

Phosphorus and Potassium Relationships in Southwestern Virginia Coal-Mine Spoils

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ABSTRACT

Nutrient deficiencies are commonly reported as a major limiting factor in reclaiming Appalachian surface-mine spoils. Our objective was to intensively study the P and K relationships of representative mine spoils and contiguous natural soils derived from the Wise Formation in southwestern Virginia. Quantity/intensity (Q/I) relationships for P and K were developed for the major occurring spoils and representative natural soil materials. Sandstones (sublitharenites) and siltstones dominate the Wise Formation and show three phases of cementation—an initial carbonate phase, a second goethite phase, and a third silica overgrowth phase. Total P ranged from 255 to 530 mg/kg in the dominant sandstone and siltstone spoil types, and the majority of P was associated with complex carbonates. Phosphorus in the weathered natural soil materials was dominantly associated with Fe oxides. Phosphorus Q/I analyses coupled with P fractionation data indicate that fixation by Fe oxides is the most likely cause of P deficiencies in rock spoils derived from the Wise Formation and may be a widespread problem limiting revegetation and reclamation success in the Appalachian region. This problem is difficult to rectify by fertilization; hence, Fe oxide-rich strata, and spoils derived from them, should be avoided during regrading to optimize surface mine reclamation. Micaceous and traces of feldspars are the dominant sources of K in the mine spoils. Potassium fixation by weathered mica occurs in natural soils derived from the Wise Formation, but not in unweathered spoils. Nonferrous rock substitutes for topsoil are therefore superior as a plant growth medium in regard to P and K availability.

Southwestern Virginia is a deeply dissected plateau underlain by a nearly flat-lying succession of coal-bearing clastic strata of Pennsylvanian age (Fig. 1). The coal is mined at the surface mainly by contour (strip) and mountaintop removal methods. More than 40 000 ha has been disturbed by surface mining in southwestern Virginia, and federal (Surface Mining Control and Reclamation Act of 1977; SMCRA) and resultant state regulatory programs mandate revegetation with a 5-yr bond release period, and return to approximate original contour.

In this region, revegetation of strip mines is complicated by steep topography. Blasted rock spoils are often employed as a substitute for topsoil, because natural soils are generally thin and acidic, and difficult to isolate during mining. Establishing and maintaining a healthy, self-sustaining vegetative cover is often complicated by the low pH, poor nutrient status, and droughtiness of the mine spoils.

In this study we examined the P and K mineralogy and chemistry of southwestern Virginia coal mine spoils. Phosphorus deficiencies are widely recognized in mine spoils of the Appalachian region, whereas K levels are not usually reported to be a major factor limiting plant growth (Barnhisel and Massey, 1969; Plass and Vogel,

1973; Smith and Sobek, 1978; Howard, 1979; Everett, 1981; Gensheimer and Stout, 1982; Daniels and Amos, 1982, 1984). Phosphorus fertilization rates as high as 780 kg/ha did not significantly increase extractable P in Wise Formation spoils similar to those used in this study (Demchak et al., 1983), and very large additions of P (336–780 kg/ha) were required to elicit a growth response.

The objectives of our study were to (i) determine the initial form and fate of P and K during mine soil weathering, (ii) predict the long-term behavior and P and K supplying potential of spoils when used as topsoil substitutes, and (iii) recommend corrective measures to optimize mine spoil revegetation strategies with regard to P and K fertility.

MATERIALS AND METHODS

Geologic Setting and Site Description

In this study, we have identified the mineral forms and the relative plant-availability of P and K in commonly occurring southwestern Virginia sandstone and siltstone mine spoils. We have also compared these spoils with naturally occurring contiguous soils at a surface mine operation in the Wise Formation near Hurley, VA (Fig. 1). A lithofacies classification of the coal-bearing strata in the study area was formulated from measured stratigraphic sections, and geologic mapping at a scale of 1:24 000 (Howard, 1979). Major soil and spoil types were identified using auger and pit descriptions from a transect between lower and middle Elk Creeks. Weathering profile descriptions of natural soils and samples of overburden materials were collected from roadcut and highwall exposures. All work was done within or in close proximity to the active mining permit area.

The study area is located in the northern tip of Buchanan County, Virginia (Fig. 1), and lies along the eastern margin of the Appalachian coal basin where the terrain is a deeply dissected plateau composed of narrow, sinuous ridges and valleys. Local relief is 300 m and sideslopes are 40 to 80%.

The coal-bearing strata sampled crop out at the head of Upper Elk Creek and Long Branch, 12 km north of Hurley, VA. We examined a stratigraphic section 150 m thick between the Campbell Creek and Cedar Grove Coal horizons (Hinds, 1918) in the middle part of the Wise Formation. The Wise Formation (Atokan), and equivalent units of the Pottsville Group, underlie a large part of southwestern Virginia, southeastern Kentucky, and western Virginia. The Wise Formation section studied consists of repeated cyclic, fining-upward sandstone-siltstone-mudrock-coal sequences probably deposited in a meandering fluvial or deltaic depositional setting (Howard, 1979). The measured section is about 70% sandstone; 20% siltstone; and 10% mudrock, conglomerate, and coal.

Mineralogical Analyses

Thirty rock thin sections were examined and modal compositions are based on grain counts of 500 points per slide. Thin sections were stained to differentiate calcite and dolomite. Clay was obtained from thoroughly ground rock samples by sieving and centrifugation. All samples were pretreated for removal of soluble salts and carbonates by washing with 0.1 M HCl. Organic matter was removed by the Dithionite-Citrate-Bicarbonate (DCB) method. Pretreatment procedures followed

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Table 2. Clay-sized minerals in rock, soil, and spoil derived from the Wise Formation.

Mineral species	Calcareous sandstone	Calcareous siltstone	Calcareous goethitic sandstone	Calcareous goethitic siltstone	%			
					Colluvium (C)	Saprolite (Cr)	B horizon (Bt)	Mine-spoil
Muscovite	45	30	30	50	15	15	10	30
Montmorillonite	10	5	40	5	35	40	5	10
Vermiculite	15	15	20	15	30	40	5	10
Interstratified 2:1 minerals	15	30	0	15	15	15	30	15
Kaolinite	10	10	10	15	0	tr	5	15
Chlorite	5	10	0	0	0	0	0	0
Quartz	0	0	0	0	tr	tr	tr	10
Feldspar	0	0	0	0	5	tr	0	5

removal on an oven-dry basis. The error due to the presence of soluble salts was thought to be small.

Phosphorus adsorption curves were obtained using thoroughly ground and mixed 1.5-g samples to which were added 50 mL of solutions that were 0.01 M with respect to CaCl₂ and which contained 1, 5, 10, 30, 50, and 100 mg P/L. The samples were equilibrated for 6 d during which time they were shaken periodically. The supernatants were collected after centrifugation and P was determined by the Murphy and Riley (1962) method. Data were plotted (Fig. 2) as P adsorbed per kilogram soil (mg/kg) vs. equilibrium P remaining in solution (EPC).

Potassium quantity/intensity (Q/I) curves (Beckett, 1964a, b, c) were obtained using varying amounts of dried, ground sample (0.2-7.0 g) weighed into 100-mL centrifuge tubes. To these samples were added 50 mL of solutions ranging from 0.0002 to 0.002 M with respect to KCl and 0.002 M CaCl₂. The samples were then shaken for 20 h at 25 °C, and the supernatants collected for analysis of K by atomic absorption spectrophotometry. The change in solution K levels (ΔK) was computed from the difference between the K in the initial and equilibrium solutions normalized to cmol_c kg soil. The activity ratio of K (ARK) values were computed from the measured concentrations of K, Ca, and Mg corrected to their appropriate activities by the Debye-Huckel equation. Data shown in Fig. 3 are plotted as described by Beckett.

RESULTS AND DISCUSSION

Mineralogic Composition of the Parent Material

In the section of Wise Formation studied, sandstones are mainly medium to fine-grained with a uniform modal composition (Fig. 4). Quartz is the principal constituent

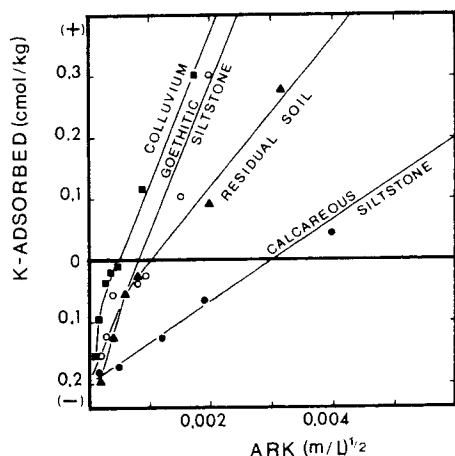


Fig. 3. Potassium quantity/intensity relations of Wise Formation parent rocks and derived soils. Detail on interpretation of Q/I curves is given by Beckett (1964a, b, c).

with lithic fragments dominant over feldspar; hence, sublitharenite is the main rock type. Detrital muscovite, biotite, and chlorite are usually present, but in minor amounts. Zircon and tourmaline with minor epidote comprise the heavy mineral suite. Siltstones have a similar composition, but are primarily quartz and mica (Howard, 1979).

Wise Formation sandstones and siltstones are 2 to 5% clay by weight. The clay mineral suite is composed mainly of muscovite or illite with variable quantities of smectite, vermiculite, mixed-layer illite/smectite, and kaolinite (Table 2).

These rocks show three episodes of cementation. An initial phase of carbonate cementation is present as a more or less continuous matrix between the majority of grains. A second, goethite phase of cementation is present, and silica, in the form of quartz overgrowths, represents the third episode. Dolomite is the main carbonate mineral present with lesser amounts of calcite and minor siderite and ankerite. Goethite is the dominant Fe oxide mineral, either as a single phase or a complex mixture with magnetite and hematite.

The spatial distribution of Fe oxides and carbonates in the Wise Formation is highly irregular; however, carbonates are most abundant in roof rocks and decrease

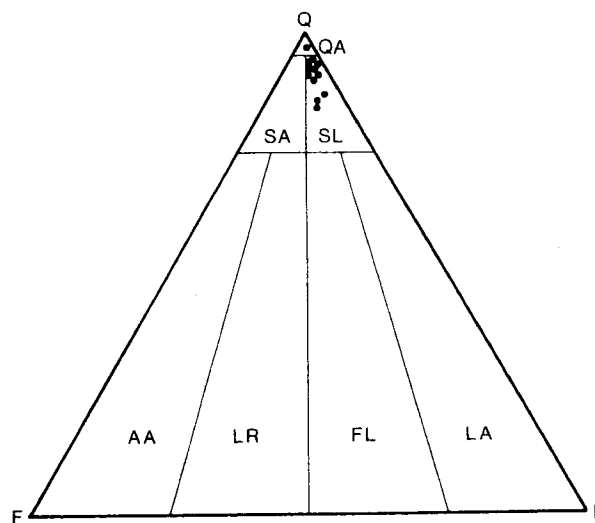


Fig. 4. Triangular diagram illustrating modal composition of Wise Formation sandstones in terms of quartz (Q), feldspar (F), and lithic fragments (L). Rock types as follows: QA, quartz arenite; SA, subarkosic arenite; SL, sublith-arenite; AA, arkosic arenite; LR, lithic arkose; FL, feldspathic litharenite; LA, lithic arenite.

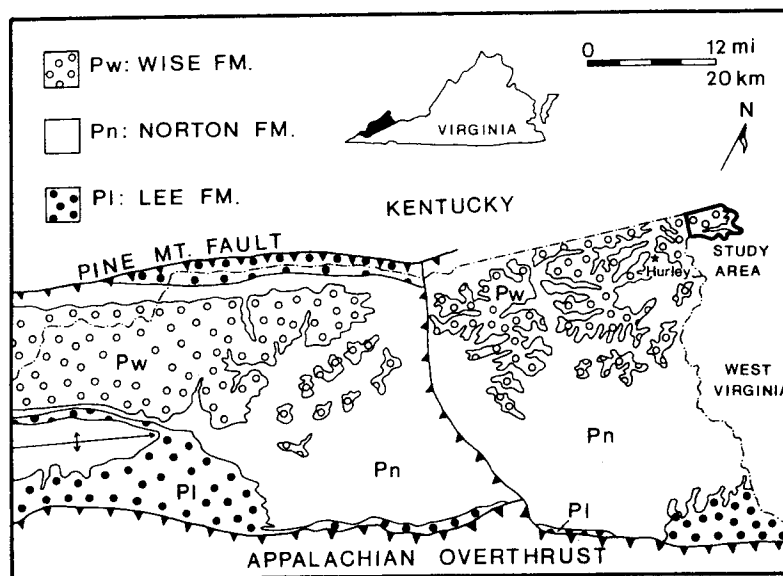


Fig. 1. Generalized geologic map of Pennsylvania strata in the coal fields of southwestern Virginia. Rocks similar to the Wise Formation examined in this study underlie large areas of the central Appalachian coal fields.

those used by Jackson (1979) and Kunze (1965). Oriented mounts were prepared using the suction on ceramic tile method (Rich, 1969). Samples were K-saturated and x-rayed at 25, 110, 300, and 550 °C and Mg-glycerol solvated and x-rayed at 25 and 110 °C. Oriented mounts were scanned from 2 to 32° 2-theta and the sand and silt fractions of rock and spoil samples in unoriented powder mounts were scanned from 2 to 62° 2-theta to identify nonclay minerals. Relative quantities of minerals present were estimated from peak intensities.

Physical and Chemical Characterization

Particle size, pH, and organic matter analyses were performed on soils and spoils by standard soil survey procedures (USDA-SCS, 1984). Dilute double acid-extractable Ca, Mg, K, and P were also determined by methods given by Donohue and Gettier (1981). Available P was also extracted in 0.5 M NaHCO₃ (pH 8.5), and solution P was determined by the Murphy and Riley (1962) method. Spoil CEC was determined using the method of Chapman and Pratt (1961) for calcareous soils. A 33-mL portion of 1 M NaOAc was added to a 4-g sample and shaken for 5 min. The procedure was repeated three times and the supernatants decanted and collected for atomic absorption analysis of Ca, Mg, and K. These data are reported as "Extractable nutrients" and "Sum of cations" in Table 1. The soils

were then washed with three 33-mL portions of 95% alcohol. Adsorbed Na was then displaced with three 33-mL portions of 1 M NH₄OAc and each washing was collected. Spoil CEC was then determined by analyzing for Na by atomic absorption spectrophotometry.

The fractionation of inorganic soil phosphates was performed according to the modified Chang and Jackson procedure of Peterson and Corey (1966) using a thoroughly mixed and ground 1-g sample. The inorganic fractions obtained, in order of extractions, were: H₂O-soluble P (soluble in 1 M NH₄Cl); Al-P (0.5 M NH₄F at pH 8.2); Fe-P (0.1 M NaOH); reductant-soluble P (0.3 M Na₂C₆H₄O₇·2H₂O and Na₂S₂O₄); occluded P (0.1 M NaOH); and Ca-P (0.25 M H₂SO₄). Total P was taken as the sum of all extractions. Excess reagents from each extraction were removed by two washings with saturated NaCl solution. Recent work by Daniels et al. (1986) has indicated that P resorption by carbonates during these procedures is minimal for these materials. Calcareous samples were run in the same manner, except the water-soluble and Al-P tests were omitted. Phosphorus was analyzed by the molybdate blue method of Murphy and Riley (1962). Excess F was neutralized with 0.8 M boric acid and pH levels adjusted to pH 2.5 to 3.0 to obtain color development. Carbonate contents were determined from these samples by weight difference before and after Ca-P

Table 1. Cation exchange capacities and sodium acetate-extractable nutrients of rocks from the Wise Formation.

Samples	Extractable nutrients			Sum of cations	Measured CEC
	Ca	Mg	K		
	cmolc/kg				
Calc. sandstone	5.5	7.7	0.8	14.0	5.2
Goeth. sandstone	6.0	16.5	0.6	23.1	17.4
Calc. siltstone	10.3	20.9	2.1	33.3	17.0
Goeth. siltstone	13.0	26.4	0.8	40.2	24.4
Goethite	1.5	7.7	0.8	10.0	13.0
Argill. shale	0.5	55.0	2.6	58.1	26.1
75:25 gss/bss†	5.8	11.0	0.6	17.4	7.8
25:75 gss/bss	6.8	14.3	0.6	21.7	13.9
75:25 bss/bsi	8.5	20.9	0.6	30.0	20.4
25:75 bss/bsi	11.8	24.2	1.0	36.9	28.3

† Simulated minespoil mixtures: gss = gray calcareous sandstone; bss = brown goethitic calcareous sandstone; bsi = brown goethitic calcareous siltstone. Ratios indicate mixtures by weight.

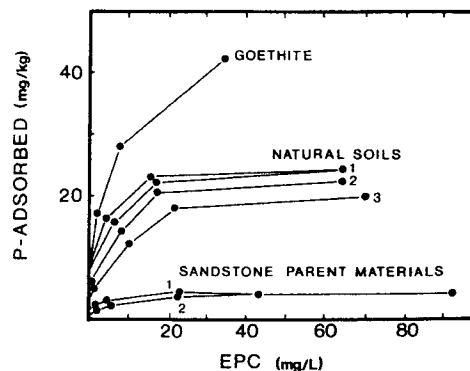


Fig. 2. Phosphorus quantity/intensity relations for Wise Formation parent rocks and derived soils. Phosphorus fixation is a problem in soils and fresh minespoils due to the abundance of goethite.

recognized mineral transformation in soils of the southeastern USA (Jackson, 1964).

In spite of the great reservoir of K in the parent rocks, natural soils derived from the Wise Formation have low to medium levels of extractable K (Table 4). Because illite and vermiculite are the clay minerals demonstrated to have the greatest potential for K fixation (Rich, 1968), it is likely that much of the K liberated from parent micas during weathering has been specifically adsorbed or fixed by pedogenic vermiculite and other clays. The remainder was probably lost by leaching or was held on the exchange complexes of clay mineral species with a low selectivity for K.

Iron oxides are the dominant P-bearing mineral phase in natural soils derived from the Wise Formation in contrast to the phosphatic carbonates in the parent materials (Table 3). No soil P is in a carbonate form, and total P levels are much lower for the soils than for the parent rocks. Substantial P has clearly been lost by long-term leaching and that remaining has altered to a totally new mineral form.

Highly insoluble Fe- and Al-phosphates are generally believed to be the predominant end-products of inorganic P during soil genesis and following P fertilization, but only at high concentrations (> 3100 mg/kg) will P react with Fe oxides in bulk and rapidly precipitate as these mineral forms (Kittrick and Jackson, 1955; Taylor et al., 1953). In dilute solutions (< 31 mg/kg), P ions are adsorbed by Fe oxides and clay minerals by chemisorption, or specific adsorption, and thus are held in a form unavailable to plants (Olsen and Wanatabe, 1957; Hsu, 1964; Muljadi et al., 1966; Hingston et al., 1967, 1968). The specific adsorption of P by clays and Fe oxides is independent of pH or concentration, and probably accounts for the very low levels of extractable P in natural soils derived from the Wise Formation (Tables 3 and 4).

Phosphorus and Potassium Supplying Potential of Mine Spoils

Blasted rock spoils are commonly used as topsoil substitutes in the Appalachians, because natural soils are generally thin and acidic. The spoils studied at this site were mainly mixtures of sandstone and siltstone and had the same mineralogic composition as the parent rocks (Table 2). The K- and P-supplying potentials of the major rock types comprising the spoils are assessed in Fig. 2 and 3, respectively.

The degree of curvature in the lower portion of a K Q/I plot is considered to be correlated with the number of specific adsorption sites present in a given sample (Beckett, 1964a, b, c). Unweathered spoils of the Wise Formation, therefore, do not have a strong specific adsorption affinity for K as indicated by their relatively linear Q/I plots (Fig. 3). The contiguous natural soils derived from the Wise Formation, however, are highly selective for K, indicating that the degree of fixation potential increases with weathering. Potassium fixation is not a problem in fresh mine spoils, but may increase with time, as indicated by the curvature in the lower portion of the Q/I plots for the weathered soil materials.

Both rock types examined had similar quantities of extractable K, but based on their Q/I curves they would differ markedly in their ability to maintain levels of K in solution as a function of plant uptake. The non-ferruginous rock has more available K initially (higher ARK at $\Delta K = 0$), but had less ability to maintain K in solution, as indicated by the shallower slope of the Q/I plot. The slope of the linear portion of a Q/I plot is proportional to CEC and the ability of a material to supply K to solution (potential buffering capacity for K). The Fe oxides in the goethitic siltstone apparently make a significant contribution to the potential buffering capacity of the mine spoils with respect to K.

These data show that a small fraction of the total K in the parent rocks is in a form readily available to plants, probably on the exchange complexes of clays and Fe oxides. The lower K status of the natural soils is most likely due to leaching and specific adsorption by illite and vermiculite. Thus, K fixation is not a problem in unweathered spoils, but may become a problem with progressive weathering of micas into vermiculite.

Nonferruginous rocks in the Wise Formation do not have a strong specific adsorption affinity for P, but the affinity of goethite for P is clearly demonstrated (Fig. 2). A residual accumulation of insoluble Fe oxides during pedogenesis accounts for the P fixation observed in the natural soils. Specific adsorption and P fixation by Fe oxides most likely causes the observed P deficiencies on mine spoils of the Appalachian region. Iron-oxides are ubiquitous throughout the Carboniferous section, and because blasting reduces the minerals into ultrafine-grained, highly reactive particles that are difficult or impossible to segregate during the mining process, serious problems with revegetation may prove to be widespread, particularly over long periods of time. This delay could be a particular problem where high P-demanding agronomic legume species are employed, as is common practice in the region. Even with substantial fertilizer additions, the problem may be difficult to remedy since P reacts with Fe oxides at high concentrations to form highly insoluble Fe-phosphates. Daniels et al. (1986) have demonstrated significant increases in Fe-bound P and P adsorption potential in similar Wise Formation mine soils over the 5-yr bond release period mandated by SMCRA.

The overall nutrient potential of mine spoils in the study area is limited by their low clay content and CEC. However, the CEC of mine spoils is enhanced by the presence of ferruginous materials, and is higher where siltstone parent rocks are present (Table 1). Mixtures of rock types made to simulate those of the mine spoils clearly indicate the positive effect of increasing the content to fine-textured siltstones on spoil base status and CEC. The measured CEC is consistently lower than that estimated by summation of extractable cations due to the presence of free salts. These water-soluble salts provide a readily available supply of plant nutrients during the initial stages of mine spoil weathering; however, soluble salt contents of the fresh spoils may exceed the tolerance limit of many plants. A lysimeter study of mine spoil leachates showed that the water-soluble component declines rapidly after the leaching equivalent of several

Table 3. Phosphorus fractionation data for rock and soil from the Wise Formation. Extracts are defined in the Materials and Methods section.

	Fe-P		Reductant sol. P		Occluded P		Ca-P		Summed total P	Carbonates	Avail.-P NaHCO ₃ -P
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
Calcareous sandstone	0	0	0	0	0	0	225	100	225.0	3.15	12.5
Calcareous siltstone	0	0	5.5	1.4	0	0	380	98.6	385.5	7.60	10.0
Goethitic sandstone	10	1.9	10.5	2.0	0	0	510	96.1	530.5	2.79	14.0
Goethitic siltstone	0	0	10.0	1.9	5	1	500	97.1	515.0	3.15	7.0
Goethitic nodule	15	12.1	14.0	11.3	15	12.1	80	64.5	124.0	2.00	8.0
Colluvium	30	66.7	3.0	6.6	12	26.7	0	0	45.0	0	3.0
Residual B horizon	18	81.8	2.0	9.1	2.0	9.1	0	0	22.0	0	0

Table 4. Morphological and chemical properties of soil and mine spoil derived from the Wise Formation.

Horizon	Depth cm	Color	Structure	Con- sistence	Sand	Silt	Clay	pH	Acid-extractable				Organic matter g/kg
									Ca	Mg	P	K	
<u>Residual upland soil no. 1</u>													
A	0-4	10YR 5/4	1vfgr	mvfr	22	54	24	4.3	69	58	3	58	59
E	4-8	10YR 6/3	1fsbk-abk	mfr-fi	22	54	24	4.4	55	47	12	58	42
Bt	8-38	10YR 6/6	2msbk	mfi	24	48	28	4.6	41	68	12	40	11
BC	38-44	7.5YR 5/6	1-2f-msbk-abk	mvfi	31	42	27	4.7	41	86	12	36	5
Cr	48-63	7.5YR 6/6	o-m	dvfi-h	35	51	14	4.8	28	98	5	32	3
<u>Residual upland soil no. 2</u>													
A1	0-8	10YR 3/4	1-2vf-fgr	mvfr	26	55	19	4.8	275	125	8	117	36
A2	8-20	10YR 5/4	1vf-fsbk	mvfr	26	54	20	4.9	69	72	5	85	9
BA	20-38	10YR 5/4	1vf-fsbk	mfr	26	54	20	5.0	42	120	5	54	2
Bt1	38-60	10YR 5/4	2f-mabk&sbk	mfi-mfr	21	52	27	5.0	28	200	3	66	2
Bt2	60-90	10YR 5/4	2msbk&abk	mfi	22	52	26	5.1	41	200	3	82	2
C	90-113	10YR 5/4	1-2f-msbk	deh	29	50	21	5.1	55	200	3	138	2
<u>Colluvial soil</u>													
A	0-19	10YR 4/2	1vfgr	mfvi	48	38	14	4.8	317	176	5	80	48
C	19-46	10YR 5/4	o-m	mfr	49	35	16	4.9	110	126	3	26	11
<u>Mine spoil</u>													
1	0-35	10YR 3/2	1msbk	mfr	31	48	21	6.5	1650	200	+138	59	27
2	35-65	10YR 4/3	o-m o-l fmsbk	mfr	16	60	24	5.8	1200	200	82	64	16
3	65-115	10YR 4/3	o-m o-l fmsbk	mfr	12	64	24	6.0	1360	200	95	58	20
4	115-165	10YR 4/3	o-m	mfr	15	69	16	6.9	1530	200	+138	73	10

upsection. Goethite is abundant throughout the section in the form of beds, nodules, concretions, fossil materials, and conglomerate clasts. The typical Wise Formation sandstone is 75 to 80% quartz (by volume), 10 to 15% lithic fragments and feldspar, with the remainder made up of mica, cementing agents, and pore space.

The main K-bearing mineral in sandstone and siltstone of the Wise Formation is muscovite or illite. Potassium-feldspar and vermiculite are present, but in minor amounts. Calcite and dolomite are the primary P-bearing mineral forms in the rocks as shown by selective dissolution (Table 3). Some P is associated with Fe oxides in the ferruginous rocks, but most is in the form of phosphatic carbonate. Even in the goethite nodule sample, most P is in a carbonate form.

Morphology and Nutrient Status of Natural Soils and Mine Spoils

The natural soils in the study area were primarily yellowish brown Typic Hapludults and Dystrochrepts

with loamy textures, containing a maximum of about 30% clay (Table 4). Residual upland soils had sola < 1 m thick, and sideslope colluvial soils had thin A-C profiles 20 to 50 cm thick. The soils were acidic and low in extractable Ca and P, whereas dilute acid-extractable K and Mg varied widely.

The mine spoils in the area were at most 2 yr old with little or no profile development other than minimal structural and organic matter accumulation at the surface. The mine spoils vary widely in texture, and generally contain 50% or more coarse fragments (> 2 mm). Mine spoil pH was moderate to high, and acid-extractable levels of Ca, Mg, and P were exceptionally high compared to the natural soils, whereas K levels were moderate (Table 4).

Fate of Phosphorus and Potassium during Weathering

Natural soils formed from the Wise Formation contain more clay-sized vermiculite and mixed-layer illite/smectite than the parent rocks (Table 2). These clays are most likely derived from weathered muscovite, a widely