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Determinants of total and available phosphorus in forested Alfisols and Ultisols of the Ozark Highlands, USA

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ABSTRACT

Phosphorus is an important nutrient limiting forest growth in many parts of world, and soil P forms and concentrations may be associated with a host of soil and environmental attributes in a complex soil landscape. The objective of this study was to identify key environmental and soil properties influencing total and available soil P concentrations in a mixed oak (*Quercus* L.)–hickory (*Carya* Nutt.) forest ecosystem. Soil samples and soil characterization data were obtained from fifty pedons sampled at the Missouri Ozark Forest Ecosystem Project (MOFEP) located in south-central Missouri, USA. Additional soil chemical analyses were conducted to measure total P, available P (Mehlich-3 P and Bray-1 P), and citrate bicarbonate dithionite (CBD) extractable Fe, Al, and Mn content. Classification and regression tree (CART) analysis was applied to explain relationships between P concentrations and environmental and soil properties. Total P concentration in the soils studied ranged from 15.6 to 410 mg kg^{-1} and the range of available P concentration was 0.29 to 30.6 mg kg^{-1}. The CART analysis identified variables, primarily soil attributes, explaining 48, 71, and 65% of the variability associated with total P, Mehlich-3 P, and Bray-1 P concentrations, respectively. Extractable Mn was the most important explanatory variable in all CART models (explaining 28–33% of soil P variation). The CART analysis provided a concise framework for coupling soil and environmental variables to understand and identify locations within a complex soil landscape that may be susceptible for nutrient depletion. Furthermore, findings of this research highlight a need to more thoroughly evaluate relationships between Mn and P forms and concentrations in soil.

1. Introduction

Relative to other macronutrients, phosphorus concentration in soil is considerably less, particularly in subsurface soil horizons (Tisdale et al., 1985; Jobbágy and Jackson, 2001). Although tree species have evolved to compensate for P deficits, overall P available for plant growth (available P) in forest soils is low and often limiting to forest growth in many parts of the world (Pritchett and Comerford, 1982; Comerford et al., 2002; Vance et al., 2003; Fox et al., 2007; Trichet et al., 2009).

A wide variety of soil factors influence P concentrations in the soil landscape (Johnson and Cole, 1980; Sollins et al., 1988; Negassa and Leinweber, 2009). Most soil P (35–70% of total P) is inorganic and bonded to metal oxides in acidic and highly weathered soils (Harrison, 1987; Pierzynski et al., 2005), and strong P adsorption and retention by metal oxides may render P less available for plant uptake (Jugsujinda et al., 1995; Arai and Sparks, 2001; Luengo et al., 2006; Mustafa et al., 2008). Mineral particle size and pH are also important regulators of soil P availability and concentration (Pierzynski et al., 2005; Oelkers and Valsami-Jones, 2008). Organic P compounds represent 30 to 65% of total soil P, resulting in soil organic matter as an additional determinant of soil P (Harrison, 1987; Turner and Engelbrecht, 2011).

With respect to environmental factors, the lithology of geologic strata underlying a soil can influence soil P concentrations and bioavailability as geochemical weathering results in the dissolution of phosphorus-bearing minerals and P release into the soil environment (Smeck, 1985; Witkowski and Mitchell, 1987; Kitayama et al., 2000). However, the relationship between lithology and soil P can be confounded by changes in P concentrations and availability through weathering processes, as well as the influence of lithology on secondary mineral formation (Crews et al., 1995; Chadwick et al., 1999; Vitousek et al., 2010). Slope position is a landscape factor influencing soil P, and concentration is often greatest at lower slope positions due to hydrologic flux (Smeck and Runge, 1971; Smeck, 1985; Day et al., 1987). Landform has also been identified as an important variable explaining soil P content (McKenzie and Ryan, 1999).

The Ozark Highlands in southern Missouri, USA are ecologically important due to extreme biological diversity and high endemism — approximately 160 species are unique and restricted to the region (USGS, 2009). Oak–hickory forests of the Ozark Highlands, growing predominantly on acidic, highly weathered soils derived from variety of parent

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materials (Hammer, 1997), are economically important to Missouri, USA. Geologic strata of the Missouri Ozarks consist of sedimentary rocks with reduced P concentrations (≤0.02% P_2O_5) relative to the Earth's continental crust (0.2%) (Connor and Shacklette, 1975; Rudnick and Fountain, 1995). Phosphorus concentrations in Ozark geologic strata are comparable to a quartz arenite formation underlying the P deficient fynbos biome of South Africa where parent material-based P limitations may occur (Soderberg and Compton, 2007; Vitousek et al., 2010). Due to reduced P concentrations in the geologic strata and advanced stages of soil weathering, there is great probability that P concentrations in Ozark Highland soils will, in general, be quite low and spatially variable. However, limited data are available to support this postulate (Hammer, 1997).

The influence of environmental properties (e.g., slope position, landform, and underlying lithology) and soil properties (e.g., pH, organic carbon content, extractable metal oxides, and clay content) on total and available P in the Missouri Ozark Highlands remains unclear, and it is difficult to ascertain the most important factors related to soil P in a complex soil landscape. While linear regression analyses are commonly used to evaluate relationships between dependent and independent environmental variables, use of parametric analyses can be hampered by the need to meet model assumptions of Gaussian distribution of predictor variables, limitations to the number of predictor variables that can be identified, and form of variance structure (Rothwell et al., 2008; Grunwald et al., 2009). To overcome these limitations, tree-based modeling has been advocated to quantify complex relationships between soil and environmental characteristics and implemented with varying degrees of success (McKenzie and Ryan, 1999; Barthold et al., 2008; Johnson et al., 2009a; Kabrick et al., 2011). The objective of this study was to identify key environmental and soil properties (Table 1) associated with total and available P concentrations in forested soils of the Ozark Highlands. Elucidating these relationships will help identify locations where soil P may limit forest productivity presently or in the future and improve sustainable forest management initiatives.

Table 1
Response and explanatory variables used in the Classification and Regression Tree (CART) analysis.

Response variables	Variable type
Total P (mg kg^{-1})	Continuous
Mehlich-3 P (mg kg^{-1})	Continuous
Bray-1 P (mg kg^{-1})	Continuous
Explanatory variables	**Variable type**
Horizon/depth	
1st mineral horizon	Categorical
1st Bt or Bw horizon	Categorical
Horizon at 100 cm depth	Categorical
Parent material	
Alluvium	Categorical
Hillslope sediments	Categorical
Hillslope sediments over residuum	Categorical
Bedrock formation	
Eminence	Categorical
Roubidoux	Categorical
Upper Gasconade	Categorical
Lower Gasconade	Categorical
Slope position	
Summit	Categorical
Shoulder	Categorical
Backslope	Categorical
Floodplain	Categorical
Landform	
Structural bench	Categorical
Ridge	Categorical
Hillslope	Categorical
Floodplain	Categorical
Ex Ca ($cmol_c$ kg^{-1}) [a]	Continuous
CEC ($cmol_c$ kg^{-1}) [b]	Continuous
pH_w [c]	Continuous
Clay content (g kg^{-1})	Continuous
TOC (g kg^{-1}) [d]	Continuous
CBD-Fe + Al (mg kg^{-1}) [e]	Continuous
CBD-Mn (mg kg^{-1}) [f]	Continuous

[a] Ex Ca, exchangeable calcium.
[b] CEC, cation exchange capacity.
[c] pH_w, pH in water (1:1 solution).
[d] TOC, total organic carbon.
[e] CBD-Fe + Al, citrate bicarbonate dithionite extractable iron plus aluminum.
[f] CBD-Mn, citrate bicarbonate dithionite extractable manganese.

2. Materials and methods

2.1. Site description

The Missouri Ozark Forest Ecosystem Project (MOFEP) located in south-central Missouri, USA, is a long term experimental project initiated by the Missouri Department of Conservation (MDC) in 1989 to comprehensively evaluate forest management practices on a wide array of upland ecosystem attributes (Brookshire et al., 1997). The study consists of nine sites ranging from 314 to 516 ha (Fig. 1). The MOFEP sites are within the Current River Forest Breaks and the Current River Oak–Pine Woodland Hills land type associations of the Ozark Highlands (Nigh and Schroeder, 2002). The Current River Oak Forest Breaks have narrow ridges and steep relief ranging from 90 to 140 m; whereas, the Current River Oak–Pine Woodland Hills have broad ridges and relief less than 90 m (Meinert et al., 1997; Kabrick et al., 2000). Moving from ridges to lower points in the landscape, other major landforms of the region consist of hillslopes, structural benches (nearly level formations occurring on backslope positions that break slope continuity and are associated with the presence of underlying bedrock that is more resistant to weathering than overlying geologic strata), and floodplains (Kabrick et al., 2000). Slope positions on these landforms are described from higher elevations to lower elevations as a summit (apex of a landform), shoulder (convex portion of the slope and transition areas between summit and backslope), backslope (steep inclining slope that is nearly linear), footslope (concave portion of the slope that occurs to limited areal extent in the study region), and floodplain (Kabrick et al., 2000; Schoeneberger et al., 2012).

The forests at MOFEP, predominantly comprise oaks (*Quercus* spp.), shortleaf pine (*Pinus echinata* Mill.), and hickories (*Carya* spp.) (Kabrick, et al., 2004), are managed according to MDC's Forest Land Management Guidelines (MDC, 1986). These forests are part of the Central Hardwood Forest Region of the United States which consists of approximately 44.5 million hectares of forested land (Johnson et al., 2009b). Globally, temperate broadleaf and mixed broadleaf–coniferous forests cover 7.5 million km^2 (Groombridge and Jenkins, 2002).

Geology of the area consists of the Roubidoux, Gasconade (each Ordovician age), and Eminence (Cambrian age) sedimentary rock formations (Thompson, 1995). The Roubidoux formation consists of interstratified sandstone, dolomite, and silicified stromatolite algal and chert beds. The Gasconade formation comprises coarsely and finely crystalline dolomite with varying quantities of chert. The upper portion of the Gasconade formation comprises coarsely crystalline dolomite interbedded with chert and layers of silicified stromatolites; whereas, the lower portion of the Gasconade formation comprises finely-crystalline dolomite interbedded with a few chert nodules and a 1- to 3-m thick sandstone and quartzose at its base (Gunter sandstone member) that is associated with the formation of structural benches. The Eminence formation is dominated by coarsely crystalline dolomite with occasional occurrence of interbedded cherts (Meinert et al., 1997; Kabrick et al., 2011). Connor and Shacklette (1975) reported a 0.010% P_2O_5 content in sandstone from the Roubidoux formation; whereas, P_2O_5 contents in carbonate residuum overlying the Roubidoux and Gasconade formations were found to be 0.017 and 0.019%, respectively.

The most common soil orders in the region consist of Alfisols and Ultisols (FAO soil classification: Luvisols and Acrisols) with low cation

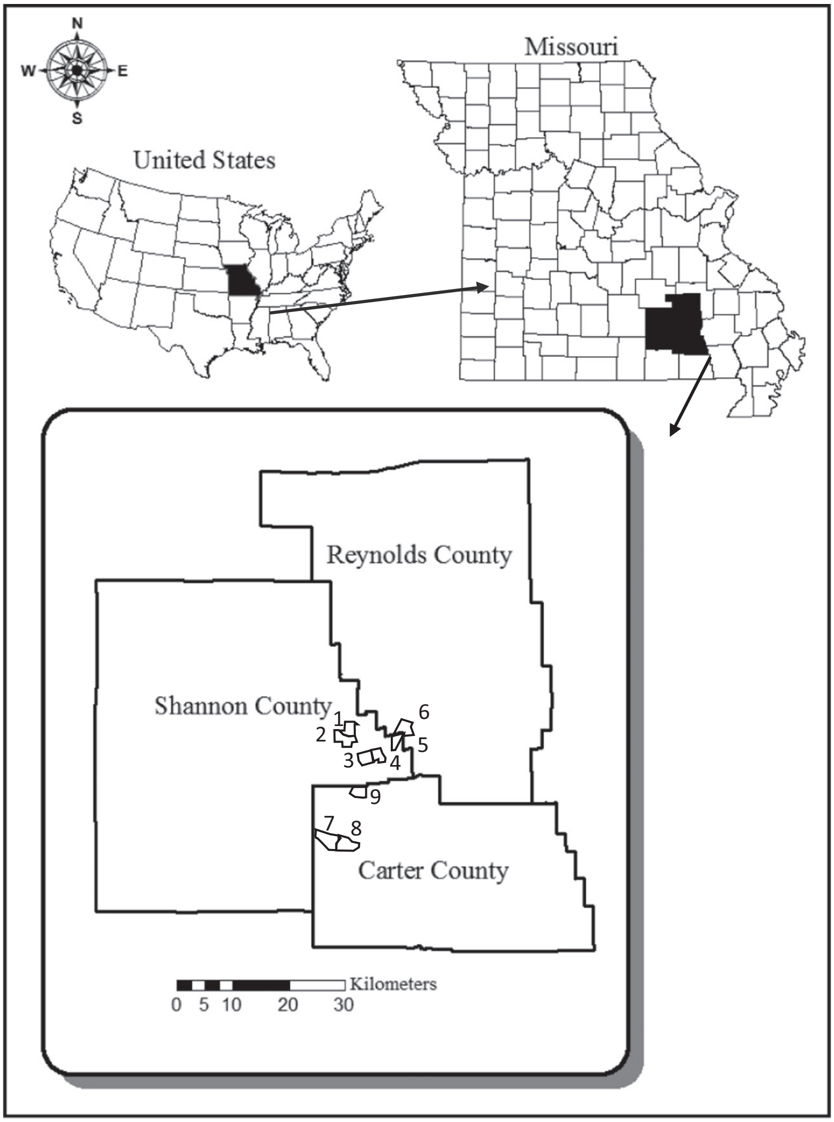

Fig. 1. Location of the nine Missouri Ozark Forest Ecosystem Project (MOFEP) sites. Samples were collected in sites 2–5 and 7 during the project establishment phase.

exchange capacity (CEC), low to moderate base saturation (BS), and relatively low to moderate concentrations of exchangeable calcium and magnesium (Meinert et al., 1997; Kabrick et al., 2011). Within the contiguous United States, Alfisols and Ultisols represent 19.9 and 15.5%, respectively, of forested lands (2.7 million km^2; Johnson and Kern, 2002), and globally there are approximately 11.7 million km^2 of forests and woodlands growing on these two soil orders (Bouwman, 1990).

Soils at the study site were formed from a variety of parent materials (e.g., residuum, alluvium, loess, and hillslope sediments — thin deposits on slopes emplaced by gravity and water from elevated landscape positions) and often times multiple parent materials (Daniels and Hammer, 1992; Hammer, 1997). Due to millennia of erosional processes dissecting the Ozark Highlands Plateau, hillslope sediments largely cover summit, shoulder, and backslope positions. However, in these same slope positions, a thinner mantle of hillslope sediments may result in soils forming from hillslope sediments overlying residuum. Alluvium is confined to narrow floodplains within the dissected landscape (Meinert et al., 1997; Kabrick et al., 2000).

Loamy-skeletal and fine-loamy Ultisols are generally associated with hillslope sediments; whereas, Alfisols with loamy-skeletal over clayey particle size class are more common to soils weathered from hillslope sediments over residuum. Fragipans are common to stable slope positions, resulting the in the presence of Fragiudults and Fragiudalfs in summit and shoulder slope positions. In the absence of a fragipan, Paleudults and Paleudalfs are generally found on the stable slope positions. Paleudalfs are also common to backslope positions. Most floodplain soils are classified as Inceptisols (Cambisols) with a loamy-skeletal particle-size class. Siliceous and mixed mineralogies are prevalent in most soils, although soils with kaolinitic mineralogy are present in the landscape (Meinert et al., 1997; Kabrick et al., 2000).

2.2. Soil sampling and sample selection

Seventy-four pedons were excavated from five of the nine MOFEP sites (Sites 2–5 and 7) at initiation of the MOFEP project, and the pedons were associated with soil mapping units located on different geologic strata and slope positions (Meinert et al., 1997). A backhoe was used to excavate each pedon to a depth of 1.5 m and soil samples from each horizon were collected and analyzed at University of Missouri Soil Characterization Laboratory using techniques described in Burt (2004). Samples were analyzed for the following parameters and applicable methodology is provided in parentheses: particle size distribution (pipette method); exchangeable base cations Ca, Mg, Na, and K

(1 M NH_4OAc at pH 7); extractable acidity [0.5 M $BaCl_2$/0.2 M triethanol-amine (TEA) at pH 8.2 and back-titrated with 0.13 M HCl]; CEC (calculated by summation of cations exchanged in NH_4OAc at pH 7); total organic carbon content (Leco C analyzer; Leco Corp., St. Joseph, MI); and soil pH (1:1 solid to solution ratio in water and 1:2 solid to solution ratio in 0.01 M $CaCl_2$).

Fifty of the 74 originally sampled pedons were used in this research (Table 2). Selection of these pedons was determined by profile depth – only pedons with a depth >100 cm were selected for study – and the ability to locate archived samples. The decision to study only pedons with a depth >100 cm is predicated on our intent to study soils supporting oak–hickory forest growth where timber harvesting occurs and nutrient depletion is a concern. In this region soils that are shallow or variable in depth to bedrock support different types of ecological communities (e.g., glades and savannas) that are not managed for timber production. Three soil horizons from fifty pedons were selected for study: (1) first mineral horizon (50 A horizons); (2) first Bt horizon and where there was no Bt horizon the first Bw was selected (47 Bt and 3 Bw horizons); (3) and the soil horizon encountered at a depth of 100 cm (47 Bt horizons, 2 Bw horizons, and 1 C horizon). Based on field observations these horizons encompass the majority of soil volume utilized by plant roots. Using USDA-Natural Resources Conservation Service (NRCS) terminology to describe roots and abundance (Soil Survey Division Staff, 1993): A horizons are characterized as having

Table 2
Site characteristics and soil classification associated with the fifty pedons studied.
Adapted from Kabrick et al. (2011).

Bedrock formation[a]	Slope position[b]	Parent materials[c]	Drainage[d]	Depth[e]	Particle-size class	Mineralogy	USDA classification
Roubidoux	Summit	Hillslope sediments	MWD	Vdeep	Fine-loamy	Siliceous	Typic Fragiudults
Roubidoux	Summit	Hillslope sediments	MWD	Vdeep	Fine-loamy	Siliceous	Typic Fragiudults
Roubidoux	Summit	Hillslope sediments	MWD	Vdeep	Fine-loamy	Siliceous	Typic Fragiudults
Roubidoux	Summit	Hillslope sediments	MWD	Vdeep	Fine-loamy/clayey	Siliceous	Typic Paleudults
Roubidoux	Summit	Hillslope sediments	MWD	Vdeep	Loamy-skeletal	Siliceous	Typic Fragiudults
Roubidoux	Shoulder	Hillslope sediments	MWD	Vdeep	Loamy-skeletal	Siliceous	Typic Fragiudults
Roubidoux	Backslope	Hillslope sediments	WD	Deep	Loamy-skeletal	Siliceous	Typic Paleudults
Roubidoux	Floodplain	Alluvium	ED	Vdeep	Loamy-skeletal	Siliceous	Cumulic Hapludolls
Roubidoux	Floodplain	Alluvium	ED	Vdeep	Loamy-skeletal	Siliceous	Humic Dystrudepts
Roubidoux	Floodplain	Alluvium	ED	Vdeep	Loamy-skeletal	Siliceous	Humic Hapludults
Roubidoux	Floodplain	Alluvium	ED	Vdeep	Loamy-skeletal	Siliceous	Typic Dystrudepts
U. Gasc.	Summit	Hillslope sediments	WD	Vdeep	Fine-loamy	Siliceous	Typic Hapludalfs
U. Gasc.	Summit	Hillslope sediments	MWD	Vdeep	Fine-loamy	Siliceous	Oxyaquic Fragiudalfs
U. Gasc.	Summit	HS/residuum	MWD	Vdeep	Fine-loamy	Siliceous	Typic Fragiudalfs
U. Gasc.	Shoulder	Hillslope sediments	WD	Vdeep	Loamy-skeletal/clayey	Kaolinitic	Typic Paleudults
U. Gasc.	Shoulder	Hillslope sediments	WD	Vdeep	Loamy-skeletal/clayey	Siliceous	Typic Paleudults
U. Gasc.	Shoulder	Hillslope sediments	WD	Vdeep	Loamy-skeletal/clayey	Siliceous	Typic Paleudults
U. Gasc.	Shoulder	Hillslope sediments	MWD	Vdeep	Fine-loamy	Siliceous	Humic Fragiudults
U. Gasc.	Shoulder	Hillslope sediments	MWD	Vdeep	Loamy-skeletal	Siliceous	Humic Fragiudults
U. Gasc.	Shoulder	Hillslope sediments	MWD	Vdeep	Loamy-skeletal/clayey	Mixed	Typic Paleudalfs
U. Gasc.	Shoulder	Hillslope sediments	MWD	Vdeep	Loamy-skeletal/clayey	Siliceous	Fragic Paleudults
U. Gasc.	Backslope	Hillslope sediments	WD	Vdeep	Loamy-skeletal	Siliceous	Typic Paleudalfs
U. Gasc.	Footslope	Hillslope sediments	MWD	Vdeep	Fine-loamy	Siliceous	Fragic Hapludults
L. Gasc.	Summit	Hillslope sediments	WD	Vdeep	Clayey-skeletal	Mixed	Typic Paleudults
L. Gasc.	Summit	Hillslope sediments	MWD	Vdeep	Fine-loamy	Siliceous	Fragiaquic Paleudults
L. Gasc.	Summit	Hillslope sediments	MWD	Vdeep	Fine-silty	Siliceous	Typic Fragiudults
L. Gasc.	Summit	Hillslope sediments	MWD	Vdeep	Fine-silty	Siliceous	Typic Fragiudults
L. Gasc.	Summit	Hillslope sediments	MWD	Vdeep	Loamy-skeletal/clayey	Mixed	Typic Fragiudalfs
L. Gasc.	Summit	HS/residuum	WD	Vdeep	Loamy-skeletal	Siliceous	Typic Paleudalfs
L. Gasc.	Summit	HS/residuum	MWD	Vdeep	Fine-loamy	Siliceous	Oxyaquic Fragiudalfs
L. Gasc.	Summit	HS/residuum	MWD	Vdeep	Fine-silty	Siliceous	Oxyaquic Fragiudalfs
L. Gasc.	Summit	HS/residuum	MWD	Deep	Loamy-skeletal/clayey	Mixed	Typic Hapludalfs
L. Gasc.	Shoulder	Hillslope sediments	WD	Vdeep	Loamy-skeletal	Siliceous	Typic Paleudalfs
L. Gasc.	Shoulder	Hillslope sediments	WD	Vdeep	Loamy-skeletal	Siliceous	Typic Paleudults
L. Gasc.	Shoulder	Hillslope sediments	MWD	Vdeep	Loamy-skeletal/clayey	Siliceous	Typic Paleudults
L. Gasc.	Shoulder	HS/residuum	WD	Vdeep	Loamy-skeletal/clayey	Mixed	Typic Paleudalfs
L. Gasc.	Shoulder	HS/residuum	WD	Vdeep	Loamy-skeletal/clayey	Mixed	Typic Paleudalfs
L. Gasc.	Shoulder	HS/residuum	WD	Vdeep	Loamy-skeletal/clayey	Siliceous	Typic Paleudalfs
L. Gasc.	Shoulder	HS/residuum	WD	Vdeep	Loamy-skeletal	Siliceous	Typic Paleudalfs
L. Gasc.	Backslope	Hillslope sediments	WD	Vdeep	Loamy-skeletal/clayey	Mixed	Typic Paleudalfs
L. Gasc.	Backslope	Hillslope sediments	WD	Vdeep	Loamy-skeletal	Siliceous	Typic Paleudalfs
L. Gasc.	Backslope	HS/residuum	WD	Deep	Loamy-skeletal/clayey	Mixed	Typic Hapludalfs
Eminence	Backslope	Hillslope sediments	WD	Vdeep	Loamy-skeletal	Mixed	Typic Paleudalfs
Eminence	Backslope	Hillslope sediments	WD	Vdeep	Loamy-skeletal	Mixed	Typic Paleudults
Eminence	Backslope	HS/residuum	WD	Vdeep	Loamy-skeletal	Siliceous	Mollic Paleudalfs
Eminence	Backslope	HS/residuum	WD	Vdeep	Loamy-skeletal/clayey	Mixed	Mollic Paleudalfs
Eminence	Backslope	HS/residuum	WD	Vdeep	Loamy-skeletal/clayey	Mixed	Typic Paleudalfs
Eminence	Floodplain	Alluvium	ED	Vdeep	Loamy-skeletal	Siliceous	Dystric Eutrudepts
Eminence	Floodplain	Alluvium	ED	Vdeep	Loamy-skeletal	Siliceous	Ultic Hapludalfs
Eminence	Floodplain	Hillslope sediments	ED	Vdeep	Loamy-skeletal	Mixed	Cumulic Hapludolls

[a] U. Gasc., Upper Gasconade; L. Gasc., Lower Gasconade.
[b] Summits; broad ridges ≥ 60 m wide with slopes < 8%; shoulders, convex, slopes 8–20%; backslopes, slopes > 20% including sideslopes, noseslopes, and headslopes.
[c] HS/residuum, hillslope sediments overlying residuum.
[d] ED, excessively drained; WD, well drained; MWD; moderately-well drained.
[e] Deep, soil depth of 101 to 150 cm; Vdeep, very deep with soil depth >150 cm.

common to many fine, medium, and coarse roots; the first Bt and Bw horizons contain few to common amounts of fine and medium roots; and horizons occurring at a depth of 100 cm contain only few fine roots.

2.3. Soil analysis

To augment available soil chemical data for this study, archived samples were analyzed for total and available P and metal oxide content. Prior to storage, archived samples were sieved to <2 mm, air-dried, and stored in sealed containers. Soil samples selected for this research were highly variable in pH ranging from pH 4.4 to 7.2. Therefore, two different available P extraction methods were employed to quantify the amount of bioavailable P: Bray-1 and Mehlich-3 available P (Bray and Kurtz, 1945; Mehlich, 1984). Both of these P testing methods are applicable to and used in Missouri, USA (Frank et al., 2012; Nathan et al., 2012).

Samples were analyzed for total P ($HClO_4$–HNO_3 digestion) (Kuo, 1996), and citrate bicarbonate dithionite (CBD) extractable Fe, Al and Mn content (Loeppert and Inskee, 1996; Burt, 2004). Each analysis was conducted in duplicate for a given sample and the two values were averaged. When results differed by greater than 10% relative to the mean, a third replicate was analyzed, and the value exhibiting greater than 10% variability was excluded from dataset.

Phosphorus concentration obtained from all extractions was measured using a spectrophotometer (Spectronic Genesys 8, Spectronic Instruments; Garforth, England) at 880 nm using the ascorbic acid method described by Kuo (1996). Concentrations of CBD extractable Fe, Al, and Mn in extracts were measured using inductively coupled plasma (ICP) — atomic emission spectrophotometer (AES) (Varian Liberty RL; Mulgrave, Australia).

2.4. Data analysis

Due to complex geology, geomorphology, and high variability of soil properties in the Missouri Ozark Highlands, it was assumed that multiple factors may be required to explain variation in total and available P concentrations. A Classification and Regression Tree (CART) analysis was used to analyze the role of soil and environmental factors associated with concentrations of various P forms in the soils studied. Classification and regression tree modeling is a non-parametric, binary recursive partitioning technique that operates using top to bottom recursive partitioning and bottom up pruning, also called the cross-validation procedure (Breiman et al., 1984). The most important advantage of employing a CART analysis is the ability of the model to utilize skewed or multi-modal, numerical and categorical data with an ordinal or non-ordinal structure (Lewis, 2000). The CART model is also capable of handling missing data during regression tree development by treating missing responses as a special category (Clark and Pregibon, 1992).

In this research, measures of total P, Mehlich-3 available P, and Bray-1 available P concentrations (mg kg^{-1}) were used as continuous response variables for the construction of three different regression trees. Predictor variables used for investigating P forms included: (1) soil horizon/depth; (2) parent material; (3) underlying bedrock formation; (4) slope position; (5) landform; (6) exchangeable Ca; (7) CEC; (8) soil pH in water; (9) clay content; (10) total organic carbon (TOC) content; (11) CBD extractable Fe and Al oxide content; and (12) CBD extractable Mn oxide content (variables are further described in Table 1).

The CART analysis consisted of two basic steps: (1) recursive partitioning of the data to create a model relating a response variable to explanatory variables and (2) cross validation to determine the optimum model for depicting relationships between the explanatory variables and the response variable. During the first iteration of the partitioning process, the response variable of the data set is split into two mutually-exclusive groups or “nodes” using explanatory variables. This is done such that the variation of the two groups or nodes created by the splitting is minimized. To handle continuous data such as available P and total P, splitting was performed to maximize the deviance criteria: SST − (SSL + SSR), where SST is the sum of squares for the data and SSR and SSL are the sums of squares for the right and left nodes created by splitting of the data (Breiman et al., 1984). During successive iterations of the partitioning process, each of the two groups or nodes created during a previous iteration was further partitioned into two subsets using the explanatory variables, further reducing overall variation in the dataset. The process of splitting was continued until a terminal node was reached (no further splitting) and residual variation of data was less than 1%.

This process results in a tree of maximum size and a data set that was likely over fitted during the analysis (Breiman et al., 1984). The cross validation is used to determine the optimal model (i.e., one that is not over fitted). We used a 10-fold cross validation procedure that partitioned the data into ten equal groups each having a similar distribution. Models are created using nine of the groups of data and the error was calculated between this model and another comprising the remaining group of the data. This process is continued until each of the ten groups of the data has served once for the error comparison with the remaining nine. The optimum model selected has the lowest overall error. The CART modeling was performed in R version 2.15.3 (part version 4.1-1, The R Foundation for Statistical Computing, Vienna, Austria).

3. Results

3.1. Mean concentrations of phosphorus forms

Total P concentrations in the soils exhibited a wide range of values with the smallest value (15.6 mg kg^{-1}) found in a Bt horizon weathered from hillslope sediment and the greatest value (410 mg kg^{-1}) observed in an A horizon weathered from alluvium. The mean concentration ± 95% confidence interval (CI) for total P across all 150 soil horizons studied was 116 ± 6.9 mg kg^{-1} (Table 3). Mean concentrations of Mehlich-3 and Bray-1 available P were 7.8 ± 0.41 mg kg^{-1} (range: 3.8 to 30.6 mg kg^{-1}) and 5.8 ± 0.48 mg kg^{-1} (range: 0.29 to 27.3 mg kg^{-1}), respectively. Based on comparison of the 95% CI, concentrations of a given P form are significantly greater in the A horizon relative to the two deeper soil horizons, but differences are nominal between mean values of the first Bt or Bw horizon and the horizon occurring at a depth of 100 cm (Table 3).

3.2. CART analysis: relationships between phosphorus forms and predictor variables

The CART analyses for total P, Mehlich-3 P, and Bray-1 P were able to explain 48, 71, and 65% of the variability, respectively, in concentrations of these three P forms in forest soils of the Missouri Ozark Highlands (Fig. 2a–c). The CART procedure indicated that CBD extractable Mn was the single most important factor explaining variation in all three forms of P studied. This single explanatory parameter explained 33, 28 and 32% of the variability in total P, Mehlich-3 available P, and Bray-1 available P, respectively.

For the total P regression tree (Fig. 2a), soil samples with ≥1183 mg kg^{-1} of CBD-Mn contained a mean total P concentration (212 mg kg^{-1}) that was two times greater than the mean total P concentration (103 mg kg^{-1}) of samples containing <1183 mg kg^{-1} CBD-Mn. No further partitioning of the data occurred for samples with ≥1183 mg kg^{-1} of CBD-Mn. However, for soils containing <1183 mg kg^{-1} of CBD-Mn, TOC accounted an additional 6.6% of the variation in total P concentration. The mean total P concentration (125 mg kg^{-1}) was greater for samples containing ≥8.6 mg kg^{-1} TOC content than samples containing TOC < 8.6 g kg^{-1} (mean total P = 90 mg kg^{-1}). Additional ability to explain total P variation for each TOC node occurred through further partitioning of the data. For soil

Table 3
Mean concentrations ± 95% confidence interval of P forms and citrate bicarbonate dithionite extractable aluminum, iron, and manganese for all soil horizons studied, the first mineral horizon, the first Bt or Bw horizon, and the horizon occurring at a depth of 100 cm.

	Total P	Mehlich-3 available P	Bray-1 available P	CBD-Fe[a]	CBD-Al[b]	CBD-Mn[c]
	$mg\ kg^{-1}$			$g\ kg^{-1}$		
All horizons (n = 150)	116 ± 6.9	7.9 ± 0.41	5.8 ± 0.48	1.45 ± 0.082	10.2 ± 0.97	0.53 ± 0.061
1st mineral horizon (n = 50)	150 ± 14	10.3 ± 0.79	9.0 ± 0.95	1.28 ± 0.066	5.4 ± 0.19	1.0 ± 0.11
1st Bt or Bw horizon (n = 50)	108 ± 8.8	6.9 ± 0.56	4.4 ± 0.59	1.2 ± 0.10	7.5 ± 0.74	0.46 ± 0.078
Horizon at 100 cm (n = 50)	94 ± 9.7	6.4 ± 0.51	4.0 ± 0.53	1.9 ± 0.19	18 ± 2.1	0.15 ± 0.046

[a] CBD-Fe, citrate bicarbonate dithionite extractable iron.
[b] CBD-Al, citrate bicarbonate dithionite extractable aluminum.
[c] CBD-Mn, citrate bicarbonate dithionite extractable manganese.

samples with a TOC ≥ 8.6 g kg^{-1}, partition of the data by landform explained an additional 5.6% of variation; soil found on hillslopes contained 1.5 times greater total P concentration than soil collected from floodplains, structural benches and ridges. Additional variation (2.8%) associated with the TOC < 8.6 g kg^{-1} node was explained by soil pH, and mean total P concentrations were 1.5 times greater in soils with pH ≥ 4.95, relative to samples with pH < 4.95.

As noted previously, CBD-Mn was the single most important variable explaining Mehlich-3 P variability (27.8%) (Fig. 2b); however, additional Mehlich-3 P variability was explained through further partitioning of the CBD-Mn nodes. For the node with CBD-Mn < 505 mg kg^{-1} and a mean Mehlich-3 P concentration of 6.2 mg kg^{-1}, a partition by soil horizon/depth explained 6.1% additional variability. Samples from the first mineral horizon contained 60% greater Mehlich-3 available P (9.3 mg kg^{-1}) than B horizon soils and those from a depth of 100 cm (5.8 mg kg^{-1}). In contrast, soil pH explained an additional 27% of Mehlich-3 P concentration when soils with ≥505 mg kg^{-1} CBD-Mn and a mean Mehlich-3 P concentration of 10.2 mg kg^{-1} were further partitioned. Mean Mehlich-3 P concentrations were twice as great in soils with a pH ≥ 6.25. Cation exchange capacity accounted for 5.5% additional variation in Mehlich-3 P concentrations when samples with a soil pH < 6.25 were further partitioned. Subsequent partitioning of the CEC nodes using underlying bedrock formation and landform explained 4.2% additional variation, cumulatively.

For the Bray-1 P regression tree, CBD-Mn was the single most important variable explaining approximately 32% of variability (Fig. 2c). Soils with a CBD-Mn concentration ≥511 mg kg^{-1} contained a 8.8 mg kg^{-1} mean Bray-1 available P concentration, which is more than double the mean Bray-1 available P concentration for samples containing <511 mg kg^{-1} CBD-Mn. Additionally, 3.3% of Bray-1 available P variation was explained by soil horizon/depth when the CBD-Mn < 511 mg kg^{-1} node was further partitioned. For the CBD-Mn ≥ 511 mg kg^{-1} node, 17% additional variation was explained when the node was partitioned by exchangeable Ca concentration as the predictor variable, and mean Bray-1 P concentration was almost two times greater when exchangeable Ca was ≥2.75 $cmol_c\ kg^{-1}$. A partition of the node with ≥2.75 $cmol_c\ kg^{-1}$ exchangeable Ca by landform explained an additional 5.8% of variation in Bray-1 P concentration. For soils with exchangeable Ca < 2.75 $cmol_c\ kg^{-1}$, an additional 7% of variation was explained by partitioning samples based on CEC and underlying bedrock formation.

4. Discussion

4.1. Soil and environmental properties explaining phosphorus variability in the landscape

4.1.1. Extractable manganese

In contrast to many previous studies demonstrating the importance of Fe and Al oxides on P sorption in soil and relationships between these metal oxides and P concentrations (Brown and Loewenstein, 1978; Jones et al., 1979; Loganathan et al., 1987; Villapando and Graetz, 2001; Burt et al., 2002; Agbenin, 2003), the CART analysis did not identify CBD Al, CBD Fe, and CBD-Al + Fe as important variables explaining concentrations of the three soil P forms studied. Instead, CBD-Mn was identified as the most important variable explaining the variability of P concentrations in the Ozark Highland forest soils studied (Fig. 2a–c).

Very few previous studies have evaluated CBD-Mn as a predictor of soil P despite literature supporting the environmental relevance and mechanistic understanding of Mn–P interactions. Jugsujinda et al. (1995) found that CBD-Mn content was positively correlated with P-sorption to acid sulfate soils, and Lair et al. (2009) observed a strong, positive correlation between CBD-Mn and oxalate extractable Mn content and P sorption to floodplain soils.

Phosphorus sorption to MnO_2 was studied as a function of pH by Mustafa et al. (2006), and P sorption was observed to increase with increasing P concentration and decrease with increasing pH. Mustafa et al. (2008) indicate that phosphate adsorbs to β-MnO_2 via an outer-sphere surface complex (indicated by ••••):

$$\equiv MnOH_2^{+} + H_2PO_4^{-} \Leftrightarrow \equiv MnOH_2^{+}\bullet\bullet\bullet\bullet H_2PO_4^{-}$$
$$\equiv 2MnOH_2^{+} + HPO_4^{2-} \Leftrightarrow \equiv 2MnOH_2^{+}\bullet\bullet\bullet\bullet HPO_4^{2-}$$

which is relatively weak compared to an inner-sphere surface complex between phosphate and β-MnO_2 at <pH 6 observed by Zaman et al. (2013):

$$\equiv MnOH + H_2PO_4^{-} \Leftrightarrow \equiv MnH_2PO_4 + OH^{-}$$
$$\equiv 2Mn(OH) + HPO_4^{2-} \Leftrightarrow \equiv Mn_2HPO_4 + 2OH^{-}$$

The findings of Zaman et al. (2013) indicate the potential for strong Mn–P complexes to form in many samples included in our study (135 samples had <pH 6).

Previous work also indicates that Mn oxides are more soluble than Fe oxides in particular soils (Narwall and Singh, 2001). If Mn oxides sorbing P in forested Ozark Highland soils are more soluble than Fe and Al oxides, this may explain the relationship between Mn and P forms found in this research. Although additional studies are needed to more thoroughly elucidate the mechanistic relationship between P and CBD-Mn in the Ozark Highland soils studied, sufficient evidence in the literature suggests that Mn oxides can be important sorbents for soil P (Jugsujinda et al., 1995; Lair et al., 2009; Mustafa et al., 2006; Mustafa et al., 2008; Zaman et al., 2013). Furthermore, our findings and the general paucity of data relating extractable Mn to soil P concentrations suggest that the relationship between Mn and P may be an important but understudied aspect of soil phosphorus cycling.

4.1.2. Total organic carbon

Total organic carbon was identified in CART analysis as second most important variable explaining total P concentration in 132 out of the 150 soil samples evaluated (Fig. 2a). Although TOC was not an important explanatory variable in the Mehlich-3 P and Bray-1 P models, soil horizon/depth was important and the first mineral horizon samples were partitioned from subsoil samples (Fig. 2b–c). This suggests that

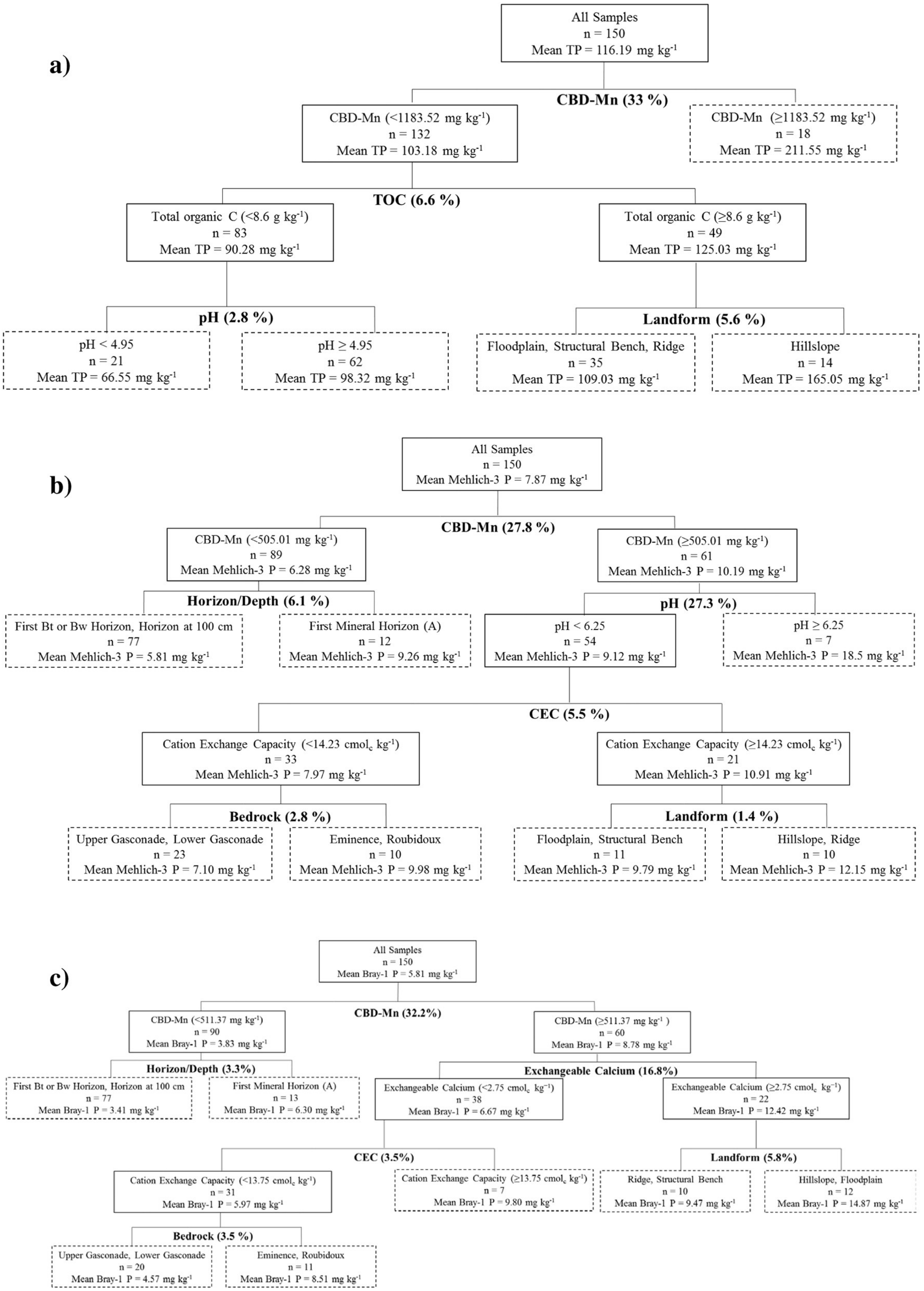

Fig. 2. Regression trees developed from classification and regression tree analysis for (a) total phosphorus (TP), (b) Mehlich-3 and (c) Bray-1 P. Each branch of the regression tree is labeled with the explanatory variable associated with partitioning of the response variable and the percent of the variation explained. Boxes represent the nodes and include information about the explanatory variable (and threshold values for continuous variables) associated with each split, the mean phosphorus concentration, and the sample size of the split. Dashed boxes represent the terminal nodes. For all three forms of phosphorus, explanatory variables included soil horizon or depth, parent material, underlying bedrock formation, slope position, landform, clay content, exchangeable calcium concentration, cation exchange capacity, soil pH in water, the sum of citrate bicarbonate dithionite extractable aluminum and iron (CBD-Al + Fe), citrate bicarbonate dithionite extractable manganese (CBD-Mn), and total organic carbon.

soil horizon/depth may be serving as a surrogate variable for TOC, as TOC within the soils studied decreased substantially with depth. The inclusion of TOC and soil horizon/depth in the model is in agreement with previous studies of P in forested soils. A large portion of P present in forest soils is bound within the structure of organic molecules in the leaf litter and surface mineral horizons (Condron and Tiessen, 2005), and these mineralizable forms of P are important to plants within forested ecosystems (Yanai, 1992).

4.1.3. pH and exchangeable calcium

The CART analysis indicated that pH explained 27.8% of the variability for Mehlich-3 P and 2.8% of the variability for total P (Fig. 2a–b). Soil pH is well known as an important factor regulating the dissolution of P-bearing minerals (Pierzynski et al., 2005; Oelkers and Valsami-Jones, 2008). With increasing pH, P bound to metal oxides maybe solubilized and become plant available; whereas, P solubility decreases with increasing pH when P is bound to Ca (Hinsinger, 2001). Exchangeable Ca content was an important explanatory variable within the Bray-1 P CART analysis and this variable explained 16.8% of the variability (Fig. 2c). At exchangeable Ca concentrations ≥2.75 cmol kg^{-1}, Bray-1 P concentrations were greater and this relationship likely results from bonding between phosphate and Ca on exchange sites (Yao and Millero, 1996).

4.1.4. Other soil and environmental predictors

There were several explanatory variables included in the CART analyses that did not explain the variability of P concentrations in the soils studied: parent material; slope position; clay content; and individual or summed concentrations of CBD extractable Al and Fe. Parent material, slope position, bedrock formation, and landform were the environmental variables considered in our analyses, but only two of the four variables (bedrock formation and landform) appeared in the pruned regression trees. These environmental attributes appeared as tertiary and quaternary variables that explained limited P concentration variability (<5.8%) (Fig. 2a–c). Due to the interrelatedness of the environmental factors evaluated (parent material and bedrock formation; slope position and landform) and their overall weak explanatory capabilities, it is sensible that not all environmental variables would appear in the pruned regression trees. However, the limited ability of landform and bedrock to explain P variation and the lack of slope position in pruned CART trees is noteworthy and contrary to other soil P studies (Richards et al., 1997; McKenzie and Ryan, 1999).

With respect to clay content, it appears that related factors (CEC and exchangeable Ca) that mechanistically govern P sorption are more important in accounting for P variability (Curtin et al., 1992; Guppy et al., 2005; Rhoton and Bigham, 2005). The specific reason resulting in absence of CBD-Al, CBD-Fe, and CBD-Al + Fe from the regression trees is less clear, but may be related to the limited range of values measured.

4.1.5. Application of classification and regression tree results

The CART analysis provided a concise framework for identifying relationships between nutrients and soil and environmental attributes in complex soil landscapes. Specifically, the CART results presented here afford forest managers an opportunity to use soil characterization and environmental data to identify locales within the Missouri Ozark Highlands that may be deficient in soil P. Subsequently, these particular locations may require greater consideration during the development of management plans for forest compartments encompassing soils with particularly reduced P concentrations. Forest scientists may also wish to initiate monitoring of total and bioavailable P in stands where nutrient depletion may be of concern. Managers also need to consider the appropriateness of even-aged and uneven-aged management, length of harvest rotation, slash management, and controlled burns in specific forest stands to maintain long-term P supplies for sustainable forest growth.

4.2. Comparison of Missouri phosphorus forms to other forested soils

The Missouri Ozark Highland soils studied had reduced concentrations of total and available P as they are found at the lower end of the range of total P, Mehlich-3 P, and Bray-1 P values reported for 21 representative U.S. soil pedons (Burt et al., 2002). The mean total P concentration for A horizons determined through our work is comparable to concentrations found in the surface horizon of Ultisols in the South Carolina Piedmont, USA under loblolly pine (*Pinus taeda* L.) forests (Richter et al., 2006), but 1.5 to 2.5 times greater than total P in fynbos communities known to be inherently P deficient (Richards et al., 1997).

However, total P concentrations in surface horizons of the Ozarks are approximately 50% less than the surface horizons of forested Amazon Ultisols (McGrath et al., 2001), some tropical forest soils from Panama (Turner, 2008), and black spruce (*Picea mariana* Mill.) forests growing on Podzols and Gleysols of western Newfoundland, Canada (Scheuner et al., 2004). Relative to the work of Cross and Schlesinger (1995), total P concentrations in Ozark A horizons are 78, 65, 60, 25, and 65% less than in Entisols (Lithosols), Inceptisols, Alfisols, Ultisols, and Oxisols (Ferralsols), respectively. Based on weathering stage, we would expect Alfisols and Ultisols of the Ozarks to contain less overall total P than Entisols and Inceptisols but more total P than Oxisols (Walker and Syers, 1976; Crews et al., 1995; Cross and Schlesinger, 1995). Given the reduced total P concentrations in the Ozark soils studied, it seems likely that the mechanisms of low-P parent material and depletion through time have interactively lead to reduced total P concentrations in Ozark soils (Vitousek et al., 2010).

The Mehlich-3 P concentrations in surface soils of southern Missouri oak–hickory forests are comparable to concentrations found under hemlock (*Tsuga canadensis* L.)–tulip (*Liriodendron tulipifera* L.) stands found on Inceptisols and oak–pine (*Quercus* spp.–*Pinus* spp.) stands growing on Ultisols in Kentucky, USA (5–13 mg kg^{-1}) (Boettcher and Kalisz, 1990; Washburn and Authur, 2003). However, Mehlich-3 P concentrations in surface soils collected from Ultisols supporting loblolly pine forests in South Carolina, USA are four-fold greater than the Ozark forested soils we studied, and likely attributable to past agronomic fertilization practices at the South Carolina site prior to reforestation (Richter et al., 2006).

While surface soil concentrations of Mehlich-3 P are substantially greater in South Carolina, USA loblolly pine forests, the same is not true for subsoil samples. Average Mehlich-3 P concentrations in subsoil horizons of the Ozarks (6.6 mg kg^{-1}) are six-fold or greater than values observed in Ultisols of South Carolina, USA (<1 mg kg^{-1}) (Richter et al., 2006). This suggests that tree species in the Ozarks with deeper rooting systems may be able to exploit a larger volume of soil to satisfy immediate P nutrition requirements; whereas, pine trees growing on South Carolina Ultisols may be limited to acquiring bioavailable P primarily from the upper surface horizons and slowly cycling P fractions in the subsoil. The difference in subsoil Mehlich-3 P concentrations between the two study areas may be associated with large differences in organic carbon at the soil surface; total organic carbon in Ozark soils is four-fold or greater than the South Carolina soils. Subsequently, we would expect greater competition for sorption surfaces to occur between organic molecules and inorganic P in the A horizon of Ozark soils (Guppy et al., 2005), potentially resulting in a translocation of inorganic P to deeper horizons. Additionally, greater organic carbon concentration at the soil surface may result in increased dissolved organic nutrient leaching and enzymatic degradation to form inorganic P in subsoil horizons (Donald et al., 1993; Suzumura and Kamatani, 1995; Tipping et al., 1999; Kaiser et al., 2003).

The average Bray-1 P concentration measured in A horizons of the Ozarks falls within the range of average Bray-1 P concentrations reported for soil samples collected from several shallow depths (0 to 15 cm) in sugar maple (*Acer saccharum* Marsh.)–black cherry (*Prunus serotina* Ehrh.)–American beech (*Fagus grandifolia* Ehrh.) stands growing on

Ultisols, Spodosols (Podzols), and Inceptisols of the Allegheny Plateau of northern Pennsylvania, USA (Long et al., 1997) and Podzols and Cambisols found under sugar maple–American Beech–hemlock stands of central Ontario, Canada (Gradowski and Thomas, 2006). In contrast, Bray-1 P concentrations in the soils we studied are 1.1 to 44 times greater than concentrations found in tropical soil pedons of Cameroon, where surface and subsurface soil concentrations ranged from 0.6 to 3.1 and 0.1 to 3.5 mg kg^{-1}, respectively (Menzies and Gillam, 1997) (See Appendix A for a summary of P extraction methods and P analysis techniques used in the literature cited during comparative analyses presented in this section.)

5. Conclusion

Concentrations of available and total P in forested Alfisols and Ultisols of the Missouri Ozark Highland soils are generally quite low; mean concentrations of total P, Mehlich-3 P, and Bray-1 P were 116.2, 7.87, and 5.81 mg kg^{-1}, respectively. The CART analysis proved to be useful for identifying multiple factors necessary to explain P concentrations in this complex landscape. From all the environmental and soil properties input into the CART models, CDB-Mn was identified as the single most important attribute explaining variation in the concentrations of all three P forms. Secondary variables identified as important were soil properties more commonly associated with soil P (i.e., TOC, pH, and exchangeable Ca), and environmental properties explained little variation in soil P. Further research is needed to elucidate the role of soil Mn in the regulation of P forms and concentrations within soils of the Ozark Highland soils and other forested ecosystems, and findings described here can be used to formulate future research efforts. This research will also help identify sites in the Missouri Ozark Highlands that are potentially vulnerable to P depletion, thus necessitating special forest management considerations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.geodrs.2015.05.001. These data include Google map of the most important areas described in this article.

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