation of acid generation and the effectiveness of biosolids for reclamation. To better estimate long-term changes in tailing geochemistry, kinetic tests, such as those using weathering cells, have been developed. Kinetic tests (i) simulate an increase in the rate of chemical weathering so that the effects of long term weathering of amended tailings, such as acid generation and metal dissolution rates, can be determined (American Society for Testing and Materials, 1996); (ii) account for differences in the kinetics of various processes, such as differences in rates of carbonate dissolution and pyrite oxidation (Scharer et al., 2000); and (iii) produce an effluent that can be tested for constituents similar to those in actual mine drainage (Hornberger and Brady, 1998). While kinetic methods provide a good simulation of weathering, they cannot predict acidic drainage through simple extrapolation of experimental results (Scharer et al., 2000).

Tailings reclamation in semiarid and arid regions presents situations quite different than in wetter climates. One such situation is the delaying of ground water contamination for tens to hundreds of years, beyond the scope of most regulations and bonding requirements, due to the slow percolation of water through the tailings impoundments (Kempton and Atkins, 2000). To estimate long-term effects of municipal biosolid additions for reclamation of Cu mine tailings in semiarid environments, a kinetic weathering experiment was performed using four tailings with differing chemical properties, amended with three rates of biosolids. The objective was to use controlled conditions of accelerated geochemical weathering to determine effects of biosolid amendments on (i) pH of leachate and tailings, (ii) leaching of NO_3^- and SO_4^{2-} , (iii) leaching and bioavailability (DTPA-extractable) of selected metals, and (iv) changes in tailing mineralogy.

A.P. Pond, S.A. White, and T.L. Thompson, Department of Soil, Water, and Environmental Science, University of Arizona, 429 Shantz Building #38, Tucson, AZ 85721. M. Milczarek, Geosystems Analysis, 2015 North Forbes, Suite 205, Tucson, AZ 85745. Received 2 Nov. 2004. *Corresponding author (thompson@ag.arizona.edu).

Published in *J. Environ. Qual.* 34:1293–1301 (2005).
 Technical Reports: Heavy Metals in the Environment
 doi:10.2134/jeq2004.0405
 © ASA, CSSA, SSSA
 677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: MCL, maximum contaminant level.

Table 1. Pre-experimental chemical properties of four copper mine tailings.

Tailing	pH	EC	NNP [†]	CaCO ₃	Pyritic S	Total S	SO ₄ ²⁻ -S	Total C	Total N	NO ₃ ⁻ -N	NH ₄ ⁺ -N
		dS m ⁻¹					mg kg ⁻¹				
1	3.3	2.9	-12	3 000	4 700	15 000	1900	1280	220	1.1	1.4
2	6.6	1.9	36	70 000	11 000	14 000	780	2060	90	1.4	0.8
3	6.8	1.3	9	43 000	11 000	13 000	560	2540	130	2.5	0.9
4	7.3	0.7	23	47 000	7 800	9 800	220	2760	120	1.2	1.5

[†] Net neutralization potential (Mg CaCO₃ per 1000 Mg material).

MATERIALS AND METHODS

Tailings and Biosolids

Copper mine tailings were obtained from a mine in southeastern Arizona located at 900 m elevation, with a mean annual rainfall of 370 mm and pan evaporation of approximately 3000 mm yr⁻¹. The mine tailings originate from the San Manuel–Kalamazoo ore body, described by Force et al. (1995) and Lowell (1968). Four tailing types differing in initial chemical properties were used in the experiment (Tables 1 and 2) with textures that ranged from loamy sand to loam (1–9% clay). Tailing Type 1 (T1) was the most weathered, and Types 2 (T2), 3 (T3), and 4 (T4) were progressively less weathered. Tailing Type 4 was composed of newly processed tailings collected as they were being deposited on a tailing impoundment and were the same used in a field experiment described by Thompson et al. (2001).

Metal concentrations (Cu, Zn, Cd, Cr, Fe, Ni, Se, As, Pb) in the tailings were determined by acid digestion (HNO₃ and HCl) (Soon and Abboud, 1993) with analysis using a Ciro AS400 inductively coupled plasma–mass spectrometry (ICP–MS) (Spectro, Kleve, Germany). Extractable Fe, Cu, Zn, Cr, Ni, Se, As, and Pb were determined in 2:1 (solution to soil) DTPA extracts followed by ICP–MS analysis (Liang and Karamanos, 1993). Total N, C, and S were measured by combustion using a CNS-2000 (LECO, St. Joseph, MI) (Gavlak et al., 1994). Inorganic N (NO₃⁻-N and NH₄⁺-N) was extracted using 1.0 M KCl and analyzed using steam distillation (Keeney and Nelson, 1982). Tailing pH and EC were measured in 1:1 water extracts, and particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986). Pyritic S was determined by total S analysis after removal of non-acid-producing sulfur by leaching with HCl and distilled water. Acidification potential (AP) was determined by multiplying percent pyritic S by 31.25 (USEPA, 1978), and CaCO₃ percentage was determined by reacting the tailings with 0.5 M HCl and then titrating with NaOH to determine the amount of acid neutralized. The acid neutralizing potential (ANP) was calculated by multiplying % CaCO₃ by 10 (USEPA, 1978), and net neutralization potential (NNP) was then calculated as ANP – AP.

The biosolids used in this experiment were Class B according to USEPA (1994) standards. They were obtained from

the City of Phoenix 27th Avenue wastewater treatment plant and had a pH of 8.1. Total N (44 g kg⁻¹), C (246 g kg⁻¹), S (24 g kg⁻¹) and metal concentrations in the biosolids were measured as described above.

Kinetic Weathering Method

The experiment was conducted in a constant temperature (20°C) growth chamber. Kinetic weathering cells were constructed following ASTM Method D5744-96 (American Society for Testing and Materials, 1996), of schedule 40 PVC pipe, 15 cm in diameter, cut into 20-cm long sections with a perforated plate glued to one end. The ends of each column were closed using PVC end caps and air flow was accomplished through plastic barbed nipples inserted into the column and caps (Fig. 1). Flow of dry and humid air was delivered to the cells through a 1.2-cm PVC pipe manifold. Compressed air was passed through a 0.5- μ m moisture/oil filter and a drierite column to remove H₂O. Humid air was generated by bubbling filtered compressed air through a humidifier.

Tailings were sieved through a 2-mm plastic sieve and stored in plastic buckets. At the beginning of the experiment, appropriate biosolid amounts (0, 40, or 60 g kg⁻¹) were added to and thoroughly mixed with 2.0 kg of each tailing type. The treatments were chosen to match those used by Thompson et al. (2001) and represent application rates of 0, 134, and 200 Mg dry matter ha⁻¹. The mixtures were then packed into triplicate cells to a bulk density of 1.48 \pm 0.04 Mg m⁻³.

Cells were subjected to 26, one-week-long cycles consisting of leaching, dry air flow, and humid air flow (American Society for Testing and Materials, 1996). Each cycle began with an addition of 1 L of distilled-deionized water to each column (1.65 pore volumes). The drainage ports were closed for 1 h, then were opened to allow free drainage for 48 h. The hydraulic conductivity on T4 was low, and 2 d were not sufficient for drainage to cease. Therefore, a vacuum of -70 kPa was applied to the bottom of each T4 cell with a hand pump and maintained until disappearance of ponded water. After leaching, the collection flasks and cells were disconnected, removed from the growth chamber, and weighed. Cells were replaced, hooked to the manifold, and dry air was blown through the cells with the drain tubes open for 1 h to remove

Table 2. Results of pre-experimental analysis of metals soluble in an HNO₃-HCl digest, and DTPA-extractable metal concentrations of the four tailings and municipal biosolids.

Metal	Metals recovered in HNO ₃ -HCl				Biosolids	DTPA-extractable metals			
	T1	T2	T3	T4		T1	T2	T3	T4
	mg kg ⁻¹								
Fe	19 300	27 300	21 100	24 700	34 000	84	65	82	112
Cu	650	1 190	750	690	520	264	90	71	65
Zn	13	150	140	160	640	5.34	2.8	2.38	2.36
Cr	7.1	8.7	12	13	74	0.12	0.16	0.14	0.08
Ni	11	12	15	15	49	4.14	0.46	ND [†]	0.36
Se	2.9	2.5	2.2	1.5	8.5	ND	0.1	0.12	ND
As	1.8	1.7	6.2	3.6	9.8	ND	ND	ND	ND
Pb	3	16	11	11	44	0.12	2.52	2.62	3.22

[†] Not detected.

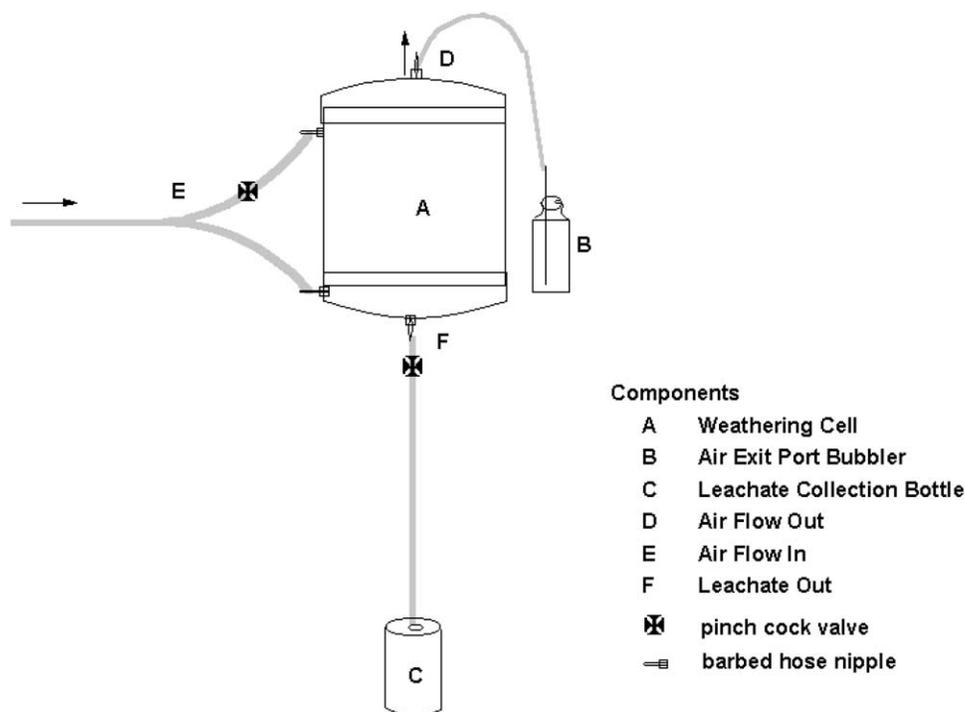


Fig. 1. Schematic of kinetic weathering cell used to simulate weathering of four copper mine tailings.

excess H_2O . The drain tubes were then sealed, bubblers attached, and air was passed through both ports of the cells at 500 mL min^{-1} for 23 h. Air flow was then shut off to the upper port and passed only through the lower port for 48 h.

After the dry air cycle, cells were removed, weighed, replaced, and reconnected to the manifold and bubblers. Humid air was passed through the system for 48 h at 500 mL min^{-1} using both upper and lower ports. Following this, the cells were removed, weighed, replaced, and attached to the collection flasks for the next cycle. Following each leaching cycle, the collection flasks were removed from the chamber and weighed, and three leachate subsamples were collected from each cell: a 40 mL sample for pH and anion analyses, a 100-mL sample that was immediately frozen, and a 15-mL sample that was frozen and composited over 26 wk for metal analysis. Leachate pH and NO_3^- -N were analyzed as described above. Sulfate S was analyzed by ion chromatography using a BioLC ion chromatograph (Dionex, Sunnyvale, CA) equipped with an Ion Pac column (AS14 $4 \times 250 \text{ mm}$ analytical), at a flow rate of 1.2 mL min^{-1} in a carbonate-bicarbonate eluent. The 26-wk composite leachate sample was analyzed for Cu, Cr, Ni, As, Se, Cd, and Pb by ICP-MS.

One week after the 26th leaching cycle, tailings were removed from the cells, placed in paper bags, and dried at 80°C . Once dry, the weathered tailings were passed through a 2-mm plastic sieve and subsampled for analysis. The pH, NO_3^- -N, and DTPA-extractable metals were analyzed in artificially weathered tailings as described above.

Tailing Mineralogy

Mineralogy of the weathered and unweathered tailings was determined using a Phillips (Eindhoven, the Netherlands) XRD 3000 X-ray diffractometer using $\text{Cu K}\alpha$ radiation, a single crystal (graphite) monochromator, and pulse height discrimination on random powder mounts from 4 to $60^\circ 2\theta$ at $2^\circ 2\theta \text{ min}^{-1}$ with peak identification using tables from Brown and Brindley (1980). Extractions were performed on the tailings

for determination of different Fe fractions: "organically bound Fe" was extracted with a 0.1 M sodium pyrophosphate solution, total "crystalline" Fe was extracted using the dithionite-citrate method, and "active/amorphous Fe" was extracted using acid ammonium oxalate (Loeppert and Inskeep, 1996). The Fe concentration in the extracts was analyzed using a Jarrell Ash (Franklin, MA) Video 12 atomic absorption spectrophotometer.

Data Analysis

Statistical analysis of leachate pH, NO_3^- -N, and SO_4^{2-} -S weekly means was performed using SYSTAT 10.2 (Systat Software, 2002). Means of dependent variables were subjected to analysis of variance with repeated measures (time dependent) analysis. Leachate metal concentrations, and tailing DTPA-extractable metals, pH, NO_3^- -N, and extractable Fe were analyzed at the end of the experiment and were subjected to analysis of variance with SAS for Windows, Release 8.1 (SAS Institute, 2000).

RESULTS AND DISCUSSION

pH

Leachate pH was not significantly different among the circumneutral tailings (T2, T3, and T4) and was not significantly affected by biosolid addition. For all three tailings and biosolid rates, leachate pH was 7.5 to 8.5, with a slight decrease with time in leachates from amended tailings (data not shown). However, acid drainage was not expected due to the positive neutralization potential of these tailings (Table 1). The final pH values of T2, T3, and T4 were not significantly different from each other, nor were they affected by biosolid treatment (Table 3).

Leachate pH from T1 increased significantly with bio-

Table 3. Tailing post weathering values and analysis of variance summary for tailing pH, total N, inorganic N, organic Fe, active Fe, free Fe, and DTPA-extractable metals as affected by tailing type (T) and biosolid rate (BS).

Tailing	Biosolid treatment	pH	Total N	NO ₃ ⁻ -N	NH ₄ ⁺ -N	Fe			DTPA					
						Organic†	Active‡	Free§	Cu	Zn	Cr	Ni	Fe	
	g						mg kg ⁻¹							
1	0	3.7	190	1.7	1.0	293	4 000	12 000	24	0.39	0.15	0.19	170	
	80	5.3	630	1.8	14.9	606	2 790	11 500	43	1.64	0.14	0.26	99	
	120	6.3	930	3.1	22.0	920	2 770	10 200	60	3.85	0.13	0.38	61	
2	0	7.3	140	1.6	0.5	190	16 800	2 550	48	1.59	0.14	0.11	28	
	80	7.3	600	2.0	1.3	380	16 800	2 490	55	3.37	0.14	0.17	33	
	120	7.2	900	2.2	3.1	771	15 400	2 450	67	6.27	0.14	0.27	41	
3	0	7.6	150	1.4	0.1	166	9 970	1 390	55	1.66	0.15	0.11	33	
	80	7.3	390	2.5	1.7	493	8 990	1 500	63	4.44	0.15	0.19	39	
	120	7.3	860	2.5	3.2	843	10 700	1 780	71	6.77	0.15	0.28	45	
4	0	7.4	130	0.9	0.2	222	15 300	2 500	75	2.39	0.14	0.14	54	
	80	7.3	480	1.5	2.2	552	16 300	2 700	87	5.05	0.14	0.22	54	
	120	7.4	870	2.1	4.9	819	16 400	2 710	92	6.82	0.14	0.27	54	
	T	**	**	*	**	**	**	**	**	**	NS¶	**	**	
	BS	**	**	**	**	**	NS	NS	**	**	NS	**	**	
	T × BS	**	NS	NS	**	NS	NS	NS	**	NS	NS	NS	**	
	replication	NS	NS	NS	NS	NS	NS	NS	*	NS	NS	NS	NS	

* Significant at the 0.05 probability level.
 ** Significant at the 0.01 probability level.
 † 0.1 M Sodium pyrophosphate extractable.
 ‡ Acid ammonium oxalate extractable.
 § Dithionite-citrate extractable.
 ¶ Not significant.

solid addition, while the leachate pH from unamended T1 remained <3.5 (Fig. 2, Table 4). The pH of amended T1 (Table 3) also increased with biosolid rate. Abbott et al. (2001) and Cravotta (1998) both reported increases

in coal mine waste pH after application of biosolids. The observed pH increases in the tailings and leachate may be short-lived, however. In the tailings amended with 80 g biosolids, the leachate pH began to decline

T1

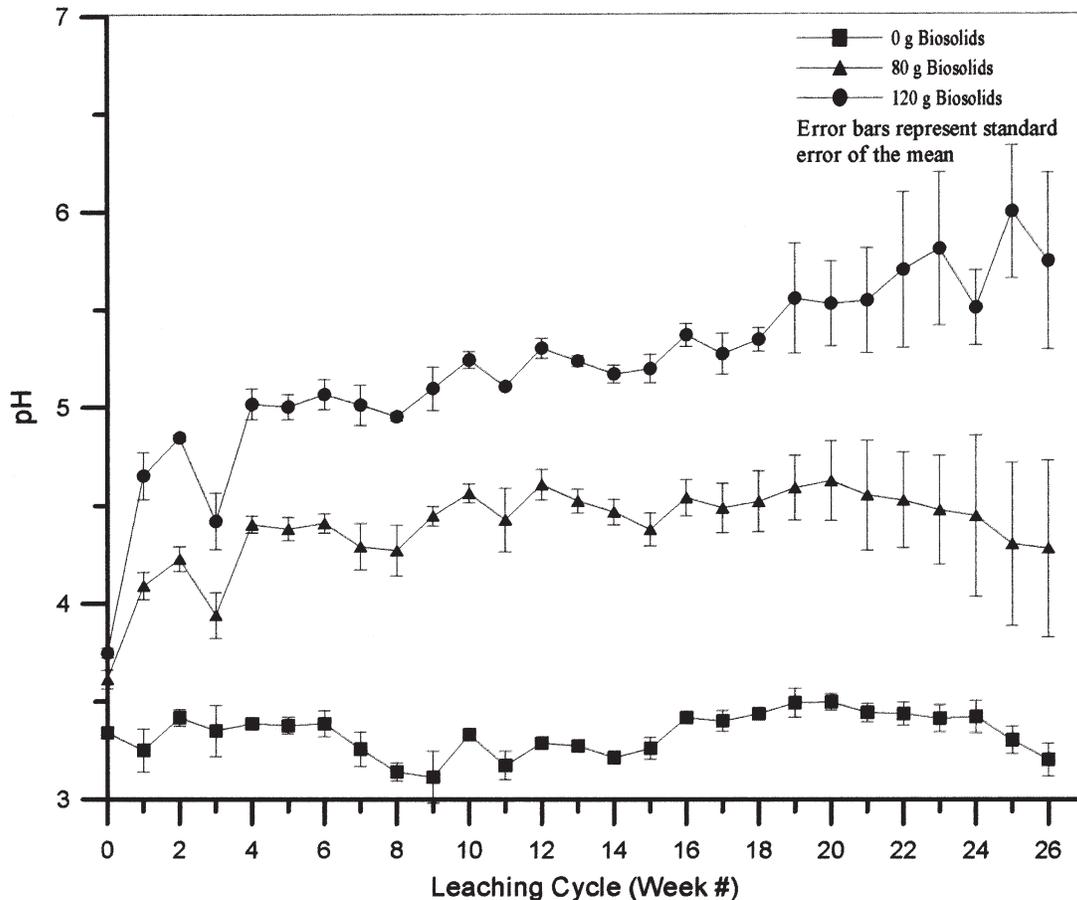


Fig. 2. pH of leachate from kinetic weathering cells for Tailing Type 1.

Table 4. Univariate and multivariate repeated measures analysis of variance for leachate pH, NO₃⁻-N, and SO₄²⁻-S as affected by tailing type (T), biosolid rate (BS), and time (W).

Source	pH	NO ₃ ⁻ -N	SO ₄ ²⁻ -S
Between subjects			
T	**	**	**
BS	**	**	**
T × BS	**	**	*
Within subjects			
W	**	**	**
W × T	**	**	**
W × BS	NS†	**	**
W × T × BS	**	**	**

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

† Not significant.

toward the end of the experiment (Fig. 2) indicating that this application rate may be insufficient for long-term neutralization of acidity. Pietz et al. (1989a), Sopper and Kerr (1982), and Sopper and Seaker (1990) all reported increases in tailing pH after biosolid application, followed by a decline in pH over several years.

Nitrate and Sulfate Leaching

Leachate NO₃⁻-N concentrations from the three circumneutral tailings (T2, T3, and T4) increased with increased biosolid rate (Fig. 3). Several weekly leachate

concentrations exceeded the USEPA maximum contaminant level (MCL) for drinking water of 10 mg L⁻¹. These high values all occurred near the beginning and middle of the experiment with concentrations decreasing toward the end. Nitrate was present in the first leachates collected from the columns containing T1. However, subsequently there was no NO₃⁻ leached from these columns until Week 18, when it was detected in leachates from columns receiving the highest biosolid application rate (Fig. 3). This delay in NO₃⁻ leaching may be due to the effect of pH on nitrifying organisms, whose activity is inhibited below pH 6 and becomes negligible below pH 5.0 (Foth and Ellis, 1997). In addition, high concentrations of bioavailable metals may have an inhibitory affect on nitrifying organisms (Seaker and Sopper, 1988). All leachates from the T1 columns initially had pH of <5.0, and only the leachates from the highest biosolid application rate increased above this value. Because of the large amounts of water applied in this experiment, compared with expected rainfall in the area, we expect that NO₃ leaching under natural conditions will be much lower than was observed from the columns. Thompson et al. (2001) used T4 in a field experiment with the same biosolid application rates and after 2 yr found NO₃⁻-N concentrations up to 400 mg kg⁻¹ in the tailings, but no evidence of NO₃⁻ movement

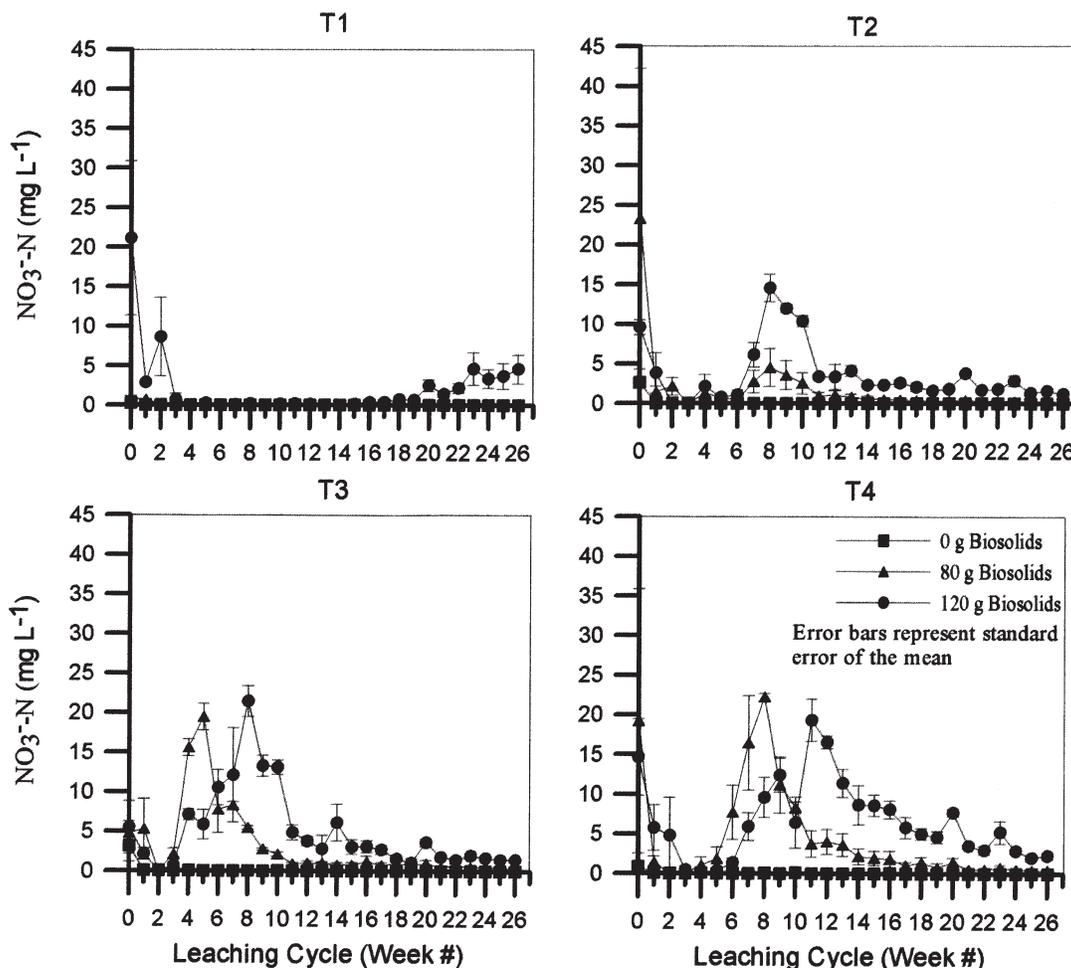


Fig. 3. Concentrations of NO₃⁻-N in leachates from kinetic weathering cells.

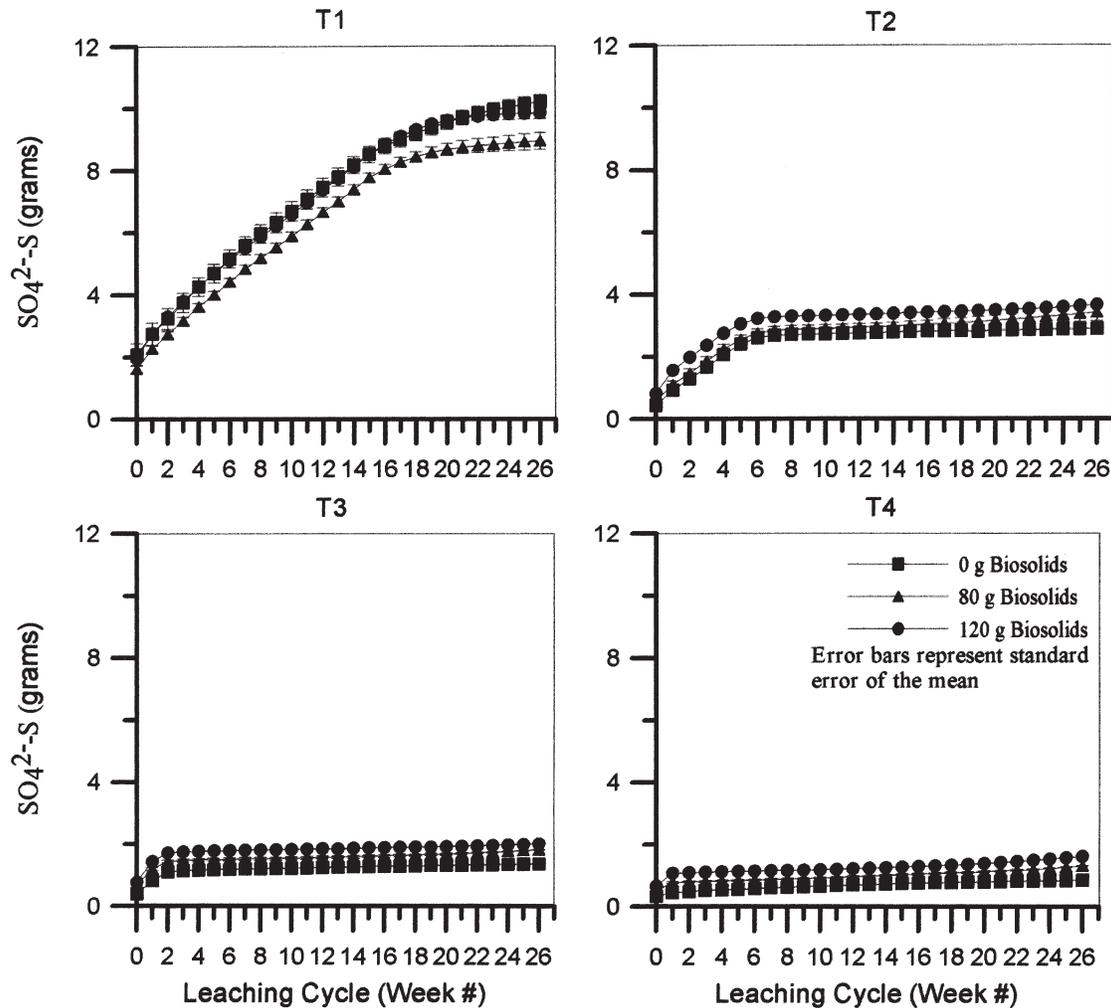


Fig. 4. Cumulative mass of $\text{SO}_4^{2-}\text{-S}$ in leachates from kinetic weathering cells.

below a 0.9-m depth in irrigated plots. Similarly, Rogers et al. (1998) applied up to 200 Mg biosolids ha^{-1} to acid mine tailings in Arizona, and found little NO_3^- below a 0.5-m depth, even with irrigation.

The cumulative mass of $\text{SO}_4^{2-}\text{-S}$ leached from the columns can provide information about weathering of pyrite in the cells (Fig. 4). The steep slopes of the $\text{SO}_4^{2-}\text{-S}$ concentration curves for T2, T3, and T4 during the first weeks of the experiment (1–2 wk for T3 and T4, 6 wk for T2) are likely due to the removal of soluble secondary minerals present in the tailings (Holmstrom et al., 1999). Once secondary minerals were removed, the main sources of SO_4^{2-} were oxidation of sulfide minerals by *Thiobacillus* sp. and release from the biosolids. Total S leached was about 33% of total S in T1, and 6 to 10% in T2, T3, and T4, which reflects the higher percentage of total S in nonpyritic forms in the more highly weathered T1 (Table 1). In T2, T3, and T4, biosolid additions led to small, but significant, increases in the mass of $\text{SO}_4^{2-}\text{-S}$ in the leachates. Cravotta (1998) and Abbott et al. (2001) also reported increases in SO_4^{2-} leaching from biosolid-amended plots compared with unamended plots.

In T1, leachates from unamended columns and those

receiving the highest biosolid rate contained similar masses of $\text{SO}_4^{2-}\text{-S}$ (Fig. 4). However, slightly less SO_4^{2-} was leached from columns receiving 80 g of biosolids. During the first few weeks, $\text{SO}_4^{2-}\text{-S}$ concentrations in leachates from columns receiving the highest biosolid application rate were much higher than those from the 80-g rate. During the last 6 wk of the experiment, $\text{SO}_4^{2-}\text{-S}$ leaching rates in these two treatments were equal at $0.04 \text{ g SO}_4^{2-}\text{-S column}^{-1} \text{ wk}^{-1}$. In comparison, the unamended tailings had a leaching rate of $0.11 \text{ g SO}_4^{2-}\text{-S column}^{-1} \text{ wk}^{-1}$ during the last 6 wk of the experiment. The lower $\text{SO}_4^{2-}\text{-S}$ leaching rate in biosolid-amended acid tailings indicates that biosolids may, at least in the short term, be effective at reducing the rate of pyrite oxidation. Possible mechanisms for this phenomenon include removal of Fe^{3+} , a primary oxidant of pyrite, from solution due to sorption onto the biosolids, and precipitation of Fe^{3+} as secondary minerals (Rose and Cravotta, 1998). Concentrations of leachate and DTPA-extractable Fe from T1 decreased with increasing biosolid rate (Tables 3 and 5), which specifically supports the removal of soluble Fe^{3+} through sorption or secondary precipitation as the primary mechanisms for reducing pyrite oxidation rate. Pietz et al. (1989b)

Table 5. Metal concentrations and analysis of variance summary for composite leachate samples as affected by tailing type (T) and biosolid rate (BS).

Tailing	Biosolid treatment	Concentration				
		Cu	Cr	Ni	As	Fe
	g column ⁻¹	mg L ⁻¹				
1	0	53.4	0.04	0.75	ND†	4.29
	80	51.1	0.02	0.92	ND	2.95
	120	26.7	ND	2.63	ND	2.56
2	0	ND	ND	ND	ND	0.76
	80	0.3	ND	ND	ND	0.86
	120	1.0	ND	ND	ND	0.92
3	0	ND	ND	ND	ND	0.39
	80	0.5	ND	ND	0.03	0.59
	120	1.0	ND	ND	0.03	0.67
4	0	ND	ND	ND	ND	0.34
	80	0.6	ND	ND	0.02	0.55
	120	1.3	ND	ND	0.03	0.73
MDL‡		0.05	0.01	0.13	0.02	0.06
	T	**	ID§	ID	ID	**
	BS	**	ID	ID	ID	NS¶
	T × BS	**	ID	ID	ID	NS
	replication	NS	ID	ID	ID	NS

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

† Not detected.

‡ Method detection limit.

§ Insufficient data for statistical analysis.

¶ Not significant.

observed similar decreases in SO_4^{2-} -S in leachates collected from biosolid-amended mine tailings during a period of 3 yr, though they then began to increase.

Differences in the patterns of SO_4^{2-} and NO_3^- leaching are likely due to the S and N forms present and the microorganisms involved in their transformations. When the experiment began, there were high concentrations of soluble SO_4^{2-} in the tailings, but little NO_3^- in tailings or biosolids (Table 1). The result was a large flush of SO_4^{2-} during the first few leaching cycles. Nitrate, however, had to be produced through mineralization and nitrification before leaching could occur. The tailing environments also affected the microbial populations, most notably in the acidic tailings (T1). Nitrifiers were likely inhibited by the low pH, resulting in low leaching rates. *Thiobacillus* spp. are acidophilic and are responsible for the oxidation of pyrite (Cravotta, 1998). Their activities were likely not inhibited by conditions in T1, thus the higher SO_4^{2-} leaching rates in these acidic tailings.

Metals

Selenium, Pb, and Cd were not detected in any of the composited leachate samples, regardless of biosolid rate. Arsenic was detected only in leachates from amended T3 and T4 (Table 5). In the four treatments with detectable leachate As, concentrations exceeded the MCL (10 $\mu\text{g L}^{-1}$). Initial concentrations of As were elevated in T3 and T4. Oxyanion forms of As would be expected to sorb, via ligand exchange, onto (hydr)oxides of Fe, thus preventing leaching from the tailings (McGeehan et al., 1998; Goldberg and Glaubig, 1988). However, during decomposition of the biosolids, organic molecules, containing COOH and phenol-catechol OH functional groups, may be released into solution. These and similar organic molecules have been shown to compete for surface adsorption sites and thus decrease sorption of As

(Grafe et al., 2001). There was no As present in the leachates from T1 or T2, which is likely due to the much lower initial As concentrations in the tailings (Table 2), and the presence of As in less mobile forms.

Chromium was detected only in the leachates from T1 and concentrations decreased with increasing biosolid rate (Table 5), though the differences were not significant. Leachate Cr concentrations did not exceed the MCL (0.1 mg L^{-1}). There was also no significant difference in DTPA-extractable Cr among tailing types or biosolid rates (Table 3). This indicates that there should be limited negative impacts on the environment from Cr due to biosolid application. Berti and Jacobs (1996) found little uptake of Cr into plant tissue after biosolid application while Alberici et al. (1989) observed a decrease in Cr concentrations in meadow voles from biosolid-amended plots compared with control plots.

Nickel was also detected only in the leachates from the acid tailings and again the differences among biosolid application rates were not significant (Table 5). In all four tailing types, DTPA-extractable Ni and Zn increased slightly but significantly with increased biosolid rate (Table 3). Berti and Jacobs (1996) found that Ni and Zn in biosolids remained in bioavailable forms when repeatedly applied to soils, leading to potential plant toxicities. Due to the low concentrations of DTPA-extractable Ni and Zn in these tailings, with only a single biosolid application there will likely be no toxic effects on plants. Thompson et al. (2001) used biosolid-amended Tailing 4 in a field experiment. They found that metal concentrations in plants were below suggested tolerance levels for agronomic crops.

Copper was detected in leachates from all treatments except for unamended T2, T3, and T4 (Table 5). In these three tailings, leachate concentrations increased slightly with biosolid amendment compared to unamended tailings, with all concentrations below the MCL (1.3 mg L^{-1}). McBride et al. (1997) reported that virtually all dissolved Cu in a biosolid amended soil was organically complexed, which led to migration as metal-organic complexes. The slight increases in leachate Cu concentration in amended T2, T3, and T4 is likely due to transport as such complexes. In T1, there was a statistically significant decrease in leachate Cu concentration with increasing biosolid rate. The decrease in Cu concentration could be caused by a decrease in Cu mobility due to the increase in pH, and precipitation of Cu hydroxides and oxides (Abbott et al., 2001). Copper concentrations in leachates from all T1 treatments exceeded the MCL. The DTPA-extractable Cu in all four tailings increased with increasing biosolid rate (Table 3), which is similar to increases found in several field experiments reported by Sopper (1993). The concentrations of DTPA-extractable Cu in the weathered tailings were lower than concentrations in tailings used by Thompson et al. (2001). They also found no significant increases in metal uptake by plants grown on tailings receiving biosolid application in a semiarid environment. Brown et al. (2003) reported that the use of high quality (i.e., Class B) biosolids generally results in no significant increase in plant metal concentrations.

Mineralogy

All four tailings were composed predominately of quartz and feldspars (microcline, plagioclase, and K-feldspars) with smaller quantities of carbonate, sulfate (fibroferrite, anhydrite, and natroalunite), sulfide (pyrrhotite, marcasite, and pyrite), and oxide minerals (diaspore, brucite, magnetite, ferrihydrite, bohemite, pyrolusite, hematite, goethite, manganite, and jarosites). Changes in the mineralogy of the tailings during the experiment were minimal. The changes in the tailings detected by X-ray diffraction (XRD) were the removal of some sulfates and sulfides, along with an intensification of the quartz and feldspar peaks (data not shown).

There was an increase in concentrations of organically bound Fe in all tailing types after addition of biosolids; this was expected due to the presence of Fe in the biosolids (34 g kg^{-1}) (Table 3). Concentrations of active (amorphous) and free (crystalline) Fe were not significantly affected by additions of biosolids to any of the tailing types, although there were differences among tailing types in concentrations of active and free Fe. Tailing T1 had a higher concentration of free iron oxides, such as goethite, indicating advanced stages of sulfide oxidation (Yanful and Orlandea, 2000). Tailings T2, T3, and T4 all had higher concentrations of active iron oxides, including jarosite, which are characteristic of "younger" tailings (Swayze et al., 2000).

CONCLUSIONS

Kinetic weathering cells were used to simulate geochemical weathering to evaluate the effects of municipal biosolid applications on the chemistry of four copper mine tailings from Arizona. Tailing T1 was acidic (pH 3.3) with negative neutralization potential. Within T1, the addition of biosolids resulted in higher leachate pH (increase of 2 to 3 pH units) and lower concentrations of Cu and Cr in leachates. Nickel concentrations in T1 leachates were increased with biosolid application. Addition of biosolids also reduced SO_4^{2-} -S leaching during the last several weeks of the experiment, possibly by reducing the rate of pyrite oxidation.

Tailings T2, T3, and T4 were circumneutral with respect to pH, with positive neutralization potential. These three tailings were similar in most chemical properties, except that T3 and T4 had higher As concentrations than T2. The addition of biosolids resulted in no significant changes in leachate Cu, Cr, and Ni concentrations in T2, T3, and T4. There were increases in As leaching from biosolid-amended T3 and T4, due to the higher initial As concentrations in the tailings. Biosolid additions did not appear to result in changes in pyrite oxidation rate in T2, T3, and T4.

Previous research has demonstrated positive outcomes from biosolid application to mine tailings, including increased plant growth and soil organic matter, and reduced plant metal uptake. Our results further suggest that application of municipal biosolids to copper mine tailings in semiarid regions should not result in adverse environmental impacts caused by increased metal leach-

ing, NO_3^- leaching, or enhanced pyrite oxidation. In addition, the increased pH of the acidic tailings after biosolid addition should aid in the establishment of a plant and microbial community. Thus, since earlier studies have shown enhanced growth of vegetation with biosolid addition to mine tailings, this practice can be recommended.

ACKNOWLEDGMENTS

This research was supported through a grant from the University of Arizona, National Science Foundation Water Quality Center. The assistance of BHP Copper, Inc., San Manuel, Arizona, is appreciated.

REFERENCES

- Abbott, D.E., M.E. Essington, M.D. Mullen, and J.T. Ammons. 2001. Fly ash and lime-stabilized biosolid mixtures in mine spoil reclamation: Simulated weathering. *J. Environ. Qual.* 30:608–616.
- Alberici, T.M., W.E. Sopper, G.L. Storm, and R.H. Yahner. 1989. Trace metals in soil, vegetation, and voles from mined land treated with sewage sludge. *J. Environ. Qual.* 18:115–120.
- American Society for Testing and Materials. 1996. Standard test method for accelerated weathering of solid materials using modified humidity cells. D 5744-96. ASTM, West Conshohocken, PA.
- Bell, L.C. 1999. A multidisciplinary approach to producing solutions for sustainable mine rehabilitation: The role of the Australian center for minesite rehabilitation research. p. 3–11. *In* M.H. Wong, J.W.C. Wong, and A.J.M. Baker (ed.) Remediation and management of degraded lands. Lewis Publ., Boca Raton, FL.
- Berti, W.R., and L.W. Jacobs. 1996. Chemistry and phytotoxicity of soil trace elements from repeated sewage sludge applications. *J. Environ. Qual.* 25:1025–1032.
- Bradshaw, A.D. 1999. The importance of nitrogen in the remediation of degraded land. p. 153–162. *In* M.H. Wong, J.W.C. Wong, and A.J.M. Baker (ed.) Remediation and management of degraded lands. Lewis Publ., Boca Raton, FL.
- Brown, G., and G.W. Brindly. 1980. X-ray diffraction procedures for clay mineral identification. p. 305. *In* G.W. Brindly and G. Brown (ed.) Crystal structures of clay minerals and their X-ray identification. Monogr. 5. Mineralogical Soc., London.
- Brown, S.L., C.L. Henry, R. Chaney, H. Compton, and P.P. DeVolder. 2003. Using municipal biosolids in combination with other residuals to restore metal-contaminated mining areas. *Plant Soil* 249:203–215.
- Cravotta, C.A. III. 1998. Effect of sewage sludge on formation of acidic ground water at a reclaimed coal mine. *Ground Water* 35:9–19.
- Ernst, W.H.O. 1988. Response of plants and vegetation to mine tailings and dredged materials. p. 54–69. *In* W. Salomons and U. Forstner (ed.) Chemistry and biology of solid waste: Dredged material and mine tailings. Springer-Verlag, Berlin.
- Force, E.R., W.R. Dickenson, and J.T. Hagstrum. 1995. Tilting history of the San Manuel-Kalamazoo porphyry system, southeastern Arizona. *Econ. Geol.* 90:67–80.
- Foth, H.D., and B.G. Ellis. 1997. Soil fertility. 2nd ed. Lewis Publ., New York.
- Gavlak, R.G., D.A. Hornek, and R.O. Miller. 1994. Plants soil, and water reference methods for the western region. Western Region Ext. Publ. WREP 125. Univ. of Alaska, Fairbanks.
- Gee, G.W., and J.W. Bauder. 1986. Particle size analysis. p. 383–411. *In* A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Goldberg, S., and R.A. Glaubig. 1988. Anion sorption on a calcareous, montmorillonitic soil- arsenic. *Soil Sci. Soc. Am. J.* 52:1297–1300.
- Grafe, M., M.J. Eick, and P.R. Grossl. 2001. Adsorption of arsenate(V) and arsenite(III) on goethite in the presence and absence of dissolved organic carbon. *Soil Sci. Soc. Am. J.* 65:1680–1687.
- Harris, M.A. 2001. The effect of sewage sludge and green manure on the erodibility of two mine tailing materials. *Environ. Geol.* 40: 1367–1376.
- Holmstrom, H., J. Ljungberg, and B. Ohlander. 1999. Role of carbon-

- ates in mitigation of metal release from mining waste. Evidence from humidity cells tests. *Environ. Geol.* 37:267–279.
- Hornberger, R.J., and K.B. Brady. 1998. Kinetic (leaching) tests for the prediction of mine drainage quality. p. 7-1 to 7-54. *In* K.B. Brady, M.W. Smith, and J. Schueck (ed.) Coal mine drainage prediction and pollution prevention in Pennsylvania. Pennsylvania Dep. of Environ. Protection, Harrisburg.
- Keeney, D.R., and D.W. Nelson. 1982. Nitrogen—Inorganic forms. p. 643–698. *In* A.L. Page, R.H. Miller, and D.R. Keeney (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Kempton, H., and D. Atkins. 2000. Delayed environmental impacts from mining in semi-arid climates. p. 1299–1308. *In* Proc. from the 5th Int. Conf. on Acid Rock Drainage, Denver. 21–24 May 2000. Soc. for Mining, Metallurgy and Exploration, Littleton, CO.
- Liang, J., and R.E. Karamanos. 1993. DTPA-extractable Fe, Mn, Cu and Zn. p. 87–90. *In* M.R. Carter (ed.) Soil sampling and methods of analysis. Lewis Publ., Boca Raton, FL.
- Loeppert, R.H., and W.P. Inskeep. 1996. Iron. p. 639–664. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI.
- Lowell, J.D. 1968. Geology of the Kalamazoo ore body, San Manuel district, Arizona. *Econ. Geol.* 63:645–654.
- McBride, M.B., B.K. Richards, T. Steenhuis, J.J. Russo, and S. Suave. 1997. Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Sci.* 162:487–500.
- McGeehan, S.L., S.E. Fendorf, and D.V. Naylor. 1998. Alteration of arsenic sorption in flooded-dried soils. *Soil Sci. Soc. Am. J.* 63: 828–833.
- Pentreath, R.J. 1994. The discharge of waters from active and abandoned mines. p. 121–132. *In* R.E. Hester and R.M. Harrison (ed.) Mining and its environmental impact. Royal Soc. of Chem., Cambridge.
- Pietz, R.I., C.R. Carlson, Jr., J.R. Peterson, D.R. Zenz, and C. Lue-Hing. 1989a. Application of sewage sludge and other amendments to coal refuse material: II. Effects on vegetation. *J. Environ. Qual.* 18:169–173.
- Pietz, R.I., C.R. Carlson, Jr., J.R. Peterson, D.R. Zenz, and C. Lue-Hing. 1989b. Application of sewage sludge and other amendments to coal refuse material: III. Effects on percolate water composition. *J. Environ. Qual.* 18:174–179.
- Rogers, M.T., S.A. Bengson, and T.L. Thompson. 1998. Reclamation of acidic copper mine tailings using municipal biosolids. p. 85–91. *In* Proc. of the 15th Natl. Meeting of the Am. Soc. Surface Mining and Reclam., St. Louis, MO. 17–21 May 1998. ASSMR, Lexington, KY.
- Rose, A.W., and C.A. Cravotta, III. 1998. Geochemistry of coal mine drainage. p. 1-1 to 1-22. *In* K.B. Brady, M.W. Smith, and J. Schueck (ed.) Coal mine drainage prediction and pollution prevention in Pennsylvania. Pennsylvania Dep. of Environ. Protection, Harrisburg.
- SAS Institute. 2000. The SAS system for Windows. Release 6.10. SAS Inst., Cary, NC.
- Scharer, J.M., L. Bolduc, C.M. Petit, and B.E. Halbert. 2000. Limitations of acid-base accounting for predicting acid rock drainage. p. 591–602. *In* Proc. from the 5th Int. Conf. on Acid Rock Drainage, Denver. 21–24 May 2000. Soc. for Mining, Metallurgy and Exploration, Littleton, CO.
- Seaker, E.M., and W.E. Sopper. 1988. Municipal sludge for minespoil reclamation 1. Effects on microbial populations and activity. *J. Environ. Qual.* 17:591–597.
- Soon, Y.K., and S. Abboud. 1993. Cadmium, chromium, lead and nickel. p. 101–108. *In* M.R. Carter (ed.) Soil sampling and methods of analysis. Lewis Publ., Boca Raton, FL.
- Sopper, W.E. 1993. Municipal sludge use in land reclamation. Lewis Publ., Boca Raton, FL.
- Sopper, W.E., and S.N. Kerr. 1982. Mine land reclamation with municipal sludge—Pennsylvania's demonstration program. p. 55–74. *In* W.E. Sopper, E.M. Seaker, and R.K. Bastian (ed.) Land reclamation and biomass production with municipal wastewater and sludge. The Pennsylvania State Univ. Press, University Park.
- Sopper, W.E., and E.M. Seaker. 1990. Long term effects of a single application of municipal sludge on abandoned mine land. p. 579–587. *Proc. Of the 1990 Mining and Reclamation Conf. and Exhibition*, Charleston, WV. 23–26 Apr. 1990. Vol. II. West Virginia Univ., Morgantown.
- Swayze, G., K. Smith, R. Clark, S. Sutley, R. Pearson, J. Vance, P. Hageman, P. Briggs, A. Meier, M. Singleton, and S. Roth. 2000. Using imaging spectroscopy to map acidic mine waste. *Environ. Sci. Technol.* 34:47–54.
- Systat Software. 2002. SYSTAT Version 10.2. Systat Software, Richmond, CA.
- Thompson, T.L., M. Wald-Hopkins, and S.A. White. 2001. Reclamation of copper mine tailings using biosolids and greenwaste. p. 429–499. *In* Vincent et al. (ed.) Proc. 18th Natl. Meeting of the Am. Soc. Surface Mining and Reclamation, Albuquerque, NM. 3–7 June 2001. ASSMR, Lexington, KY.
- USEPA. 1978. Chemical methods—Overburdens & mine soils. 600/2-78-054. USEPA, Washington, DC.
- USEPA. 1994. A plain English guide to the EPA part 503 biosolids rule. 832-R-93-003. USEPA, Washington, DC.
- Yanful, E., and M. Orlandea. 2000. Controlling acid drainage in a pyritic mine waste rock. Part II: Geochemistry of drainage. *Water Air Soil Pollut.* 124:259–284.