

# SOIL FERTILITY ASSESSMENT FROM INITIAL CHEMICAL ANALYSES OF COPPER MINE TAILINGS, DUCKTOWN, TENNESSEE.<sup>1</sup>

by

J L. Branson, T. E. Cook, J. T. Ammons, and V. C. Stevens<sup>2</sup>

**Abstract.** In 1907, 23,000 acres in the southeastern corner of Tennessee, known as the Copper Basin, were denuded as a result of mining activities. Bereft of vegetation, native soils became extremely eroded and acid. Wastes from ore processes were pumped into an 800 acre tailings pond. Over 350 acres remain unsuitable for plant growth. Original assumptions postulated that vegetal growth was inhibited by an acid pH. In 1998, this study was undertaken to 1) determine acidity levels of the tailings and 2) determine the presence/absence of plant nutrients for revegetation. A transect of four soil pedons was extracted, described, and sampled for laboratory analysis. Acidity levels were measured through acid-base accounting and pH. Sodium bicarbonate phosphorus, Melich double acid extraction, and total elemental dissolution analysis were used to determine the potential deficits or toxicities of nutrients and metals. In three pedons, pH ranged from 6.6 to 8.2 with NP's from 109 to 323 tons per thousand tons CaCO<sub>3</sub> equivalent. In the fourth pedon, pH below 40 cm decreased to levels of 3.0-3.8 with NP's of <59 tons per thousand tons CaCO<sub>3</sub> equivalent. Total elemental analysis and bicarbonate P indicated a maximum of 416 mg kg<sup>-1</sup> P in the tailings material with essentially none plant available. Potassium was available in sufficient quantity and would not be a limiting factor. Although total elemental concentration of some metals was high, the metals were probably in forms unavailable to plants and presented no toxicity problems. As related to revegetation, lime additions should alleviate the low pH in specific sections of the tailings pond. The major concern was the phosphorus deficiency which would require amending for any possible vegetative success.

**Additional Key Words:** Ducktown, phosphorus, copper mine tailings

## Introduction

The Copper Basin encompasses 60,000 acres within three counties: Polk County, Tennessee, Cherokee County, North Carolina, and Fannin County, Georgia (Fig. 1). Beginning in the mid-1800's, this section of the Appalachian Mountains was a major source of copper, iron, zinc, and sulfuric acid.

As a result of mining and its associated activities, tremendous environmental changes have occurred to the landscape. By 1907, a combination of

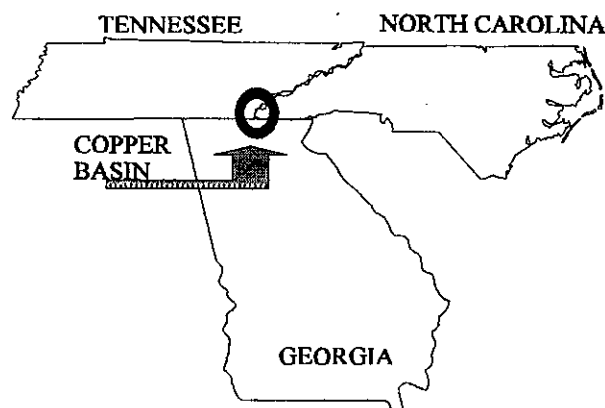


Figure 1. Location of the Copper Basin at the juncture of North Carolina, Georgia, and Tennessee.

<sup>1</sup>Paper presented at the 2000 National Meeting of the American Society of Surface Mining and Reclamation, Tampa, Florida, June 11-15, 2000.

<sup>2</sup>J. L. Branson is a post doctoral research associate, T. E. Cook is a graduate research assistant, J. T. Ammons is a professor, and V. C. Stevens is a senior research assistant, Department of Plant and Soil Sciences, The University of Tennessee, P. O. Box 1071, Knoxville, TN 37901-1071.

factors, including clearcutting of timber for fuel and sulfur emissions from processing, resulted in 23,000 acres of barren land. Erosion of native soils removed much of the fertile topsoil leaving a thin veneer of acidic, clayey subsoil over Pre-Cambrian saprolite.

By the 1990's, much of the native soil had been revegetated with pines. One of the sites remaining to be reclaimed was an 800 acre tailings pond. Native soil was layered over a 450 acre section of the tailings and revegetated. A 350 acre parcel received no soil cover and was barren of any vegetation even though deposition of wastes had ceased in the late 1980's.

Primary concerns centered around the 350 acre region which appeared disadvantageous for plant life. An investigation was initiated with the objectives of 1) determining the acidity levels of the tailings material and 2) establishing the presence or absence of essential nutrients for plant growth.

### Milling Process

Following ore extraction, rock materials were crushed to pass a 200 mesh sieve. These <2 mm particles were then subjected to flotation processes (Maher, 1966).

In most flotation operations, pH values generally range from 7 to 13. To control pH, the reagents commonly used are lime (CaO), soda ash (Na<sub>2</sub>CO<sub>3</sub>) for alkaline circuits, and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in acid circuits. In addition, lime may be added for the precipitation of toxic salts in water and the depression of pyrite. Depressing agents react with certain minerals to prevent them from floating. Sodium, potassium, and calcium cyanides are commonly added as zinc-depressing agents and occasionally to depress copper sulfides (Richards and Locke, 1940).

Waste matter did not float but was drawn off at the bottom of the float machines and pumped to a waste disposal lake, the tailings pond (Maher, 1966). In 1922, flotation was introduced at the Tennessee Copper Company in Copper Hill. Until that time, iron and zinc could not be recovered, only copper, and, in 1907, sulfuric acid began to be produced (Maher, 1966)

### Characteristics of Waste Materials from Mining

Plant available nitrogen is a common deficiency in minesoil. This is often due to a lack of source for the element. Any nitrogen present would most likely be in low concentrations. Successful conversion of nitrogen into plant usable forms would be hindered by small populations of microorganisms. Sustainable levels of N can be difficult to produce for maintaining vegetation (Grandt and Lang, 1958).

Heavy metals in tailings ponds often occur in concentrations higher than that of native soils. Total concentrations of the more common metals in native soil are (†Lindsay, 1979; †† Kabata-Pendias and Pendias, 1992):

Copper †	2-100 mg kg <sup>-1</sup>
Lead †	2-200 mg kg <sup>-1</sup>
Nickel †	5-500 mg kg <sup>-1</sup>
Manganese †	20-3000 mg kg <sup>-1</sup>
Zinc †	10-300 mg kg <sup>-1</sup>
Cadmium ††	0.06-1.1 mg kg <sup>-1</sup>
Chromium ††	54 mg kg <sup>-1</sup>

High levels of such elements can be toxic to vegetation. Heavy metals decrease water and nutrient uptake by plants, decrease root respiration, inhibit cell mitosis in root meristematic regions, and reduce enzymatic activity and microbial communities in soil (Gemmell, 1977; Clark and Clark, 1981).

### Materials and Methods

#### Field Methods

Using Soil Taxonomy, Cook et al (1999) classified the soils of the tailings material as mixed, mesic Typic Udipsamments. To determine soil physical and chemical properties of the tailings materials which would influence plant growth, a transect of four pedons was extracted across the barren portion of the tailings pond. Soil morphology was described using methods outlined in the soil survey manual (Soil Survey Staff, 1993). Each horizon was sampled for laboratory analysis. In a section suspected of having a low pH, only a surface grab sample labeled as C' (prime) was sampled.

#### Laboratory Methods

Particle size analysis was measured on selected samples by the pipette method (Kilmer and Alexander, 1949). Sands were fractionated by sieving into very coarse, coarse, medium, fine, and very fine sand sizes (Gee and Bauder, 1986).

Soil pH was measured using a 1:1 ratio of water and soil (Olsen and Ellis, 1982). Total sulfur and sulfur fractions were determined with a Leco CNS 2000. Acid - base accounting (Sobek et al., 1978; Jackson, 1958) was used in assessing potential acidity or alkalinity of the tailings materials.

Fizz tests for CaCO were measured using the following criteria (Freeman, 2000; Sobek et al, 1978):

Fizz Rating	HCl	
	(ml)	(Normality)
0 None	20	0.1
1 Very Slight	20	0.1
2 Slight	40	0.1
3 Moderate	40	0.5
4 Strong	80	0.5
5 Very Strong	80	0.5

Double-acid-extractable K, Ca, Mg, Na, Cu, and Fe (Sims and Heckendorn, 1987) was determined by atomic absorption spectrophotometer. Sodium bicarbonate extractable P (Olson et al., 1954) was determined to complete the suite of chemical properties to be monitored in the test plots. To measure total P, Cd, Cr, Cu, Mn, Ni, Pb, and Zn, total dissolution analysis (Ammons et al., 1995) was performed on the initial transect and grab samples.

## Results and Discussion

Over a long period of time, waste materials had been deposited in the tailings pond. As a result of multiple depositions, stratification was evident in the soil profiles. Each layer was designated as a C horizon indicating an absence of pedogenic influence (Table 1).

All four pedons were relatively uniform in soil morphology and particle size distribution. As a result of the milling process, particle size (Table 2) of the four pedons ranged from fine sand to loamy fine sand. Silt sized particles comprised 7 (site 2) to 26% (site 4) of the soil texture. All four sites contained less than 8% clay sized particles. The structureless single grain (0 SG) grade and shape of the soil structure indicated no pedogenic aggregation of the sand sized particles (Table 1).

Table 1. Soil morphology for sites 1, 2, 3, and 4 of the initial transect.

	Horizon	Depth (cm)	Color		Texture	Structure
Site 1	C1	0-30	2.5Y 4/2	dark grayish brown	Sand	0 SG
	C2	30-50	10YR 4/4	dark yellowish brown	Sand	0 SG
	C3	50-70	10YR 4/6	dark yellowish brown	Sand	0 SG
	C4	70-90	5YR 4/6	yellowish red	Loamy sand	0 SG
Site 2	C1	0-30	10YR 4/2	dark grayish brown	Sand	0 SG
	C2	30-55	10YR 4/4	dark yellowish brown	Sand	0 SG
	C3	55-100	10YR 4/6	dark yellowish brown	Sand	0 SG
	C4	100-125	2.5YR 3/6	dark red	Loamy sand	0 SG
	C5a	125-150	2.5YR 2.5/0	reddish black	Sand	0 SG
	C5b	125-150	5Y 3/2	dark olive grey		
Site 3	C1	0-5	2.5YR4/4	reddish brown	Loamy sand	0 SG
	C2	5-32	5YR 4/6	yellowish red	Loamy sand	0 SG
	C3	32-79	2.5Y 5/6	light olive brown	Loamy sand	0 SG
	C4	79-130	5Y 4/6	olive	Loamy sand	0 SG
	Cg	130+	5BG 4/1	dark greenish grey	Sand	0 SG
Site 4	C1	0-15	2.5Y 4/2	dark grayish brown	Loamy sand	0 SG
	C2	15-40	10YR 3/6	dark yellowish brown	Loamy sand	0 SG
	C3	40-60	5YR 3/4	dark reddish brown	Loamy sand	0 SG
	C4	60-85	5YR 4/6	yellowish red	Loamy sand	0 SG
	C5	85-110	2.5YR 4/6	red	Loamy sand	0 SG
	C6	110-130	7.5YR 3/2	dark brown	Loamy sand	0 SG
Grab Sample	C'	0-20	5YR 4/6	yellowish red	Loamy sand	0 SG

Table 2. Particle size analysis of sites 1, 2, 3, and 4.

	Horizon	Depth (cm)	% VCOS	% COS	% MS	% FS	% VFS	% SAND	% SILT	% CLAY
Site 1	C1	0-30	0	10	19	43	16	88	11	1
	C2	30-50	0	15	15	43	14	87	12	1
	C3	50-70	3	24	14	38	10	88	12	0
	C4	70-90	0	17	17	40	13	86	13	2
Site 2	C1	0-30	0	5	11	53	22	91	9	0
	C2	30-55	0	13	21	43	14	92	8	0
	C3	55-100	1	16	14	41	14	87	11	2
	C4	100-125	0	7	13	42	18	81	12	7
	C5	125-150	1	20	15	46	11	92	7	1
Site 3	C1	0-5	0	2	5	44	31	83	15	1
	C2	5-32	0	6	7	49	20	82	15	3
	C3	32-79	0	4	10	52	20	86	12	2
	C4	79-130	0	3	6	56	21	86	13	1
	Cg	130+	0	5	10	50	24	89	11	0
Site 4	C1	0-15	1	10	11	39	25	86	14	0
	C2	15-40	6	23	15	26	10	80	19	1
	C3	40-60	6	21	12	23	10	72	26	2
	C4	60-85	13	20	10	26	9	78	19	3
	C5	85-110	2	18	14	31	11	76	21	3
	C6	110-130	NA	NA	NA	NA	NA	NA	NA	NA
Grab Sample	C' (prime)	0-30	7	31	10	20	7	75	22	3

Total sulfur was variable by horizon with no concentration greater than 9% (Table 3). Most was in the form of sulfate or organic sulfur. Pyritic sulfur was present at levels of less than 0.8%. Soil pH decreased in horizons with measurable pyritic sulfur. Over the four pedons, pH ranged from 8.2 (site 2) to 3.0 (site 4) (Table 4). In three pedons, pH ranged from 6.6 to 8.2 with NP's from 109 to 323 tons per thousand tons CaCO<sub>3</sub> equivalent. In site 4, pH decreased in the four horizons between 40 to 130 cm. These horizons contained measurable levels of pyritic sulfur (Table 3), but neutralization potential of the system was less than 60 tons per thousand tons CaCO<sub>3</sub> equivalent (Table 4).

In some small localized sectors, the surface soil was suspected of possibly being acidic and a grab sample labeled C' was extracted. Taking sulfur fractions into account, out of all samples analyzed only the C' sample, required additional neutralization (Table 4). Soil pH in the C' was very acidic at 1.9. All of the sulfur present was in the form of sulfate or organic sulfur. The low pH possibly was a result of pyritic sulfur oxidation prior to the present time which

has since been removed from the system. Since there was evidence of a specific sector with surface soil having a low pH, it was recommended in the vegetation management plan to incorporate additional neutralizing amendments such as lime.

The plant nutrients, calcium, magnesium, and potassium were available at adequate levels (Table 5). Potassium in the C' surface sample measured at 25 mg kg<sup>-1</sup>, indicating the possibility of a K deficiency in localized regions. Phosphorous was a limiting factor for plant growth as all horizons analyzed contained <0.5 mg kg<sup>-1</sup>. Total P only reached a maximum of 416 mg kg<sup>-1</sup> in the C1 horizon of Site 3.

Comparing the four pedons, double acid extractable iron was higher in site 4 (Table 6). As pH decreased, plant available iron increased. Sodium was very low (< 11 mg kg<sup>-1</sup>), and plant available copper was nearly undetectable in sites 1, 2, and 3. Site 4 contained levels of copper ranging from 0.25 to 132 mg kg<sup>-1</sup>.

Table 3. Sulfur forms analyzed by an independent laboratory.

	Horizon	Depth (cm)	Total Sulfur %	Pyritic Sulfur %	Sulfate Sulfur %	Organic Sulfur %
Site 1	C1	0-30	1.79	0.00	1.54	0.44
	C2	30-50	8.22	0.00	6.57	1.72
	C3	50-70	1.94	0.00	1.81	0.18
	C4	70-90	2.76	0.10	2.42	0.24
Site 2	C1	0-30	0.94	0.03	0.58	0.33
	C2	30-55	2.85	0.00	2.66	1.33
	C3	55-100	8.26	0.00	5.90	2.36
	C4	100-125	5.63	0.33	4.18	1.12
	C5a	125-150	3.26	0.00	2.86	1.67
	C5b	125-150	2.78	0.00	2.51	1.43
Site 3	C1	0-5	2.06	0.00	1.70	1.34
	C2	5-32	3.43	0.00	3.11	0.36
	C3	32-79	1.31	0.06	1.24	0.01
	C4	79-130	1.73	0.14	1.54	0.05
	Cg	130+	1.56	0.00	1.41	0.72
Site 4	C1	0-15	4.16	0.00	3.63	1.06
	C2	15-40	7.10	0.06	4.84	2.20
	C3	40-60	4.84	0.16	4.35	0.33
	C4	60-85	4.19	0.21	3.90	0.08
	C5	85-110	6.91	0.40	5.43	1.08
	C6	110-130	7.14	0.76	5.65	0.73
Grab Sample	C'	0-20	7.42	0.00	5.63	2.22

Table 4. Acid-base accounting data calculated from pyritic sulfur values.

	Horizon	Depth (cm)	Fizz Test	Color	%S	Max. From %S	N. P. CaCO <sub>3</sub> Equiv.	Max Needed (pH 7)	Excess CaCO <sub>3</sub>	pH 1:1 H <sub>2</sub> O
Site 1	C1	0-30	4	2.5Y 6/2	<.001	.03	219.47	219.44	7.2	
	C2	30-50	4	10 YR 4/4	<.001	.03	211.79	211.76	7.4	
	C3	50-70	4	10 YR 6/3	<.001	.03	166.34	166.31	7.4	
	C4	70-90	3	10 YR 5/4	.099	3.09	109.25	106.16	7.6	
Site 2	C1	0-30	4	2.5Y 6/3	.028	.88	174.02	173.14	8.2	
	C2	30-55	5	10 YR 6/3	<.001	.03	245.73	245.70	8.0	
	C3	55-100	5	10 YR 5/4	<.001	.03	323.45	323.42	7.4	
	C4	100-125	4	7.5 YR 5/4	.330	10.31	143.43	133.12	6.6	
	C5a	125-150	5	2.5Y 5/3	<.001	.03	217.31	217.28	7.0	
	C5b	125-150	4	2.5Y 6/2	<.001	.03	233.02	232.99	7.0	
Site 3	C1	0-5	4	10 YR 5/4	<.001	.03	208.08	208.05	7.8	
	C2	5-32	4	7.5YR 5/4	<.001	.03	148.11	148.08	7.0	
	C3	32-79	4	2.5Y 6/4	.064	2.00	109.97	107.97	7.6	
	C4	79-130	4	2.5Y 6/4	.142	4.44	112.73	108.29	7.4	
	Cg	130+	4	2.5Y 6/1	<.001	.03	172.10	172.07	7.4	

Site 4	C1	0-15	3	2.5Y 5/3	<.001	.03	144.39	144.36	7.6
	C2	15-40	3	10YR 4/4	.060	1.88	110.69	118.81	6.6
	C3	40-60	1	10YR 4/6	.160	5.00	40.46	35.46	3.0
	C4	60-85	2	10YR 5/6	.214	6.69	59.48	52.79	3.0
	C5	85-110	1	10YR 5/4	.400	12.5	40.77	28.27	3.8
	C6	110-130	1	2.5Y 4/4	.757	23.66	30.90	7.24	3.6
Grab Sample	C'	0-20	0	10YR 4/6	<.001	.03	-3.62	3.65	1.9

Table 5. Available plant nutrients analyzed by an independent laboratory.

	Horizon	Depth (cm)	Phosphorus (mg kg <sup>-1</sup> )	Total P (mg kg <sup>-1</sup> )	Potassium (mg kg <sup>-1</sup> )	Calcium (mg kg <sup>-1</sup> )	Magnesium (mg kg <sup>-1</sup> )
Site 1	C1	0-30	<0.5	166	111	6900	272
	C2	30-50	<0.5	93	89	6750	264
	C3	50-70	<0.5	231	138	6550	331
	C4	70-90	<0.5	242	281	4780	615
Site 2	C1	0-30	<0.5	312	191	6600	2200
	C2	30-55	<0.5	289	122	7000	273
	C3	55-100	<0.5	237	92	6750	303
	C4	100-125	<0.5	355	73	4745	376
	C5a	125-150	<0.5	199	106	6700	363
	C5b	125-150	<0.5	199	119	6550	320
Site 3	C1	0-5	<0.5	416	128	6450	225
	C2	5-32	<0.5	254	236	6500	322
	C3	32-79	<0.5	260	269	6500	352
	C4	79-130	<0.5	278	178	6600	381
	Cg	130+	<0.5	160	156	6400	298
Site 4	C1	0-15	<0.5	279	141	5900	471
	C2	15-40	<0.5	201	163	4920	840
	C3	40-60	<0.5	74	217	4570	600
	C4	60-85	<0.5	231	112	4795	920
	C5	85-110	<0.5	190	148	4180	990
	C6	110-130	<0.5	151	85	3965	790
Grab Sample	C'	0-20	2.7	88	25	4520	805

**Table 6. Double acid extractable metals analyzed by an independent laboratory.**

	Horizon	Depth (cm)	Iron (mg kg <sup>-1</sup> )	Sodium (mg kg <sup>-1</sup> )	Copper (mg kg <sup>-1</sup> )
Site 1	C1	0-30	479	7.8	<.1
	C2	30-50	900	4.5	<.1
	C3	50-70	960	7.3	<.1
	C4	70-90	2020	10.9	.45
Site 2	C1	0-30	331	7.3	<.1
	C2	30-55	705	6.6	<.1
	C3	55-100	770	4.6	<.1
	C4	100-125	1260	9.8	.15
	C5a	125-150	1580	6.4	<.1
	C5b	125-150	1450	7.5	<.1
Site 3	C1	0-5	276	6.4	.2
	C2	5-32	590	5.8	<.1
	C3	32-79	650	7.0	<.1
	C4	79-130	920	7.5	<.1
	Cg	130+	1210	6.9	<.1
	Site 4	C1	0-15	1255	6.8
C2		15-40	2880	5.9	10.6
C3		40-60	2770	7.2	57
C4		60-85	2780	7.6	49.8
C5		85-110	4035	7.4	132
C6		110-130	3415	6.0	19
Grab Sample		C'	0-20	3510	4.3

Total metal concentrations were averaged for each pedon (Table 7). Levels of specific elements of interest were compared with those generally found in native soils (Lindsay, 1979; Kabata-Pendias and Pendias, 1992). Nickel fell within the range normal for native soils, while cadmium, chromium, manganese, and lead were slightly higher. As expected, Copper and zinc were present in much greater quantities. Since the double acid extractable copper content (Table 6) was extremely low compared with total copper (Table 7), plant toxicity should not be a problem. Double acid extractable data was unavailable for the other elements, however, these metals, as with copper, were probably unavailable in sufficient quantity to pose a problem for revegetation.

#### Conclusions

1. Total sulfur concentrations were less than 9%. Most was present as sulfate or organic sulfur. No horizon contained greater than 0.8 % pyritic sulfur.

2. Calcium carbonate content was sufficient to neutralize the acid production potential of the pyritic sulfur.

3. Potassium was available in adequate amounts for plant growth.

4. There were exceptions as evidenced by the C' grab sample. Analysis of the C' sample indicated a pH of 1.9 and double acid extractable K content of 25 mg kg<sup>-1</sup>. To insure the successful establishment of vegetation, additions of neutralizing materials and potassium would be advisable to enhance revegetation success rate.

5. Soil pH ranged from 8.2 to 3.0, with most > 6.0.

6. Phosphorus was deficient in the tailings material. For successful revegetation, an amendment of P was required.

7. Total elemental concentration of nickel were comparable with those of native soils, while

Table 7. Specific total elemental content of native soils as compared with the total elemental concentrations in the four pedons from the tailings pond († Lindsay, 1979; †† Kabata-Pendias and Pendias, 1992).

ELEMENT	% COMMON IN NATIVE SOILS (mg kg <sup>-1</sup> )	SITE 1 (mg kg <sup>-1</sup> )	SITE 2 (mg kg <sup>-1</sup> )	SITE 3 (mg kg <sup>-1</sup> )	SITE 4 (mg kg <sup>-1</sup> )
Cadmium	0.06 - 1.1 ††	3	3	2	4
Chromium	54 ††	64	62	57	24
Copper	2 - 100 †	839	737	666	2537
Manganese	20 - 3000 †	3723	3592	3678	3356
Nickel	5 - 500 †	75	63	316	57
Lead	2 - 200 †	100	94	96	286
Zinc	10 - 300 †	1738	1922	1637	2861

cadmium, chromium, and lead were slightly higher. Total copper and zinc were much greater than in native soils.

8. Although total copper concentrations were high, double acid extractable copper was very low and should not be present in amounts toxic to plant life.

#### Acknowledgements

Special thanks to Glen Springs Holdings, INC, a subsidiary of Occidental Petroleum Co. for funding this research.

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