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Nutrient concentrations in tree leaves on brown and gray reclaimed mine soils in West Virginia

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HIGHLIGHTS

- Tree leaf nutrient concentrations growing in four mine soils were lower than those in native forests.
- Phosphorus and potassium were lower in all three tree species.
- Brown mine soil had similar foliar and soil nutrient values as those in native soils.
- After 6 yrs, amended and Brown mine soils supported healthy tree growth.

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ABSTRACT

Surface mining in Appalachia disrupts large areas of forested land. Federal and state laws require disturbed lands be reclaimed by re-constructing the landscape and replacing soil materials to provide a rooting medium. If insufficient quantities of native topsoil are available, substitute materials derived from the overburden may be used as soil media. This study examined soil and foliar nutrient concentrations of three hardwood tree species on areas where brown and gray sandstone overburden were applied as substitute growth media at the Birch River mine in West Virginia. Soil and foliar nutrient concentrations found in four experimental plots were compared to soil and foliar nutrient concentrations found in a nearby native Appalachian forest. Many foliar nutrients such as phosphorus and potassium were lower in all three tree species on most mine soils compared to trees growing in nearby native forest soils and to tree nutrient concentrations from the literature. Foliar and soil nutrient concentrations in the Brown mine soil were similar to those found in native forest soil, while the Gray mine soil provided significantly lower levels of nutrients. Overall, low nutrient availability in mine soils translates into generally lower foliar nutrient concentrations in trees growing on mine soils. After six years, amended topsoil substitutes and Brown mine soil produced higher foliar nutrient concentrations than Gray mine soil.

1. Introduction

The Appalachian region of the eastern USA is home to some of the most ecologically diverse temperate deciduous forests in the world (Showalter et al., 2007; Riitters et al., 2000). Every year more than 10,000 ha of land in Appalachia are disturbed for the purpose of surface coal mining (Zipper et al., 2011). In the USA, West Virginia is the second largest coal producing state. In 2012, West Virginia produced 126,483,400 tonnes of coal from both underground and surface mining operations. Currently, there are 232 active surface mines in West Virginia which produced 43,599,824 tonnes of coal in 2012 (West Virginia Coal Association, 2012).

In 1977 the U.S. government passed the Surface Mining Control and Reclamation Act (SMCRA) due to growing concerns about environmental and safety issues with surface mining. SMCRA mandates performance standards for coal operators to meet before, during, and after mining operations including restoring the land to its approximate original contour, minimizing disturbances to the hydrologic system, reclaiming the land in a timely manner, and establishing a permanent vegetative cover (Public Law 95-87, 1977). In an effort to quickly and economically establish a permanent vegetative cover as mandated by SMCRA, coal operators frequently planted a variety of rapidly establishing grasses and legumes. However, aggressive non-native forage species such as red clover (*Trifolium pretense* L.), Kentucky-31 tall fescue (*Festuca arundinacea* Schreb), and sericea lespedeza (*Lespedeza cuneata* L.) impede the re-colonization of native herbaceous and tree species by outcompeting them for nutrients, water, and solar energy (Franklin et al., 2012; Emerson et al., 2009).

Recently however, there has been a shift in reclamation philosophy in the Appalachian region. The U.S. Office of Surface Mining (US OSM) launched the Appalachian Regional Reforestation Initiative (ARRI)

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with assistance from several state regulatory agencies and university researchers to encourage mine operators to re-establish native hardwood tree species. Reforestation of mined land enhances wildlife habitat, supports ecosystem diversity, promotes soil and water conservation, aids in the sequestration of atmospheric CO_2, and eventually provides an economically valuable post-mining land use for the landowner (Burger, 2009; Amichev et al., 2008; Larkin et al., 2008). ARRI recommends using Forestry Reclamation Approach (FRA) technology. The five FRA steps are (Burger et al., 2005): 1) create a suitable rooting medium for tree growth; 2) loosely grade the topsoil or topsoil substitute; 3) seed a tree compatible ground cover; 4) plant early successional tree species and commercially valuable crop trees; and 5) use proper tree planting techniques. Research has shown that these techniques foster natural succession of native plant species, increases the survival and growth of trees, and promotes the re-colonization of wildlife communities (ARRI, 2012; Zipper et al., 2011).

The designation of forestry post-mining land uses in West Virginia requires the placement of 1.2 m of soil material. This performance standard was established in the West Virginia surface mining regulations to optimize the growth of commercially valuable trees and to re-establish a sustainable forest ecosystem on mined lands. Steep topography and thin native soils characterize the coal mining regions of southern West Virginia and make topsoil salvage extremely hazardous and expensive. Therefore, regulations allow coal operators to use topsoil substitutes derived from weathered and unweathered geologic strata from the overburden to achieve required depths of soil material (Emerson et al., 2009). In West Virginia, the predominant overburden rock type is sandstone; as either brown sandstone, which is weathered and moderately acidic, or gray sandstone, which is unweathered and slightly- to moderately-alkaline (Emerson et al., 2009).

Several studies conducted in the Appalachian coal fields have shown that selecting the appropriate material from the overburden to create mine soils suitable for reforestation is imperative for proper tree growth and survival. Angel et al. (2008) found that average tree height on brown sandstone was significantly greater (66 cm) than average tree height on gray sandstone (35 cm) after three years. Skousen et al. (2013) reported that the average height of chestnut (*Castanea* spp.) seedlings was 90 cm on brown mine soil compared to 62 cm on gray mine soil after the third year. Eight years after reclamation, Wilson-Kokes et al. (2013) found that average tree volume index (diameter^2 × height) was significantly greater on brown mine soils (3853 cm^3) than on gray mine soils (407 cm^3). In a greenhouse study, Showalter et al. (2010) attributed better tree performance on brown sandstone overburden to lower pH and a higher percentage of fine soil material (<2 mm).

As a consequence to coal mining, many surface-mined sites lack sufficient organic matter to support optimum soil function (Bendfeldt et al., 2001). Several studies have shown that mine soils exhibit limited nitrogen and phosphorus availability, micronutrient imbalances, high electrical conductivity, and low water holding capacity (Daniels and Zipper, 1988; Torbert et al., 1989, 1988), all of which are influenced by the low amount of organic matter in these soils.

The application of soil amendments to reclaimed surface mines can improve tree growth by alleviating the problems mentioned above. Bark mulch helps to deter erosion, provides soil nutrients, protects tree seeds and seedlings, and helps retain moisture for plant uptake (Conrad et al., 2008). Angel et al. (2006) found the addition of organic soil supplements (hardwood bark mulch and composted straw and manure) to a shale and sandstone topsoil substitute improved tree growth by adding nutrients to the soil. Showalter et al. (2010) found the addition of forest topsoil to unweathered shale topsoil substitute improved the growth of native hardwood trees. It was reported that the addition of forest topsoil significantly increased mineralizable nitrogen from 0.35 to 4.24 mg kg^{-1} compared with non-amended unweathered shale. In addition to providing soil nutrients, the application of soil amendments such as bark mulch to mine soils may reduce levels of iron or other heavy metals by forming metal complexes with the organic matter (Harman et al., 2007).

Past research involving tree growth on mined lands primarily focused on the physical and chemical properties of mine soils which affect tree growth and development. Often these studies focused on compaction, electrical conductivity, pH, and available nutrients (Rodrigue and Burger, 2004; Emerson et al., 2009; Conrad et al., 2008). Only a few studies have been conducted which examine mine soil nutrient concentrations and the foliar nutrient concentrations in trees grown on the reclaimed mine sites. Torbert et al. (1990) found nutrient availability in the soil varied with pH of overburden materials, which influenced the overall tree volume of pitch × loblolly hybrid pine (*Pinus × rigitaeda*). They reported that mine soil pH had the greatest effect on available manganese. Manganese availability decreased as soil pH increased, resulting in low concentrations in the soil and foliage. This deficiency directly affected tree volume (Torbert et al., 1990). Showalter et al. (2007) found a correlation between nutrient availability in mine soil and foliar nutrient concentration of white oak (*Quercus alba* L.). The researchers reported that mine soil nitrogen levels were deficient, consequently resulting in reduced foliar nitrogen levels. Foliar nitrogen concentrations found in the mine soil were significantly lower than foliar nitrogen concentrations of white oak from a nearby native Appalachian hardwood forest.

The objectives of this study were to determine the effects of topsoil substitute (brown vs. gray sandstone topsoil substitutes) and amendment (bark mulch vs. no bark mulch) on nutrient concentrations in soil and leaves of three deciduous hardwood tree species at the Birch River mine in Webster County, West Virginia. We compared these soil and foliar nutrient concentrations in mine soils to trees growing in a nearby native Appalachian forest and to foliar nutrient concentrations in the literature.

2. Methods

The location of this study was Arch Coal's Birch River mine (approximately 1620 ha) located near Cowen in Webster County, West Virginia (38° 26′ 31.4154″ N 080° 36′ 39.9594″ W). In November 2006, a 2.8-ha experimental plot was established using two different topsoil substitutes. Half of the plot was constructed with approximately 1.5 m of weathered brown sandstone and the other half with approximately 1.5 m of unweathered gray sandstone. Measures were taken to limit compaction by allowing only one or two passes of the bulldozer to level the area, which resulted in a 1.2-m depth of roughly graded material throughout the plot. The following spring, a 15-cm layer of hardwood bark mulch was applied to an area over the top of both mine soil types. The hardwood bark was obtained from a local sawmill which had accumulated at the log landing. The material included soil, bark and other woody debris, and ground up limestone (added as aggregate for traction), all of which was scraped up and hauled to the mine site. Seedlings (2/0 bare root) of twelve tree species were then planted on 2.4-m centers by a professional planting crew for a stocking rate of about 1450 trees per ha. The tree seedlings were purchased from commercial growers. Four topsoil substitute treatments were used in this study: Brown mine soil, Brown mine soil with bark mulch, Gray mine soil, and Gray mine soil with bark mulch (B, BM, G, and GM). A native Appalachian hardwood forest (FOR) located within the permitted boundaries of the Birch River mine was used as a control site for collection of soil and foliar samples for nutrient analyses (38° 25′ 22.48″ N 080° 40′ 04.44″ W). Fig. 1 illustrates the location of the forest in relation to the experimental plot. The predominant soil type in the forested area sampled is Dekalb channery sandy loam (loamy-skeletal, mixed, mesic Typic Dystrochrepts) with naturally low fertility and extremely acid to strongly acid. However, the potential productivity for trees on this soil is considered moderately high (Carpenter, 1992).

Black cherry (*Prunus serotina* Ehrh.), tulip-poplar (*Liriodendron tulipifera* L.), and red oak (*Quercus rubra* L.) were three of the twelve

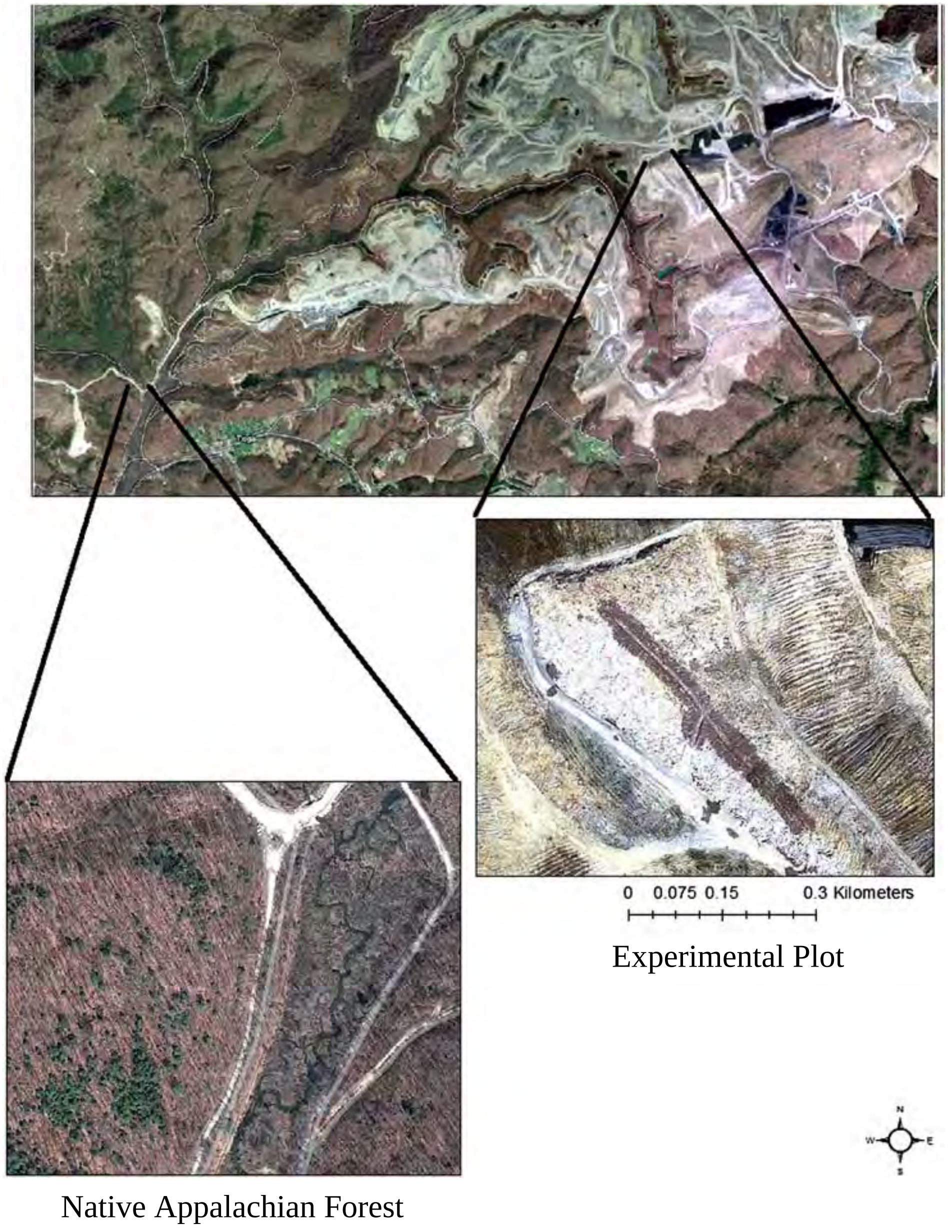

Fig. 1. Aerial view of Arch Coal's Birch River mine with close-up views of the experimental plot and the native Appalachian forest in Webster County, WV (Google Maps, 2013).

species planted in 2007, so the trees were six years old when sampled and they varied in height from 1 to 5 m. Tree growth was determined by a tree volume index (diameter^2 × height) (DeLong, 2010; Wilson-Kokes et al., 2013). These three species were selected for this foliar nutrient study due to their importance within the forest ecosystem and their commercial value. Three individuals of each species were randomly selected in each topsoil treatment (Brown mine soil with and without bark mulch, and Gray mine soil with and without bark mulch). In July, a minimum of ten leaves were collected from the mid-section of the current season's terminal shoot growth from the upper portion of the crown. Two leaves from each terminal shoot were sampled.

Three individuals of each species were also randomly selected in a nearby native forest for comparison. The stand was an intact, 40-year-old forest composed primarily of maple (*Acer spp.*), black cherry, tulip-poplar, several oak species, black locust (*Robinia pseudoacacia* L.), and some hickories (*Carya spp.*) and beech (*Fagus grandifolia* Ehrh.). For these larger native forest trees, canopy shooting was used to collect leaves from the three species also in July. We were careful to sample the current season's growth. Foliage samples were used for analyzing foliar nutrient concentrations.

The harvested leaves were oven-dried at 65 °C for 24-h. Dry foliage was ground with a Capresso Cool Grind Blade coffee grinder to pass a 1-mm sieve. Precisely 0.50 g of foliage were digested overnight in 10 mL concentrated HNO_3, followed by microwave assisted acid digestion (Showalter et al., 2010). Digests were diluted to 50 mL with DDI water and filtered through Whatman No. 42 filter paper. Potassium, calcium, magnesium, manganese, phosphorus, aluminum, and iron were determined using a Perkin Elmer Optima DV 2100 emission spectrophotometer (Perkin Elmer Corp., Norwalk, CT). Peach leaf standards from the National Institute of Standards and Technology (SRM 1547) were digested along with blank samples for control comparison.

Soil samples were collected to a depth of 15 cm and within a 50-cm radius from the base of each tree. On mulched sites, much of the organic material had decomposed and moved downward into the mine soil. If any of the thin layer of organic matter was still present, it was scraped away and the soil beneath was sampled. Soil samples were air dried and sieved to pass a 2-mm screen. The fine soil fraction was used for measuring pH and extractable nutrients. Soil pH was determined using 5 g of soil with 5 mL of DDI water with a Fisher Scientific Accumet pH meter model 915 (Thermo Fisher Scientific Inc., Pittsburgh, PA). Extractable nutrients were determined using a Mehlich 1 extracting solution (0.025 N H_2SO_4 + 0.05 N HCl). The extracted solution was analyzed for potassium, calcium, magnesium, manganese, phosphorus, iron, and aluminum using a Perkin Elmer Optima DV 2100 emission spectrophotometer (Perkin Elmer Corp., Norwalk, CT).

A one-way ANOVA was used to analyze soil and foliar nutrient concentrations for each species. Since there are inherent differences in nutrient concentrations in leaves among species (McJannet et al., 1995; Mellert and Gottlein, 2012; Ricklefs and Matthew, 1982), ANOVA was performed on each species across treatments to minimize the species effect. A Tukey's HSD test was used to determine significant differences at a level of $p < 0.05$. All statistical analyses were conducted using the R language (R Development Core Team, 2013).

3. Results and discussion

Average tree volume index increased from 2007 to 2012 by 30 times on the Gray mine soil to 300 times on the other mine soils (Table 1). Clearly, tree volume indices in the Brown, and the Brown and Gray with bark amendment were substantially greater than that in the Gray mine soil.

3.1. Black cherry

Foliar and soil phosphorus concentrations were significantly lower on all four mine soils compared with those found in the native forest (FOR) (Table 2). Among the four mine soils, foliar phosphorus concentrations were significantly greater on Brown (2145 mg kg^{-1}) versus Gray (888 mg kg^{-1}). Extractable soil phosphorus on Gray mine soil was low because the soil fines fraction was also low (40% compared to 60% on Brown; Wilson-Kokes et al., 2013), causing less phosphorus to be available to plants (Bolland et al., 2003). Similar studies have reported deficiencies of foliar phosphorus in hardwood species which limited tree growth (Showalter et al., 2010; Andrews et al., 1998; Torbert et al., 1988). Mulch further decreased the phosphorus concentrations in both Brown and Gray mine soils probably due to organic matter adsorbing extractable phosphorus or to microbial uptake of available phosphorus for organic matter decomposition.

Foliar potassium concentrations of black cherry in Gray mine soil were significantly lower (10,659 mg kg^{-1}) than foliar potassium concentrations (20,621 mg kg^{-1}) in FOR (Table 2). The Gray mine soil also had the lowest soil potassium levels at 47 mg kg^{-1} (Table 2). Low levels of potassium in Gray mine soil may be due to low levels of potassium initially available as well as subsequent leaching of available potassium or plant uptake (Bradshaw, 1997). Potassium deficiencies are not commonly reported in mine soil studies in the Appalachian region, however Showalter et al. (2010) found that foliar potassium concentrations were below literature-based values for white ash (*Fraxinus americana* L.) grown on weathered and unweathered sandstone overburden at a surface mine in West Virginia.

Foliar calcium concentrations in mine soils were above the mean foliar calcium concentration in FOR (7063 mg kg^{-1}), with the exception of the Brown Mulch treatment (Table 2). It is unknown why foliar concentrations were so low on Brown Mulch when soil calcium concentrations were high (9000 mg kg^{-1}) and soil pH (7.8) was suitable for plant-availability of this nutrient (Table 2). Although the mean foliar calcium concentrations in the four mine soils were not significantly different, each treatment had a wide range of values (supplemental material in Appendix A).

Foliar magnesium concentrations were not significantly different across soil treatments ranging from 2052 to 4175 mg kg^{-1}. However, the highest magnesium concentrations were on Brown Mulch and Gray (Table 2). Low foliar magnesium on Brown mine soil corresponded to the low magnesium levels in the soil which are most likely due to the strongly acidic pH value of 4.5 measured in this soil.

Mean foliar aluminum concentrations ranged from 59 mg kg^{-1} on Brown Mulch to 152 mg kg^{-1} on Brown (Table 1). The highest values were on Brown and FOR, which also had the lowest soil pH values that resulted in the highest soil aluminum values (Table 2). Currently, no literature is available which gives the concentration at which aluminum becomes toxic to black cherry growth. Henry (1973) reported that black cherry requires an average of 32 mg kg^{-1} of aluminum for healthy growth, a value that all soil types exceeded in this study. Schaedle et al. (1988) described black cherry as highly resistant to aluminum toxicity. However, without literature-based values it is uncertain if the measured

Table 1
Mean tree volume index (cm^3) of three species after the first year and the sixth year of growth on four mine soils. Data from DeLong (2010) and Wilson-Kokes et al. (2013).

Tree Species	Soil type			
	G	B	GM	BM
Black Cherry				
2007	11[b*]	10[b]	18[a]	13[b]
2012	377[c]	7380[a]	6988[a]	2344[b]
Red oak				
2007	11[b]	12[b]	20[a]	15[ab]
2012	361[c]	3612[a]	3503[a]	2440[b]
Tulip-poplar				
2007	20[ab]	25[a]	33[a]	15
2012	605[c]	4948[a]	3001[ab]	1981[b]

*Means for each volume index for each year within species with the same letter are not significantly different at $p < 0.05$. Means with no letters signify no significant difference. Tree volume index in cm^3 was calculated as $diameter^2 \times height$ (Emerson et al., 2009).

Table 2
Mean foliar nutrient concentrations of black cherry and mean soil pH and nutrient concentrations around black cherry trees in five soil types.

	Soil type				
	G	B	GM	BM	FOR
Foliar concentrations					
P (mg kg^{-1})	888[c*]	2145[ab]	1756[bc]	1065[c]	2798[a]
K (mg kg^{-1})	10,659[b]	14,980[ab]	15,893[ab]	14,982[ab]	20,621[a]
Ca (mg kg^{-1})	8755	8880	9230	6186	7063
Mg (mg kg^{-1})	4158	2052	3490	4175	3009
Al (mg kg^{-1})	105[ab]	152[a]	69[b]	59[b]	143[a]
Fe (mg kg^{-1})	83[ab]	97[a]	69[b]	61[b]	69[b]
Mn (mg kg^{-1})	66[b]	2051[a]	73[b]	259[b]	145[b]
Soil pH and concentrations					
pH (s.u)	7.4[a]	4.5[b]	7.8[a]	7.7[a]	4.7[b]
P (mg kg^{-1})	38[b]	80[b]	10[b]	15[b]	153[a]
K (mg kg^{-1})	47[c]	62[bc]	164[ab]	195[a]	164[ab]
Ca (mg kg^{-1})	1500[b]	660[b]	11,400[a]	9060[a]	1040[b]
Mg (mg kg^{-1})	468[ab]	132[b]	660[a]	696[a]	288[ab]
Al (mg kg^{-1})	45[b]	384[b]	12[b]	10[b]	1531[a]
Fe (mg kg^{-1})	98[ab]	97[ab]	9[b]	9[b]	158[a]
Mn (mg kg^{-1})	115	34	72	72	256

*Means for each foliar or soil property within rows with the same letter are not significantly different at $p < 0.05$. No letters signify no significant difference.

Table 3
Normal nutrient concentrations in leaves of three tree species from the literature. We use the term "normal" simply because these values were found in the literature.

Nutrient	Black cherry[a]	Red oak[b]	Tulip-poplar[b]
P (mg kg^{-1})	3500	1810	1780
K (mg kg^{-1})	10,900	7990	12,130
Ca (mg kg^{-1})	13,600	7520	18,320
Mg (mg kg^{-1})	3500	2240	3160

[a] Normal nutrient concentrations for black cherry are from Blinn and Bucker (1989).
[b] Normal nutrient concentrations for red oak and tulip-poplar are from a group of good growth populations from the literature compiled by van den Burg (1985) and Mellert and Gottlein (2012).

foliar aluminum concentrations on Brown mine soil and FOR were growth limiting.

Nutrient concentrations in tree leaves across species from the literature showed wide variation (Table 3). When comparing black cherry nutrient values in leaves for phosphorus, the values in trees in our soils were all lower than "Normal" values as reported by Blinn and Bucker (1989). Foliar phosphorus concentrations were 20% lower in the FOR soil and 75% lower in the Gray mine soil. Foliar potassium concentrations in trees growing on our soils were equal to and up to double the Normal amounts (Tables 2 and 3). Foliar calcium concentrations in black cherry trees in mine soils were about half the Normal concentrations, while magnesium concentrations were similar to Normal concentrations.

3.2. Red oak

Foliar phosphorus concentrations in Gray mine soil showed less than half than that available in FOR (Table 4). Almost all mine soils were significantly different from one another with regards to foliar phosphorus levels, and the Gray Mulch treatment had the highest concentration at 1583 mg kg^{-1} compared to 621 mg kg^{-1} on Gray alone (Table 4). In a greenhouse study, Showalter et al. (2010) reported similar findings for red oak with foliar phosphorus concentrations being low on four soil types (forest topsoil, weathered sandstone, unweathered sandstone, and unweathered shale). The authors reported that those levels were strongly correlated with poor tree growth suggesting that phosphorus was a growth limiting factor on those mine soils (Showalter et al., 2010). For this study, soil phosphorus concentrations were very low in the mine soils varying from 6 to 50 mg kg^{-1} and greatest in FOR at 652 mg kg^{-1}. But the amounts found in leaves did not correlate well with the phosphorus levels in soils (Table 4). The low phosphorus concentration in FOR leaves even while having high extractable phosphorus in the soil may be due to extremely high concentrations of soil aluminum at 2122 mg kg^{-1} and a soil pH of 3.7. At pH less than 5.8, phosphorus can react with aluminum and iron to produce insoluble aluminum and iron phosphates (Abaye et al., 2006).

Foliar potassium concentrations in red oak were the lowest (6083 mg kg^{-1}) on Gray mine soil, which mirrored the low soil potassium levels at 53 mg kg^{-1} (Table 4). Red oak growing in mulch treatments had significantly higher foliar potassium concentrations than no mulch treatments (Table 4). Showalter et al. (2010) reported in a greenhouse study that foliar potassium concentrations in red oak grown on unweathered sandstone (5900 mg kg^{-1}) were below literature-based norms of 8000 mg kg^{-1}.

Foliar calcium and magnesium concentrations were significantly greater on mulch treatments than in FOR and Brown alone (Table 4). The FOR soils and Brown mine soil also had the lowest mean soil calcium and soil magnesium concentrations compared to the Gray mine soil, Gray Mulch, and Brown Mulch (Table 4). These high calcium values in the mulch treatments were largely due to the limestone added at the log landing for traction and which was incorporated into the sawmill bark mulch. Mean pH values on FOR and Brown mine soil were very strongly to extremely acidic at 3.7 and 4.5, respectively (Table 3). On acidic soils, calcium and magnesium are generally found in lower abundance and therefore are less plant-available (Abaye et al., 2006). When calcium is deficient, the rooting system is negatively affected thereby making the roots shorter and denser, and making plants more susceptible to aluminum toxicity on very acidic soils (Abaye et al., 2006; Brady and Weil, 2002).

There were no significant differences among mine soils for red oak foliar aluminum concentrations, even though there was a wide difference among soil aluminum concentrations (Table 4). However, the range of foliar aluminum concentrations in FOR included samples with values up to 172 mg kg^{-1}.

Normal foliar concentrations of phosphorus in red oak (1810 mg kg^{-1}) were higher than those found in red oak leaves growing in our soils (621 to 1583 mg kg^{-1}). All other nutrients for which we have data (potassium, calcium, and magnesium) were similar between the Normal concentrations and those found in tree leaves in our study.

3.3. Tulip-poplar

As with the previous two tree species, foliar phosphorus levels were significantly lower in tulip-poplar growing on the mine soils than in FOR soil (Table 5). Tulip-poplar trees growing in FOR contained a mean foliar phosphorus concentration of 2356 mg kg^{-1} compared to mean concentrations less than 1600 mg kg^{-1} in the mine soils (Table 5). In a greenhouse study, Showalter et al. (2010) reported deficient foliar phosphorus concentrations in tulip-poplar grown in forest topsoil, weathered sandstone, and unweathered sandstone. Mean values ranged from 680 mg kg^{-1} in unweathered sandstone to 980 mg kg^{-1} in weathered sandstone, which were generally lower than those found in our study. Although the mean foliar phosphorus concentrations in the four mine soils were not significantly different, each treatment had a wide range

Table 4
Mean foliar nutrient concentrations of red oak and mean soil pH and nutrient concentrations around red oak trees in five soil types.

	Soil type				
	G	B	GM	BM	FOR
Foliar concentrations					
P (mg kg^{-1})	621^{d*}	1393^{ab}	1583^{a}	923^{c}	1266^{b}
K (mg kg^{-1})	6083^{c}	8528^{b}	10,591^{a}	11,535^{a}	9529^{ab}
Ca (mg kg^{-1})	7879^{b}	6591^{bc}	11,356^{a}	11,760^{a}	5281^{c}
Mg (mg kg^{-1})	5740^{a}	1960^{cd}	2446^{c}	3577^{b}	1331^{d}
Al (mg kg^{-1})	108	138	94	100	99
Fe (mg kg^{-1})	96	108	122	119	109
Mn (mg kg^{-1})	275^{b}	4714^{a}	624^{b}	771^{b}	740^{b}
Soil pH and concentrations					
pH (s.u.)	7.3^{a*}	4.5^{b}	7.7^{a}	7.7^{a}	3.7^{c}
P (mg kg^{-1})	50^{b}	6^{b}	7^{b}	16^{b}	652^{a}
K (mg kg^{-1})	52^{b}	58^{b}	128^{a}	123^{a}	99^{ab}
Ca (mg kg^{-1})	1960^{b}	260^{b}	14,800^{a}	11,060^{a}	240^{b}
Mg (mg kg^{-1})	432^{b}	204^{b}	828^{a}	936^{a}	77^{c}
Al (mg kg^{-1})	45^{c}	212^{b}	45^{c}	59^{c}	2122^{a}
Fe (mg kg^{-1})	131^{b}	67^{c}	5^{d}	49^{c}	461^{a}
Mn (mg kg^{-1})	106	32	119	159	36

*Means for each property within rows with the same letter are not significantly different at $p < 0.05$. No letters signify no significant difference.

Table 5
Mean foliar nutrient concentrations of tulip-poplar and mean soil nutrient concentrations around tulip-poplar trees in five soil types.

	Soil type				
	G	B	GM	BM	FOR
Foliar concentration					
P (mg kg^{-1})	927^{b*}	1102^{b}	1552^{b}	1173^{b}	2356^{a}
K (mg kg^{-1})	10,285^{b}	11,382^{b}	13,909^{ab}	14,650^{ab}	21,251^{a}
Ca (mg kg^{-1})	12,505^{a}	7010^{bc}	12,941^{a}	9581^{ab}	5548^{c}
Mg (mg kg^{-1})	8596^{a}	7058^{a}	3909^{b}	3268^{b}	2076^{b}
Al (mg kg^{-1})	64^{c}	313^{b}	100^{c}	53^{c}	404^{a}
Fe (mg kg^{-1})	94	79	83	74	85
Mn (mg kg^{-1})	49^{c}	1098^{a}	113^{c}	76^{c}	444^{b}
Soil pH and concentrations					
pH	7.1^{a*}	4.9^{b}	7.8^{a}	7.7^{a}	3.8^{c}
P (mg kg^{-1})	31^{b}	7^{b}	10^{b}	11^{b}	528^{a}
K (mg kg^{-1})	55^{b}	82^{b}	173^{a}	138^{a}	90^{b}
Ca (mg kg^{-1})	1400^{c}	540^{c}	13,460^{a}	16,300^{a}	160^{c}
Mg (mg kg^{-1})	396^{b}	432^{b}	732^{a}	648^{a}	60^{c}
Al (mg kg^{-1})	38^{c}	274^{b}	49^{c}	35^{c}	2179^{a}
Fe (mg kg^{-1})	87^{b}	80^{b}	8^{c}	11^{c}	442^{a}
Mn (mg kg^{-1})	99^{a}	62^{b}	53^{b}	67^{b}	15^{c}

*Means for each property within rows with the same letter are not significantly different at $p < 0.05$. No letters signify no significant difference.

of values (supplemental material in Appendix A). As expected, the soil phosphorus concentrations in tulip-poplar were significantly higher in FOR than in the four mine soils (Table 5).

Foliar potassium concentrations of tulip-poplar in Gray and Brown mine soils were significantly lower than in FOR (Table 5). The Gray and Brown mine soils also had the lowest soil potassium levels (Table 5). Showalter et al. (2010) reported that foliar potassium concentrations in tulip-poplar grown on weathered and unweathered sandstone were below literature-based norms; 5810 mg kg^{-1} on weathered sandstone and 4400 mg kg^{-1} on unweathered sandstone, both of which were far below the values we found in our study with tulip-poplar.

Foliar calcium concentrations in tulip-poplar were the highest in Gray, Gray Mulch, and Brown Mulch mine soils. Tulip-poplar is a calcium-demanding species which requires high levels of calcium for adequate growth (Table 3; Craul, 1992; Adams et al., 2006), and the high levels in these mine soils supplied the high calcium demands of tulip-poplar (Table 5). Not surprisingly, foliar calcium concentrations were the lowest where soil and foliar aluminum concentrations were the highest, i.e., in Brown and FOR soils (Table 5). Other studies dealing with foliar nutrient status in native hardwood species reported decreased foliar calcium concentrations with increases in foliar aluminum concentrations on acidic forest soils (White et al., 1999; Adams et al., 2006).

For tulip-poplar, foliar magnesium concentrations were significantly higher in the Gray and Brown mine soils, and more than double that found in trees in the corresponding Mulch treatments and FOR (Table 4). Soil magnesium concentrations were also the lowest in FOR (60 mg kg^{-1}) compared to the four mine soils, which ranged from 396 to 732 mg kg^{-1} (Table 5). The native forest soil may contain little magnesium due to its highly weathered nature and low pH.

Foliar aluminum concentrations of tulip-poplar in Brown mine soil and FOR soils were significantly higher than Gray, Gray Mulch, and Brown Mulch (Table 5). Brown mine soil and FOR soils once again contained the highest mean soil aluminum concentrations at 274 mg kg^{-1} and 2179 mg kg^{-1} and the lowest soil pH values at 4.9 and 3.8, respectively (Table 5). Aluminum may be forming humic substance-metal complexes in the mulch treatments which could reduce the concentration of exchangeable aluminum (Thomas, 1975) and thereby reduce deleterious effects on plant growth due to high levels of aluminum.

Foliar phosphorus concentrations in the mine soils for tulip-poplar were all lower (<1500 mg kg^{-1}) than Normal phosphorus concentrations (1780 mg kg^{-1}; Table 3) listed for this species. Foliar concentrations in tulip-poplar in FOR were above the Normal range, which is the first time this occurred for any of the three species. Foliar potassium concentrations in the mine soils were close to the Normal concentration of 12,130 mg kg^{-1}, while the concentrations in FOR were much higher at 21,251 mg kg^{-1} (Tables 3 and 5). Foliar calcium concentrations in the mine soils were all lower than the Normal concentration of 18,320 mg kg^{-1}. Magnesium showed wide variation in foliar concentrations on the mine soils, but in general these concentrations were higher than Normal magnesium foliar concentrations for tulip-poplar.

Bulk density of the soils is an additional factor that probably influenced the differences in foliar nutrient concentrations between mine soils and the FOR soil. In a companion study at another site with similar mine soil and FOR treatments, bulk density of the mine soils ranged from 1.6 to 1.8 Mg m^{-3}, while the FOR soil was 1.1 Mg m^{-3} (DeLong et al., 2012). If these mine soils were similarly high in bulk density, root expansion could be diminished thereby reducing the chances for obtaining nutrients. Water holding capacity and water movement in the soil may have also hindered nutrient uptake by trees. Therefore, the bulk density differences between the mine soils and the FOR soil could have been an important controlling factor to foliar nutrient concentrations than the actual nutrient concentration in the soil and their availability and movement.

4. Conclusions

This study found that foliar phosphorus concentrations were significantly lower in all three tree species growing in the four mine soils compared to trees growing in the native forest soil. Mine soils are known to have phosphorus deficiencies and even when phosphorus is present in soil solution it tends to sorb to fine soil particles or organic matter (mulch treatments) rendering it unavailable to plants. Further, if aluminum and iron are in high concentrations, as we found in the Brown mine soil and FOR soil, phosphorus can also be bound by these elements. Foliar potassium concentrations were consistently low on the Gray mine soil for all three tree species and soil potassium concentrations were always lowest on Gray mine soil. Foliar calcium and magnesium concentrations were variable depending on tree species and soil type; abundant for some and low for others. Foliar aluminum concentrations were consistently higher on Brown mine soil and FOR soil for all tree species. Foliar and soil nutrient concentrations in Brown mine soils were similar to values measured in FOR, as might be expected since the Brown mine soil was partially composed of FOR native soils and subsoils. Mulch treatments supplied potassium and magnesium for all three tree species comparable to FOR and significantly reduced foliar uptake of aluminum for black cherry. Gray mine soil displayed low concentrations of several nutrients, which may be indicative of nutrient deficiencies and slow release of nutrients, both of which would limit hardwood tree growth. Tree volume index was significantly lower on Gray mine soils compared to the other three. High bulk density and poor soil water availability on these rocky, coarse-textured mine soils may exacerbate these nutrient deficiencies.

Overall, this study showed that nutrient availability in mine soils for tree growth is usually low compared to concentrations found in native forest soils. We also found that the foliar concentrations of trees in this study were often lower than Normal foliar concentrations from the literature, especially for phosphorus. Calcium was also deficient for black cherry and tulip-poplar. However, organic soil amendments such as bark mulch can add nutrients and improve water holding capacity, but we also saw that mulch can bind up nutrients such as phosphorus and make them less available for plant uptake. Coal mine operators should work closely with foresters and soil scientists to ensure that adequate amounts of native topsoil or other organic matter-rich amendments are being replaced during reclamation and that fertilizer is applied to increase the amount of plant-available nutrients to ultimately re-establish a healthy, productive and sustainable forest ecosystem.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.02.015.

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