SOIL PHOSPHORUS POOLS AND HARVEST EFFECTS ON SOIL SOLUTION CHEMISTRY IN THE MISSOURI OZARK HIGHLANDS

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By
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Master of Science 

And hereby certify that, in their opinion, it is worthy of acceptance. 

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ABSTRACT

Forests ecosystems are governed by complex and dynamic nutrient cycles where soil is a major provider of nutrients essential for plant growth. Disturbances occurring in forested ecosystems (timber harvest, fire, and disease breakouts) lead to removal of living biomass which may impact nutrient cycling and can cause changes in soil solution chemistry, nutrient flux, and alter soil moisture and temperature. Missouri Ozark Highland soils are highly weathered and, to maintain long-term sustainability and productivity of forests supported by these soils, understanding harvest operations effect on nutrient loss is of utmost importance. Therefore, the primary objective of this study was to enhance understanding of nutrient dynamics and pools in forested soils of the Missouri Ozark Highlands. The study was divided into two specific research objectives: (1) quantify the influence of clearcutting (CC) and single tree selection forest (STS) regeneration on soil solution chemistry and nutrient flux in low and medium nutrient status soils at Missouri Ozark Forest Ecosystem Project (MOFEP); and (2) identify the importance of geomorphic and soil properties on total and available P concentrations in Ozark Highland soils.

To address concerns regarding the depletion of soil nutrients in association with timber harvest in the Missouri Ozark Highlands, soil solution and nutrient flux in low and medium nutrient status soils was monitored in clearcut, single tree selection, and no-harvest management sites (NHM) at MOFEP. Pre-harvest and post-harvest solution samples were collected with throughfall and zero-tension soil solution (ZTS) samplers (15 and 40 cm depths), and samples were analyzed for pH and electrical conductivity (EC), anions (F⁻, Br⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, PO₄³⁻), cations (K⁺, Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, and total aluminum), dissolved organic carbon (DOC), and total nitrogen (TN). Ion exchange resin (IER) samplers
(15 and 40 cm soil depths) were used to capture cumulative flux. Pre-harvest and one year post harvest soil samples were collected and analyzed for soil pH, exchangeable concentrations of Ca$^{2+}$, Mg$^{2+}$, and K$^+$, effective cation exchange capacity (ECEC), base saturation (base sat.), extractable acidity (EA), extractable aluminum (EAl), aluminum saturation (Al sat.), total organic carbon (TOC), and total nitrogen (TN). Post-harvest soil solution samples contained significantly greater concentrations of NO$_3^-$, Mg$^{2+}$, and TN and greater values of EC in the clearcut sites relative to STS and NHM. Mean daily flux measurements captured by IER samplers show significantly greater flux of NO$_3^-$ and Mg$^{2+}$ in post-harvest clearcuts relative to pre-harvest measures. Despite morphological and some chemical differences between low and medium nutrient status soils, no influence of soil nutrient status was observed in this research. Study results demonstrate increased nutrient leaching after clearcutting but minimal changes were observed in STS harvested sites relative to control sites. Missouri forest managers may need to reevaluate and modify this practice to minimize the losses triggered after timber harvesting in order to maintain long-term sustainability and productivity of Ozark forests.

To meet the second objective, archived soil samples and soil characterization data were obtained for 50 pedons sampled at MOFEP. Soil chemical analyses were conducted to measure total P, available P, and citrate bicarbonate dithionite (CBD) extractable Fe, Al, and Mn in the samples studied. Linear regression and classification and regression tree (CART) analyses were applied to elucidate relationships between soil P pools and geomorphic and soil chemical properties. Total P and available P in the soils studied ranged from 15.55 to 410.13 mg kg$^{-1}$ and 3.81 to 30.61 mg kg$^{-1}$, respectively. Linear regression analyses indicated a moderate correlation of CBD extractable Mn with total P ($r^2 = 0.77$), Bray-1 available P ($r^2 = 0.69$), and Mehlich-3 available P ($r^2 = 0.71$) for soils overlying Eminence bedrock. The
CART analysis identified (1) CBD extractable Mn and total organic C as important variables explaining 39% of cumulative variation in total P; (2) CBD extractable Mn, and exchangeable Ca as important variables explaining 49% of cumulative variation of Bray-1 available P; and (3) CBD extractable Mn, and pH as important variables explaining 55% of cumulative variation of Mehlich-3 available P. This research aids in understanding and identifying locations in Missouri Ozark forests where P pools may be relatively small, thus necessitating careful management and monitoring before and after timber harvest.

Results from the soil solution study and P forms enhance our understanding of nutrient leaching and budgets in Ozark Highland soils and can help better understand the impact of timber harvesting on nutrients in highly weathered soils. Study results will serve as a tool to better manage Missouri forests and to formulate future management policies. Furthermore, this research can aid in identifying soils which are at risk of depletions for P concentrations after harvesting in Ozark highland landscape.
1.1 Introduction

Missouri is ranked seventh out of the 20 northeastern states in the amount of forested acreage, having more than 5.6 million hectares of forested land which covers approximately one-third of the state (MDC, 2000). Of these 5.6 million hectares, 83 percent is owned by private landholders and 15 percent is public land, and the majority of forested land is located in the Ozark Highlands. The large forested land in Missouri is both ecologically and economically significant for the state. Subsequently, there is substantial scientific interest in developing and evaluating silvicultural practices that promote long-term forest sustainability. The Missouri Department of Conservation (MDC) initiated the Missouri Ozark Forest Ecosystem Project (MOFEP) in 1989 to understand the complex nature of multiple ecological systems operating in forests managed in differing manners and to investigate the sustainability of these management practices.

One factor that must be considered while addressing forest sustainability is soil nutrient changes following harvest. Soils of the Ozark Highlands are highly weathered and are unproductive to marginally productive for conventional agricultural practices (Brookshire et al., 1997). Therefore, it is very important to understand nutrient changes in the soil system following harvest and its potential impact on species diversity and biomass production. Toward this end, MOFEP provides an opportunity to monitor various nutrient changes in soils located within differing forest management systems before and immediately after harvest.

Ozark Highlands soils are dynamic and highly weathered materials formed from a variety of parent materials (e.g., residuum, alluvium, loess, and pedisediments) (Hammer, 1997).
most common soil orders present in the Ozark Highlands are Alfisols and Ultisols generally expressing low cation exchange capacity (CEC) and low quantities of exchangeable bases, although significant variability is exhibited in soils of this region (Kabrick et al., 2011). Due to variability in soil nutrient capital and different harvesting methods, MOFEP permits specific combinations of soil and forest management to be evaluated. For example, soils at MOFEP can be subdivided on the basis of nutrient capital or status (low, medium and high), and these different soils are nested in forests managed using even-aged management (EAM), uneven-aged management (UAM) and no harvest management (NHM). Furthermore, each management practice can utilize different regeneration techniques [e.g., clear-cutting (CC), single tree selection (STS), and shelterwood harvest].

Soil samples collected and stored at the time of MOFEP initiation also permit the investigation of geomorphic and soil property influences on nutrient pools (Kabrick et al., 2011). Phosphorus is a macronutrient of importance for plant growth, and it is considered a limiting nutrient for forest growth in some regions of the world (Fox et al., 2011). Being highly weathered, soils of Ozark Highlands may have insufficient P to supplement tree growth after harvest, which may impact long term productivity of these forests. It becomes very important to quantify various forms of P and identify soil and geomorphic properties related to P supply (e.g., landscape position, parent material, bedrock, and soil depth). Through greater understanding of factors governing P, we may be able to avoid or reduce timber harvest on sites low in P and maintain forested stands in P depleted sites.

The overall objective of this research is to enhance understanding of nutrient dynamics and nutrient pools in forested Missouri Ozark Highland soils. More specifically, research presented in this thesis is divided into two different studies. The first study is focused on understanding soil solution chemistry in forested stands harvested using CC, STS and no harvest through the comparison of pre- and post-harvest data from low and medium nutrient
status soils (low, ≤20% base saturation; and medium, 20-50% base saturation). It was hypothesized that nutrient concentrations in soil solution would increase post-harvest with a greater magnitude of change occurring in CC relative to STS harvested stands. The second study was intended to quantify phosphorus pools in forested soils collected from MOFEP and to elucidate geomorphic and soil properties that aid in predicting P pools. It was hypothesized that total and available P concentrations would differ with parent material, landscape position, bedrock, depth, clay content, pH, CEC, and the quantity of iron, aluminum and manganese oxides in the soil. Results from these studies will aid in identifying nutrients more prone to loss in soils with marginal nutrient content. Additionally, the results will help to formulate better forest management practices for sustaining oak dominated forests of southern Missouri.
1.2 Objectives and Hypothesis

Primary Objective

To enhance understanding of nutrient dynamics and pools in forested soils of the Missouri Ozark Highlands.

Specific Research Objectives

1. To quantify the influence of CC and STS forest regeneration on soil solution chemistry and nutrient flux in low and medium nutrient status soils at MOFEP.

2. To identify the importance of geomorphic and soil properties on total and available P concentrations in Ozark Highland soils.

Specific Research Hypotheses

1. Due to mineralization of slash and soil organic matter, concentrations of total nitrogen, dissolved organic carbon, base cations, $\text{NO}_3^-$, $\text{PO}_4^{3-}$, $\text{SO}_4^{2-}$, $\text{H}^+$ and total Al in soil solution will increase post-harvest and changes will be most pronounced in CC sites. Solute concentrations will be greater in medium nutrient status soils than low nutrient status soils.

2. Phosphorus concentrations will differ with parent material, landscape position, bedrock, depth, clay content, pH, CEC, and the quantity of iron, aluminum and manganese oxides in the soil.
1.3 Literature Review

1.3.1 Missouri Ozark Forested Ecosystem Project (MOFEP)

The Missouri Ozark Forest Ecosystem Project is a long term experimental project started by MDC in 1989. This project was started to comprehensively evaluate forest management practices on wide array of upland ecosystem attributes. The MOFEP sites are located within the Ozark Highlands of south-central Missouri, and more specifically within the Current River Forest Breaks and the Current River Oak-Pine Woodland Hills land type associations (Nigh and Schroeder, 2002). In terms of political boundaries, the sites are located in Shannon, Carter and Reynolds Counties, and lands in these counties are primarily forested (84%) (Hahn, 1991). The forests at MOFEP are predominantly comprised of oaks (*Quercus sp.*), shortleaf pine (*Pinus echinata* Mill.), and hickories (*Carya sp.*) (Kabrick et al., 2004), and they are managed according to MDC’s *Forest Land Management Guidelines* (MDC, 1986).

The MOFEP sites are arranged in a completely randomized block design consisting of three blocks and each block has three sites summing to a total of nine sites (Figure 1.1). Each site within a single block is managed with one of three types of treatments (EAM, UAM and NHM) and within each treatment differing types of timber regeneration methods are used (e.g., CC for EAM sites and STS for UAM sites) (Brookshire et al., 1997). Each of the nine sites range from 291 to 514 hectares in size and the sites are also referred as compartments (Sheriff and He, 1997). The MOFEP project is intended to last one to three full rotations (100-300 yr) within these operational forest compartments. Harvest event occurs approximately every 15 years and during each harvest re-entry 10 to 12% of a site is harvested with the designated treatment. Five years of pretreatment ecological data were collected at MOFEP before the first timber harvesting entry began in May 1996 and
concluded in Nov. 1996 (Brookshire et al., 1997; Shifley and Brookshire, 2000). Biological data collected at MOFEP included vegetative composition and structure, site characteristics, and wildlife communities. Physical site characteristics and soil samples were collected before the first harvest entry (Meinert et al., 1997; Kabrick et al., 2000) and soil samples from 74 pedons were characterized for general physical and chemical properties.

These highlands are an assemblage of nearly level to deeply dissected plateaus comprised primarily of Ordovician dolomites or sandstones. Dominant bedrock formations are the Roubidoux sandstone, upper and lower Gasconade dolomite, the Gunter sandstone member, and Eminence dolomite (Figure 1.2, Meinert et al., 1997). Each bedrock unit is considerably different in lithology. The Roubidoux bedrock formation is interstratified with sandstone, dolomite, and silicified stromatolite algal and chert beds. The Gasconade formation is subdivided into the upper and lower Gasconade formations. The upper Gasconade is comprised of coarsely crystalline dolomite and the lower Gasconade is comprised of finely crystalline dolomite. Where the upper Gasconade is interbedded with chert and layers of silicified stromatolites, the lower Gasconade is interbedded with a few chert nodules and the base of this formation is a 1 to 3 m bed of sandstone and quartzose. The Eminence formation is dominated by coarse crystalline dolomite with occasional occurrence of interbedded cherts (Meinert et al., 1997; Kabrick et al., 2011).
Figure 1.1. Location of nine MOFEP sites in three Missouri counties and the management treatment (adapted from Kabrick et al., 2011).
Ozark Highland soils are dynamic and highly weathered materials formed from a variety of parent materials (e.g., residuum, alluvium, loess and pedisediments) (Hammer, 1997), although most landscapes of this region are covered with extensively weathered residual soils and pedisediments. The most common soil orders at MOFEP are Alfisols and Ultisols with low CEC, low base saturation (BS), and relatively low concentrations of exchangeable calcium and magnesium (Meinert et al., 1997; Kabrick et al., 2011).

Several soil nutrient studies have been completed at MOFEP related to carbon and sulfur pools and how seasonal differences change the production rate of organic sulfur by (Spratt, 1998). Spratt (2002) was also able to correlate changes occurring in a clearcutting plots to decreased organic sulfur, total carbon, total sulfur and total nitrogen after harvest. Carbon pools were determined by Li et al. (2007) in different harvest treatments at MOFEP. Total pools of carbon including live tree biomass and coarse woody debris were greatest for NHM and least for EAM eight years after harvest; whereas, organic carbon in mineral soils significantly increased in UAM while there was no significant effect of harvest on soil under the EAM treatment. Kabrick et al. (2011) found that bedrock lithology and depth to bedrock are correlated to Ca and Mg concentrations in Ozark Highland soils. They compared shallow soils (<1 m to bedrock) to deeper soils (>1 m to bedrock) and concluded that Ca and Mg concentrations were greater in shallow soils. In deeper soils, underlying bedrock formation was found to be secondary variable explaining Ca and Mg concentrations; greater concentrations were found in soils overlying dolomites of the Eminence and lower Gasconade formations.
Figure 1.2. Stratigraphy of bedrock geology and relative locations of soil nutrient status groupings at MOFEP experimental sites (Updated, Albers, 2010).
Albers (2010) studied mixed hardwood forests of MOFEP and collected soil samples from CC and STS plots ten years after the first harvest at MOFEP. Albers (2010) observed that the CC regeneration method increased soil nutrient concentrations while STS appeared to decrease soil nutrient levels. In STS plots, overall concentrations of calcium, total organic carbon, total nitrogen and stable and labile nitrogen were smaller and in CC plots they were greater than corresponding paired controls, and these nutrient differences were attributed to differences in slash distribution within the treatments.

In an *ex-situ* leaching experiment conducted for three months by Gaddie (2012), a pronounced effect of temperature was observed for certain nitrogen species and soil microbial activity. Leachate NH$_4^+$ concentration in soil columns incubated at 23°C was significantly greater than soil columns incubated at 26°C. Additionally, β-glycosidase activity was significantly greater in soils incubated at 21°C than soils incubated at 26°C. Gaddie (2012) also collected pre-harvest soil solution samples *in-situ* and these data will be used for meeting the first research objective of this thesis. In this pre-harvest data, Gaddie (2012) observed seasonal fluctuations in pH, base cations, non-purgable organic carbon (NPOC) and total nitrogen (TN) concentrations; however, ion composition was very similar in solution samples collected from low and medium nutrient status soils.

### 1.3.2 Forest Management Systems and Harvest Techniques

Timber is a valuable natural resource and it is significant source of economic well-being for Missouri (MDC, 2000); therefore, it is essential to identify and optimize forest management to ensure sustainability of Missouri’s forested ecosystems. Forest management is a broad concept involving integration of silvicultural practices and business objectives ultimately focused on achieving long-term objectives of landowners (Bettinger et al., 2010). There is wide array of forest management considerations ranging from ecology to economics...
which includes activities such as tree planning, herbaceous weed control, fertilization, forest thinning, forest harvest, harvest for habitat improvement and preservation, etc. In forest management, trees are harvested for a variety of purposes including: (1) improving forest health; (2) preferential growth of desired tree species; (3) enhanced wildlife habitat; (4) supplementing landowner income; (5) producing forest products; and (6) improving forest access for recreational purposes (Bettinger et al., 2010).  Forest management plans may utilize different forest regeneration methods (e.g., clearcutting, shelterwood, seed tree, group selection and single tree selection) to achieve particular goals. Each method has its own benefits and drawbacks and no method is ideal for all situations (Jacobs et al., 1992).

The most cost effective forest regeneration method is clearcutting associated with EAM. One of the objectives of EAM within a compartment is to attain a forest stand with different age classes, and within each age class trees are allowed to grow to a specific age called rotation age (Johnson et al., 2009). Once the trees reach to rotation age they are harvested with an appropriate regeneration method. Clearcutting is useful for regenerating shade intolerant or early-successional tree species (Johnson et al., 2002). In a clearcut, all merchantable trees are removed while any tree greater than two inches in diameter at breast height (DBH) are felled or deadened. In this management system approximately 10 to 12% of a compartment is harvested every 10 to 15 years and the remainder of the compartment is reserved for harvest over a period of 100 years. (MDC, 2000). Immediately following clearcutting, a large amount of slash is left onsite and it is commonly distributed in a relatively uniform manner across the stand and left to degrade and return nutrient capital to the soil.

Two other natural regeneration methods used in EAM are shelterwood and seed tree methods. The most important objective of the shelterwood regeneration method is providing a congenial environment for reproduction of desired tree species below the parent stand
(Johnson et al., 2009). Thinning of parent stand is common practice and only those trees providing shade and protection to a developing age class are left behind (Helms, 1998). The seed tree method is least efficient method for regeneration of oak stands, and it involves leaving ten or less trees per acre in a stand for seed production (Smith, 1996).

Uneven-aged management is focused on maintaining and sustaining an uneven aged forest stand which can keep up an even flow of forest products. When comparing EAM to UAM, fewer trees are generally removed from UAM stands per unit area, resulting in shading of the forest floor which is beneficial for the regeneration of shade tolerant tree species (Johnson et al., 2009). Group tree selection (GTS) and STS forest regeneration methods are commonly used in UAM. Uneven-aged management requires multiple entries into a stand over a full rotation compared to relatively few entries for EAM. After one rotation, UAM trees may be less likely to be injured as many trees selected for removal are smaller (Bruhn et al., 2002). In STS, individual trees are harvested periodically so that desired stand age, size and species composition is maintained. There are some standard management characteristics which should be considered for each STS periodic harvest: (i) the distribution of tree ages; (ii) the distribution of tree diameters; (iii) stand stocking; (iv) reproduction; and (v) species composition (Johnson et al., 2002). In STS harvested stands, slash distribution and site disturbance are less uniform (Shifley and Kabrick, 2002), which may result in areas of nutrient depletion around stumps (Albers, 2010). A common challenge associated with STS is the high-grading of forest stands which can result in inferior quality stands and undesirable species (MDC, 2000). In GTS, trees are harvested from larger area typically 0.2 to 0.5 acre and the objective is regeneration of shade intolerant and mid-tolerant species. Applicability of GTS to oak stands is not well documented and derives inconclusive and undemonstrated long term impacts (Hill and Dickmann, 1988; Golden, 2001).
Differences in canopy cover under EAM and UAM managed forests result in a shift of tree species distribution (Jensen and Kabrick, 2008).

1.3.3 Forest Harvest and Soil Nutrients

In an undisturbed forest ecosystem, nutrient loss is very low or negligible as all the nutrient pools are balanced and regulated by biomass present in the area (Hedin et al., 1995). However, disturbances occurring in a forested ecosystem will disrupt nutrient cycling and the degree of disruption may be proportional to intensity of disturbance (Kimmins, 1995). Biomass removal associated with forest harvest can potentially alter the forest ecosystem through the loss of nutrients via increased rates of nutrient leaching (Belleau et al., 2006). The intensive removal of timber via clear-cutting requires more concentrated use of heavy equipment and greater direct physical disturbance of soil. Opening of the canopy and surface biomass removal increases exposure of soil to sun and other chemical elements, increasing possible loss due to leaching and erosion. Physical disturbances along with removal of woody biomass alters nutrient pools and nutrient cycling in forest ecosystems (Kimmins, 1997; Binkley and Fisher, 2012). Johnson et al. (1997) documented an increased mobilization rate of exchangeable cations from the forest floor which accumulated in spodic B-horizons following clearcutting. Two years after stem only harvest (SOH), Belleau et al. (2006) observed increases in total Ca, K, Mg, and pH in forest floor soil horizons, but no change was observed in the mineral soil.

Clearcutting removes more biomass per unit area when compared to other management systems, and large quantities of slash remaining on the surface degrade over time. However, clearcutting has been observed to increase stream temperatures, sediment loading, and outflow of nutrients from the forest floor (Qualls et al., 2000; Johnson et al., 2002; Spoelstra et al., 2010). Clearcutting increases soil moisture compared to uneven-aged methods in the
larch/fir forests of the Northern Rockies (Schmidt, 1980). Soil temperature and moisture monitoring by Londo et al. (1999) indicated greater temperature and lower moisture levels in CC plots and seasonal fluctuations in temperature and moisture levels were also significant. Mahendrappa et al. (2006) reported changes in surface organic materials and soil solution chemistry after harvest events. Solution pH decreased after SOH relative to whole tree harvest (WTH). Changes in pH were attributed to proton release as organic matter was mineralized and ammonium (NH₄⁺) was converted to nitrate (NO₃⁻). Decreases in the concentration of exchangeable base cations and soil pH in the upper soil horizons was shown by Johnson et al. (1997) over a period of 3 years following clearcutting. Several studies have reported that nutrient uptake and the subsequent harvesting of above-ground biomass causes soil acidification (Akselsson et al., 2007; Vanguelova et al., 2010; Brandtberg and Olsson, 2012). By removing trees through conventional SOH or WTH method, nutrients are irreversibly removed from the ecosystem, and the WTH harvesting type is typically the most conducive to soil acidification (Vanguelova et al., 2010). After harvesting, the decomposition of soil roots, branches, and twigs will release cations, which may partly neutralize the acidification by nutrient uptake (Nilsson et al., 1982).

When minimal slash materials are left behind in sites harvested with WTH regeneration, effects on the ecosystem are often amplified. Increased base cation concentrations were observed by Dahlgren and Driscoll (1994) in soil solution collected from WTH sites relative to soil solution from a reference watershed, and this difference can be attributed to enhance leaching from the forest floor. Whole-tree harvest methods were found to increase concentrations of dissolved silicate and potassium in New Hampshire streams (Romanowicz et al., 1996; Conley et al., 2008). Whereas Johnson and Todd (1998) reported higher levels of soil exchangeable base cations in SOM compared to WTH harvested sites; soil Ca increases were in close relation to Ca estimated from slash during a 15-year period following harvest.
Clearcutting in the Northern Limestone Alps of Austria have been well documented for post-harvest hydrological losses of potassium (Katzensteiner, 2003). Hendrickson et al. (1989) found that three years after harvest, SOH created significantly greater Ca$^{2+}$ and Mg$^{2+}$ concentrations in the forest floor than in uncut plots and WTH plots of a pine-aspen stand in northern Ontario. In a long term study conducted in the eastern USA, it was estimated that WTH removed 20-60% of Ca, and 2–10% of K, P and Mg over a 120 year time period (Federer et al., 1989; Vance, 1996). Yanai (1991) observed greater concentrations of P in forest floors (Oa horizon) of WTH sites when compared to un-harvested sites in a northern hardwood forest and this was attributed to a decrease in plant biomass after harvesting.

The effect of timber harvest has also been observed on micro-ecosystems operating on the forest floor. Nutrient loss via sawlog removal and leaching losses post-harvest harvesting may be very intense in clearcut (Mann et al., 1988). Slash which is left behind after a harvesting event, particularly in clearcut, increases the net mineralization rate of nitrogen (O'Connell et al., 2004) resulting in nutrient leaching and decreasing overall vegetative growth potential of forest (Fahey et al., 1991). Many changes occur in the forest floor after harvesting including soil moisture, soil temperature and substrate quality which impairs the microbial cycling of nutrients (Pietikäinen and Fritze, 1993; Baldock et al., 1999). Carmosini et al. (2002) observed more rapid rates of NH$_4$-N production in mixed stands of northern Alberta after harvesting whereas NO$_3$-N production remained unchanged. In contrast, Bock and Van Rees (2002) found minimal changes in forest floor soil properties and nutrient content after harvesting of a mixed wood forest of the Northwest Territories of Canada. Soil respiration can be significantly increased in the forest after harvest due to increased root growth and micro-floral activity associated with forest regeneration processes (Londo et al., 1999).
Forest fires play a significant role in governing forest ecosystems, but the role of fire in harvested areas is ambiguous with respect to soil nutrient cycling. There are a few studies available comparing the impact on soil nutrients after harvesting and natural fires (Bååth et al., 1995; Pietikäinen and Fritze, 1995; Smith et al., 2008). Pietikäinen and Fritze (1995) observed significantly lower total microbial C in plots burned after clearcutting. Microbial biomass and community structure were studied in humus by Bååth et al. (1995) using phospholipid fatty acid analysis and they observed a significantly lower fungal/bacterial ratio in burned plots than in harvested plots. Smith et al. (2008) compared soil microbial communities in four treatments: control, harvest, burn, and burn plus timber salvage in boreal forests of Alberta and microbial biomass carbon was found to decrease 18%, 74%, and 53% in the harvest, burn, and burn-salvage treatments, respectively. Microbial biomass N decreased in the harvested plots; whereas, it increased in the burned plots and this change was attributed to microbial assimilation of increased amounts of available NH$_4^+$ and NO$_3^-$ released during burning.

The influence of UAM on soil properties and nutrient leaching is less understood. UAM has also been shown to sequester more carbon (21% greater) and improve tree species diversity (32% greater) in Norway spruce stands when time between harvest re-entry is increased (Buongiornoa et al., 2012). Carbon-dioxide respiration levels following UAM regeneration methods have shown the potential of this management system to sustain larger sinks of soil carbon in forested ecosystems (Li et al., 2007). However, localized regions of nutrient depletion surrounding tree stumps in UAM stand harvested using the STS regeneration method were found by Albers (2010) and extractable carbon and nitrogen were also significantly lower in STS sites compared to CC sites. The general lack of knowledge regarding UAM regeneration methods on nutrient pools and cycling suggests a need for more research on this topic.
We hypothesize if low nutrient status soils are intensively managed with EAM using clearcutting, these soils may suffer long-term degradation that may not be realized in short timber harvest regeneration cycles. On the other hand UAM with STS removes fewer trees during each entry which can reduce nutrient removal after harvesting and due to less amount of slash left behind after harvesting, losses due to mineralization and leaching would be less relative to EAM (Figure 1.3).

![Figure 1.3. Hypothetical relationships between nutrient availability and clearcutting and single tree selection forest regeneration methods (J. Kabrick, unpublished).](image)

1.3.4 **Soil Solution Sampling**

Soil solution is defined as the “aqueous liquid form of the soil and its solutes” (SSSA, 2009). It has also been defined as “aqueous liquid form of soils whose composition is influenced by flow of matter and energy between it and its surroundings and by gravitational field of earth” (Sposito, 2008). Nutrients present in soil solution reflect the availability of nutrients for plant roots where processes such as root absorption, soil chemical reactions, and solute redistribution occur (Sparks, 2003). Thus, understanding the fluxes and composition of soil solution is very important for comprehensive geochemical studies. Soil solution can be collected using destructive and nondestructive sampling techniques. Destructive sampling
techniques include collecting a soil sample and extracting the soil solution in the laboratory, also known as *ex-situ* soil solution sampling. Non-destructive techniques involve extracting or capturing soil solution in the field by installing a solution sampler, meeting the specific research objectives of a project, is referred to as *in-situ* soil solution sampling. When sampling a soil solution for chemical analysis, it is necessary to extract solution from the soil without altering chemical composition (Wolt, 1994). A wide range of *ex-situ* soil solution samplers have been employed and tested for accuracy in field by many scientists (Wolt, 1994; Fares, 2004).

Various collection techniques have been employed to capture soil solution, and the differing scientific approaches include using a wide range of materials and modified sampling devices. However, sampling devices and construction materials have different advantages and disadvantages (Parizek and Lane, 1970; Barbee and Brown, 1986; Marques et al., 1996; Goyne et al., 2000; Weihermuller et al., 2007). *In-situ* soil solution samplers include the tension or suction cup lysimeter, the zero-tension sampler (ZTS) or lysimeter, and the passive capillary sampler or wick lysimeter. The material used in sampler fabrication can alter the composition of solution collected by soil solution samplers (Goyne et al., 2000; Reynolds et al., 2004). Negative pressure soil solution samplers with suction devices have been widely used for extraction of soil solution and include porous cups, vacuum lysimeters and suction plates (Barbee and Brown, 1986; Fares, 2004; Weihermuller et al., 2007). Barbee and Brown (1986) found that suction cup samplers perform poor in strongly structured clay soils. Mean concentration of DOC, silicon, iron and aluminum were found to be greater in ZTS than in suction cups by Fares (2004) and he concluded that ZTS appear to collect soil solution from macropores whereas suction cups collect soil solution from micropores.

Zero-tension samplers are the most widely used samplers, and sampling with ZTS depends on the formation of a saturated soil zone above the sampler before drainage can
occur by gravitational flow (Brye et al., 1999). The ZTS are very efficient in capturing rapidly draining soil water and solutes from macropores (Brosofske et al., 1997). Although ZTS may significantly under sample vadose soil water, they are less likely to contaminate the collected solution (Jemison and Fox, 1992; Dahlgren et al., 1994). However, leachates collected by ZTS may not represent actual concentrations of nutrients discharged by soil matrix to groundwater (Boll et al., 1997; Weil, 2003). Nevertheless, ZTS are cheaper to construct and easier to install than other commercially available lysimeters (Evans, 1986; Abdou and Flury, 2004). Zero-tension samplers can also be used at shallow depths (e.g., under organic or forest litter layers) and they are most conveniently used for observing nutrient inputs and outputs in forested ecosystems (Marques et al., 1996). Channeled flow of soil solution collected by ZTS in unsaturated soils was well documented by Russell and Ewel (1985) and soil solution collected by these samplers mostly represents macropore flow which has not fully reacted with surfaces of soil solids (Essington, 2004).

The efficiency of varying types of ZTS has always been under question. Nachabe et al. (1995) demonstrated that even if soil is not fully saturated, free flow of soil solution can occur and this free flow depends on soil moisture and rainfall observed previously at the site. Jemison and Fox (1992) reported that pan collection efficiency can be increased by increasing surface area of pan which further increases the chances of capturing water through capillary attraction. Zero tension samplers can be fabricated from a variety of materials but the overall objective is to reduce contamination of collected soil solution. Youngil et al. (2010) used ZTS troughs made from PVC and filled with acid washed sand to study the effect of liming at Hubbard Brook Experimental Forest in New Hampshire. Sanderman et al. (2008) used ZTS and isotopic techniques in forest and grassland soils for determining the composition of dissolved organic carbon (DOC) and reported that the humified fraction of
the soil OM pool and its exchange with the aqueous phase regulates DOC composition. More than one type of soil solution sampler is generally used to validate the results of a study.

Porous cup vacuum samplers along with ZTS were used by Qualls et al. (2000) to collect soil solution after harvesting and the soil solution was analyzed for DOC, dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP). Three different soil solution samplers, PVC tension-free samplers, porous polytetrafluorethene tension samplers and porous polymer tension samplers, were used by Buckingham et al. (2008) to compare DOC chemistry in soils of northern England. Concentrations of DOC captured from tension-free samplers was greatest when compared to tension samplers, and it was postulated that differences were attributable to variation in construction of samplers, localized compaction created by vacuum samplers and sorptive removal of DOC by tension samplers (Buckingham et al., 2008).

There are a few demerits associated with ZTS: (1) during high rainfall events, the tension-free samplers drain too slowly to capture all soil solution (2) roots can penetrate these samplers and extract nutrients from acid-washed quartz (3) physical damage can occur to these samplers from underground fauna, and (4) in studies where these samplers are placed for many years, soil can move into acid-washed quartz within the ZTS. Considering all implications of samplers, ZTS were selected for this research as they suited our needs and research objectives.

Nutrient cycling in forested ecosystems can be estimated using a variety of techniques, and ion exchange resin (IER) samplers are an alternative to traditional soil solution sampling. Ion exchange resins have been employed in soil science in many studies focused on plant nutrient-uptake (Durán et al., 2008; Rodgers et al., 2008; Siddique et al., 2008), ion leaching (Szillery et al., 2006) and N immobilization and mineralization studies (Burns and Murdoch, 2005; Homyak et al., 2008). Many studies concluded that the availability of nutrients to plant
roots is well mimicked by IER samplers (Binkley, 1984; Hart and Binkley, 1985; Binkley et al., 1992; Giblin et al., 1994). The IER samplers behave similar to soil particles and are more reliable to use over traditional soil solution sampling techniques (Skogley and Dobermann, 1996). Important merits of using IER are: (1) sample holding time prior to analysis is flexible (Giblin et al., 1994); (2) less time is required for installation and collection of samplers (Johnson et al., 2001); (3) and the disturbance created by IER samplers is minimal (Gibson, 1986).

Resin samplers are designed by placing a layer of resin sandwiched between two layers of acid-washed sand inside a polyvinyl chloride (PVC) tube, and IERs designed to trap nutrients from soil solution under saturated conditions (Susfalk and Johnson, 2002). Low fabrication cost makes IER samplers suitable for studies examining spatial heterogeneity of nutrient flux in the soil landscape (Lehmann et al., 1999; Weihermuller et al., 2007). Considering the merits and shortcomings of each type of solution sampler, it is always beneficial to use multiple sampler designs which can serve as cross checks for complete evaluation of in situ soil solution chemistry.

1.3.5 Soil Phosphorus

Phosphorus is important limiting factor of forest growth in many parts of world (Fox et al., 2007; May et al., 2009; Trichet et al., 2009). Annually, more than 100 kg of N and 10 kg of P per hectare is needed for pine stands to maintain maximum volume production (Ducey and Allen, 2001; Battaglia et al., 2004). The role of forest floor in tree nutrition is well documented by Berg and Laskowski (2005). Phosphorus content in the forest floor depends on climate, soil type, tree species and age of forests and it varies from 10 kg ha\(^{-1}\) to more than 300 kg ha\(^{-1}\) (Pritchett and Fisher, 1988). Yanai (1992) estimated a P budget over period of 70 years in Hubbard Brook Experimental Forest. It was found that 61% of P which is
assimilated by trees every year comes from forest floor and this pool represented only 5% of total P present in the soils studied. Phosphorus turnover rates were also calculated by Yanai (1992) and it was estimated that forest floor contributed 7% yr\(^{-1}\), whereas mineral soils contributed 0.3% yr\(^{-1}\). It was reported that on annual basis only 0.007 kg ha\(^{-1}\) yr\(^{-1}\) of P is leached from a forest ecosystem in northern hardwood forests (Wood et al., 1984).

Phosphorus is a rock-derived nutrient and the amount and availability of P decreases with time, therefore younger-aged sites are generally rich in soil P. As primary mineral weathering proceeds, P availability increases and intermediate-aged sites often have the greatest content of readily available P. As soil weathering continues through time, P availability decreases and is lowest in older-aged soils (Crews et al., 1995; Chadwick et al., 1999; Porder et al., 2006; Vitousek et al., 2010). Phosphorus is universally low in soils and most P is occluded in inorganic and organic substrates with less P availability in subsurface horizons (Brady and Weil, 2010). Soil P can be divided into two broader chemical forms: inorganic P (Pi) and organic P (Po) (Pierzynski et al., 2005; Turner et al., 2007; Dou et al., 2009), and these P forms differ in their behavior and fate in soils. Most of P (35% to 70% of the total P) is inorganic and bounded with Fe and Al oxides in acidic soils and apatite \([\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F})]\) in alkaline soils (Harrison, 1987). Phosphorus has low bioavailability for organisms due to slow diffusion and high fixation in soils. The Pi in soils is often bonded in the minerals apatite, strengite, and variscite (Walker and Syers, 1976). Geochemical weathering results in the dissolution of P-bearing minerals and releases P into the soil environment where it can be absorbed by plants, adsorbed to Al and Fe oxides, precipitated as a secondary Ca-P mineral, or leached from the root zone (Smeck, 1985).

Soil pH and the size of mineral particles play a very important role in regulating the dissolution of P-bearing minerals (Pierzynski and McDowell, 2005; Oelkers and Valsami-Jones, 2008). With increasing pH, P bounded with Fe and Al oxides is solubilized and
becomes available for plants; whereas, solubility of calcium phosphates decreases with increasing pH (Hinsinger, 2001). The specific surface area of clay minerals and Fe/Al oxides is often quite large which provides a large number of adsorption sites for P (Arai and Sparks, 2007). The adsorption of P to soil can be easily enhanced by increasing ionic strength, with further reaction P is occluded in nanopores of Fe/Al oxides thus making P unavailable to plants. (Luengo et al., 2006; Arai and Sparks, 2007). Jugsujinda et al. (1995) reported a significant correlation between P-sorption capacity and oxides of Fe, Al and Mn for acid sulfate soils. Phosphorus adsorbed on various clays and Al/Fe oxides can be released into solution via desorption reactions which play an important role in nutrient dynamics. Figure 3 explains the concept of P quantity, intensity and buffer capacity in forest soils and the following reactions regulating P buffer capacity in forest ecosystems: dissolution/precipitation; mineralization/immobilization; and ligand exchange (Fox et al., 2011).

Phosphorus also accumulates via addition of organic materials deposited by vegetation. Trees may also change the distribution of P in soil by concentrating P in O and A horizons through litterfall. The importance of organic P (Po) in forest ecosystems has been discussed by many researchers (Wood et al., 1984; Yanai, 1991; Binkley and Fisher, 2012), and Harrison (1987) reported that this fraction represents 30% to 65% of total P in soils. Mineralization of Po depends on microbial activity and extracellular phosphate enzymes produced by plant roots and soil microorganisms (Tate, 1984). Release of Pi from Po is governed by decomposition reactions and that can help sustain plant available P within a forest ecosystem (Cross and Schlesinger, 1995; Binkley and Fisher, 2012).
Figure 1.4. Schematic representing the quantity, intensity and buffer capacity of P pools in forest soils and processes that convert P into labile forms (adapted from Fox et al., 2011).

Tree species have evolved to compensate for deficits in P through a variety of mechanisms: (1) adaptations in root morphology; (2) symbiosis with mycorrhizal fungi; (3) preferential root growth into more fertile soil; (4) enhanced phosphatase activity in rhizosphere; (5) and secretion of low molecular weight organic acids that enhance mineral dissolution (Vance et al., 2003). Despite these modifications to the rhizosphere, overall P availability in forest soils is low and P availability often limits plant growth and production (Vance et al., 2003).

Phosphorus pools can be affected by several factors including landform or slope position, clay content, parent material (PM), depth to bedrock, pH, organic carbon, oxides/hydroxides of Fe Al Mn, exchangeable calcium, and cation exchange capacity (CEC). Day et al. (1987) evaluated the distribution of various P pools in northwest Florida and found that total-P
content in soil was directly associated with clay content present in lower landscape positions. Total-P was greater in coarser sand fractions dominated by quartz and ironstone. Furthermore, residual P was most abundant among all P forms which implies that the soils were weathered and evolved from parent material containing considerable residual-P occluded in sesquioxides. Guzel and Ibrikci (1994) reported that two-thirds of total P and organic P was associated with the clay plus silt fractions of soil, and Fe, Al and P content was greater in surface horizons than in subsurface horizons. In a study conducted by Brubaker et al. (1993) on soils of eastern Nebraska, the availability of P decreased with soil depth, whereas calcium carbonates, extractable Ca and Mg increased with soil depth. Smeck and Runge (1971) indicated that pedons on upper landscape positions tend to lose P and, in contrast, pedons on lower landscape position tend to accumulate P. Phosphorus movement in the landscape was studied by Smeck (1985) and it was concluded that greatest content of P was at lower end of the hydraulic gradient. King (1997) indicated that stratified parent material, landscape position, clay content, CEC and organic carbon are important factors affecting distribution and availability of P in the Missouri Ozarks.

Parent material has profound effect on the type of soil that develops in an ecosystem and the amount of P present in a soil is directly related to parent material (Kitayama and Aiba, 2002; Porder et al., 2007; Vitousek et al., 2010). Dieter et al. (2010) indicated a strong control of parent material on soil P in tropical rainforests of central Panama. Vinegla et al. (2006) found that two similar forest sites differing in parent material showed no differences in total P concentration, although available P concentrations were significantly different. Richards et al. (1997) investigated differences in total P, pH, total N, organic carbon, and various cations on the basis of parent material. They reported that soils derived from limestone parent material had the greatest values of all factors when compared to soils derived from sandstone parent material. Safford and Harrison (2004) observed contrasting
results while comparing soil P in burned versus unburned plots, and reported that soils derived from sandstone parent material had greater levels of P than soils derived from limestone parent material. Soils under grasslands in Canterbury, New Zealand were studied to determine the influence of parent material on P content on the accumulation of C, N, S and organic P materials, and results show that total P content of the soils was closely related to P content of parent material (Walker and Adams, 1958).

Geologic strata of the Missouri Ozarks consist of sedimentary rocks dominated by cherty limestone and dolomite with small contributions of sandstone and shale which are low in P content (King, 1997). Some soils in the region have weathered from multiple parent materials (e.g., pedisedsiments over residuum) and many Ozark Highland soils are leached and acidic. Thus the influence of parent material, underlying bedrock and other factors on total and available P in the Missouri Ozarks is not clear.

1.3.6 Summary of Literature Review and Relationship to Current Study at MOFEP

Given a broad spectrum of forested ecosystems with a diversity of results from various studies, it is difficult to apply the findings of previous researchers to Missouri Ozark Highland soils. Forests supported by MOFEP soils are mixed hardwood forests, which differ in geology and landform and limit the applicability of nutrient cycling studies (Johnson et al., 1997) directly to MOFEP. Differences in soil type, climatic conditions and weathering rates account for disagreement when comparing studies from various forested ecosystems. Additionally, soils of the Ozark Highlands are highly weathered and underlying bedrock formations are less likely to continue supplying soil base cations to support biomass after harvesting.

To study soil solution before forest harvests at MOFEP, zero tension samplers were chosen as the primary sampler to monitor soil solution chemistry (Gaddie, 2012) and, in
continuation, the post-harvest study described in this thesis has utilized the same soil solution samplers and monitoring locations. Collection efficiency, losses, implications and fabrication of ZTS have been well documented by many researchers over time (Jemison and Fox, 1992; Marques et al., 1996; Goyne et al., 2000), and these sampler were determined suitable for this study. Check samplers (IER) were also installed and, if they are constructed well, they are very reliability in predicting nutrient fluxes (Lehmann et al., 2001; Susfalk and Johnson, 2002).

Soils at MOFEP are generally acidic soils, and in soils of this nature P is dominantly adsorbed by Al/Fe oxides and hydroxides, such as gibbsite, hematite, and goethite (Parfitt, 1989; Brady and Weil, 2002). King (1997) observed that P pools are affected by stratified parent material, landscape position, clay content, CEC and organic carbon in a Missouri Ozark watershed but conclusions from this research cannot be transferred to MOFEP due high variability in landform and a larger study area. Geologic strata of the Missouri Ozarks consist of sedimentary rocks dominated by cherty limestone and dolomite with small contributions of sandstone and shale which are low in P content (King, 1997). Some soils in the region have weathered from multiple parent materials (e.g., pedisediments over residuum) and many Ozark Highland soils are leached and acidic. Thus, the influence of parent material, underlying bedrock and other factors on total and available P is not clear in the Missouri Ozarks.
CHAPTER 2: SOIL SOLUTION CHEMISTRY: PRE- AND POST-HARVEST LEACHING IN MIXED HARDWOOD FORESTS OF THE MISSOURI OZARKS

2.1 Abstract

Forest production has an important economic function in Missouri but nutrient depletion due to forest harvest may reduce sustainable tree growth especially in low nutrient status soils. In particular, changes in soil solution chemistry and nutrient flux are observed due mineralization of slash remaining after harvest. Soils of Missouri Ozark Highlands are diverse in nature and they support the growth of mixed hardwood forests; however, most soils of this region are highly weathered with inherently low nutrient supply capacity. To address concerns regarding the depletion of soil nutrients in association with timber harvests in the Missouri Ozark Highlands, the objective of this study was to quantify the influence of clearcutting (CC) and single tree selection (STS) forest harvesting on soil solution chemistry and nutrient flux in low and medium nutrient status soils within the Missouri Ozark Forest Ecosystem Project (MOFEP). The forests of MOFEP are managed using three forest management systems, even-aged management (EAM) with CC, uneven-aged management (UAM) with STS and group selection, and no-harvest management (NHM). Pre-harvest and post-harvest solution samples were collected with throughfall and zero-tension soil solution (ZTS) samplers (15 and 40 cm depths), and samples were analyzed for pH and electrical conductivity (EC), anions (F⁻, Br⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, PO₄³⁻), cations (K⁺, Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, and total aluminum), dissolved organic carbon (DOC), and total nitrogen (TN). Ion exchange resin (IER) samplers (15 and 40 cm soil depths) were used to capture cumulative flux. Pre-harvest and one year post harvest soil samples were collected and analyzed for soil pH, exchangeable concentrations of Ca²⁺, Mg²⁺, and K⁺, effective cation
exchange capacity (ECEC), base saturation (base sat.), extractable acidity (EA), extractable aluminum (EAl), aluminum saturation (Al sat.), total organic carbon (TOC), and total nitrogen (TN). Post-harvest soil solution samples contained significantly greater concentrations of NO\textsubscript{3}\textsuperscript{-}, Mg\textsuperscript{2+}, and TN and greater values of EC in the CC sites relative to STS and NHM sites. Mean daily flux captured by IER samplers showed significantly greater flux of NO\textsubscript{3}\textsuperscript{-} and Mg\textsuperscript{2+} in post-harvest clearcutting relative to pre-harvest data. Despite morphological and some chemical differences between low and medium nutrient status soils, no influence of soil nutrient status was observed in this research. Study results demonstrate increased nutrient leaching after clearcutting. Missouri forest managers may need to reevaluate and modify this practice to minimize the losses triggered by timber harvesting in order to maintain long-term sustainability and productivity of Ozark forests.

2.2 Introduction

Ozark Highland soils are dynamic and highly weathered materials formed from a variety of parent materials (e.g., residuum, alluvium, loess and pedisediments) (Hammer, 1997), although most landscapes of this region are covered with extensively weathered pedisediments and residual soils. The most common soil orders in this region are Alfisols and Ultisols (Meinert et al., 1997) with low cation exchange capacity (CEC), low base saturation (BS), and relatively low concentrations of exchangeable calcium and magnesium (Kabrick et al., 2011). Due to variability in soil nutrient status and differences in timber harvest, changes in soil solution chemistry and nutrient flux from forested Ozark Highland soils may not be proportionate or comparable across the landscape or between differing timber regeneration methods. Subsequently, some soils in this region may be prone to nutrient depletion if not managed properly.
Forest ecosystems are generally well balanced with very low or negligible nutrient loss (Hedin et al., 1995). However, any disturbances occurring in this ecosystem will disrupt nutrient cycling and the degree of disruption may be proportional to intensity of disturbance (Kimmins, 1995). Biomass removal associated with forest harvest can potentially alter the forest ecosystem through the loss of nutrients via increased rates of nutrient leaching (Belleau et al., 2006). Opening of the forest canopy and surface biomass removal increases exposure of soil to sun and other elements, increasing possible nutrient loss via leaching and erosion. For example, clear-cutting, which is associated with even-aged management (EAM), increases soil moisture compared to other uneven-aged methods in the larch/fir forests of the Northern Rockies (Schmidt, 1980). Johnson et al. (1997) documented increased mobilization rates of exchangeable cations from the forest floor which accumulated in underlying spodic B-horizons following clear-cutting. Two years after stem only harvest, Belleau et al. (2006) observed increases in total Ca, K, Mg, and pH in the forest floor soil horizons, but no change was observed in the mineral soil.

Uneven-aged management (UAM) methods are less understood with relationship to changing soil properties and nutrient leaching after harvest. Uneven-aged management has also been shown to sequester more carbon (21% greater) and sustain greater tree species diversity (32% greater) in Norway spruce forests when rotation length is increased from 5 years to 20 years (Buongiornoa et al., 2012). Carbon-dioxide respiration levels following UAM methods have shown the potential of these management systems to sustain larger sinks of soil carbon in forested ecosystems. However, localized regions of nutrient depletion surrounding tree stumps in UAM stands harvested with single tree selection (STS) were found by Albers (2010), and extractable carbon and nitrogen were also significantly lower in STS compared to CC sites. Therefore, there is need to further identify nutrient changes in UAM stands, particularly those regenerated using STS.
Soil solution is defined as “aqueous liquid form of soils whose composition is influenced by flow of matter and energy between it and its surroundings and by gravitational field of earth” (Sposito, 2008). Soil solution composition is an efficient indicator of nutrient supply available to the plant root system where processes such as root absorption, soil chemical reactions, and solute redistribution occur (Sparks, 2003). Thus, understanding the fluxes and composition of vadose zone soil water is very important for environmental studies. Soil solution can be collected using destructive and nondestructive techniques. A wide range of *in-situ* soil solution techniques have been employed and tested for accuracy in the field (Wolt, 1994; Fares, 2004). *In-situ* soil solution samplers include the tension or suction cup lysimeters, zero-tension samplers (ZTS) or lysimeters, and passive capillary samplers, and the material used in sampler fabrication can alter the composition of solution collected by soil solution samplers (Goyne et al., 2000; Reynolds et al., 2004). Zero-tension samplers are most widely used, and their function depends on soil saturation above the sampler before drainage occurs via gravitational flow (Brye et al., 1999). The ZTS are very efficient in capturing rapidly draining soil water and solutes from macropores (Brosofske et al., 1997), and ZTS are less expensive to construct and easier to install than other commercially available samplers (Evans, 1986; Abdou and Flury, 2004).

Ion exchange resin (IER) samplers are an alternative to traditional soil solution sampling techniques. The IER samplers have been employed in soil science in many studies focused on plant nutrient-uptake (Durán et al., 2008; Rodgers et al., 2008; Siddique et al., 2008), ion leaching (Szillery et al., 2006), and N immobilization and mineralization studies (Burns and Murdoch, 2005; Homyak et al., 2008). Ion-exchange resin samplers are designed by placing a layer of resin sandwiched between two acid-washed sand layers inside a polyvinyl chloride tube (pvc) and they are designed to trap nutrients from soil solution under saturated conditions (Susfalk and Johnson, 2002). Low fabrication cost and the ability to estimate
solute flux makes IER samplers suitable for studies examining spatial heterogeneity in soil landscape (Lehmann et al., 1999; Weihermuller et al., 2007). Acknowledging that merits and shortcomings exist for each type of solution sampler, it is always beneficial to employ multiple sampler designs in an experiment to serve as cross checks for complete evaluation of in situ soil solution chemistry.

The overall objective of this study was to enhance understanding of nutrient dynamics in forested soils of the Missouri Ozark Highlands with specific focus on quantifying the influence of CC and STS forest regeneration methods on soil solution chemistry and nutrient flux in soils with differing nutrient and morphological properties.

2.3 Materials and Methods

2.3.1 Site Characteristics and Experimental Design

Research for this study was conducted at the Missouri Ozark Forest Ecosystem Project (MOFEP), a long-term experimental project started by MDC in year 1989. MOFEP was started to comprehensively evaluate forest management practices on wide array of upland ecosystem attributes. The MOFEP sites are located within the Ozark Highlands of southern Missouri (37°6’3 ′′7 N latitude and 91°6′4 ′′5 W longitude), and more specifically within the Forest Breaks of the Current River and the Current River Oak-Pine Woodland Hills land type associations (Nigh and Schroeder, 2002). The forests of this region are predominantly composed of oaks (Quercus sp.) and hickories (Carya sp.).

The nine MOFEP sites or compartments are arranged in a complete, randomized block design consisting of three blocks and three sites per block. Each site within a single block is managed with one of three types of treatments [EAM, UAM and no harvest management (NHM)] and within each treatment differing timber regeneration methods are used (i.e., CC for EAM sites and STS for UAM sites) (Brookshire et al., 1997). Each of the nine sites range
in size from 291 to 514 hectares (Sheriff and He., 1997). The MOFEP project is intended to last one to three full rotations (i.e., 100-300 yr.) within these operational forest compartments. Harvest events occur approximately every fifteen years and over the course of each harvest re-entry, 10 – 12% of a site is harvested with the designated treatment. Five years of pretreatment ecological data were collected including vegetation composition and structure, site characteristics, and wildlife communities before the first timber harvest began in May 1996 and concluded in Nov. 1996 (Brookshire et al., 1997; Shifley and Brookshire, 2000). The second harvest at MOFEP started on 3/31/2011 and ended at 12/26/2011, and this particular harvest is the focus of this study.

Physical site characteristics and soil samples were collected before the first harvest entry by Meinert et al. (1997) and Kabrick et al. (2000), and soil samples were characterized for general physical and chemical properties. Nutrient status of the soils was determined by percent base saturation (BS) and associated parent material for grouping the soils into low, medium and high nutrient status soils (Kabrick et al., 2000). For this study two soil groups, low nutrient status (≤20% BS in the diagnostic subsoil horizon) and medium nutrient status (20 - 50% BS in the diagnostic subsoil) were considered. Four MOFEP soil mapping units representative of low and medium nutrient status soils were considered during sample site location: (1) low nutrient status map units included 80F (loamy-skeletal, Typic Paleudults) or 63F (loamy-skeletal, Typic Hapludults); and (2) medium nutrient status map units included 82F (very-fine, Typic Paleudults) or 75F (loamy-skeletal, Typic Hapludults). High nutrient status soils (≥ 50% BS) were not considered for this research as these soils are mostly associated with glades, and these soils have variable depth to bedrock (0-1 m) and seldom support the growth of marketable timber. Meinert et al. (1997) described 80F/63F mapping units in loamy-skeletal and loamy-skeletal/clayey textural classes with low base saturation (< 20% BS) whereas 82F/75F mapping units in loamy-skeletal and loamy-skeletal/clayey
textural classes with low to high base saturation. Following extensive ground-truthing, two sampling sites (one site each in low and medium nutrient status soils) were identified in each of the nine experimental sites.

Each of the eighteen soil solution sampling sites were excavated up to depth of 1 m using backhoe or, for sites inaccessible by the backhoe, by manual excavation. During excavation the integrity and firmness of soil pit sidewalls, upslope, and lateral areas were not disturbed. All excavated material was piled downslope at a reasonable distance where it would not disturb the sampling area. Morphological characteristics of each soil exposed soil profile were described in detail (Table 2.1) (USDA-NRCS, 1999).

Pre-harvest soil samples were collected in 10 cm increments from a 0 to 40 cm depth, air-dried, and sieved to < 2 mm. Samples were then characterized for the following properties using procedure described in Burt (2004): soil particle size using standard pipette analysis; pH measured in water and 0.01 M CaCl₂ soil slurry (1:1 and 1:2 w/v, respectively); exchangeable concentrations of Ca²⁺, Mg²⁺, and K⁺ [1 M ammonium acetate (CH₃COONH₄) and ammonium chloride (NH₄Cl) extraction techniques]; effective cation exchange capacity (ECEC) was calculated by summation of BaCl₂-triethanolamine released extractable acidity and NH₄Cl exchangeable bases; extractable aluminum (EAl) (1 M KCl extract and ICP-AES analysis); and total organic carbon (TOC) and total nitrogen (TN) (dry combustion method). Post-harvest soil samples were also collected one year after the harvest around the 18 soil pits. Triplicate subsamples were collected in 10 cm increments to a depth of 40 cm and samples were bulked by sampling increment for each site to create a composite sample for soil characterization. These samples were not collected from the walls of soil pits as wooden enclosures protecting the soil pit walls from collapse prohibited pit wall access. Post-harvest samples were air-dried, sieved to <2 mm, and characterized as described previously with exception for particle size analysis which was omitted.
(a) Low nutrient status soil.

Table 2.1. Example, qualitative soil pit and sampling site descriptions (obtained from Gaddie 2012).

<table>
<thead>
<tr>
<th>#</th>
<th>Horizonation</th>
<th>Boundary</th>
<th>Texture</th>
<th>Color</th>
<th>Structure</th>
<th>Soil Features</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Prefix</td>
<td>Master</td>
<td>Sub</td>
<td>No</td>
<td>Depth (cm)</td>
<td>Dist</td>
</tr>
<tr>
<td>1</td>
<td>O</td>
<td>i</td>
<td>-</td>
<td>3-0</td>
<td>A/S</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>C/S</td>
<td>70% VGR</td>
</tr>
<tr>
<td>3</td>
<td>E</td>
<td>-</td>
<td>-</td>
<td>33</td>
<td>C/S</td>
<td>30% GR</td>
</tr>
<tr>
<td>4</td>
<td>B w 1</td>
<td>52</td>
<td>C/S</td>
<td>25%</td>
<td>GR</td>
<td>loam</td>
</tr>
<tr>
<td>5</td>
<td>B w 2</td>
<td>72</td>
<td>C/S</td>
<td>50%</td>
<td>GR</td>
<td>loam</td>
</tr>
<tr>
<td>6</td>
<td>B t</td>
<td>100+</td>
<td>-</td>
<td>40%</td>
<td>GR</td>
<td>-</td>
</tr>
</tbody>
</table>

Abbreviation Code:
- A=abrupt
- C=clear
- G=gradual
- S=smooth
- W=wavy
- GR=gravelly
- Gr=granular
- CB=cobbly
- PR=prismatic
- VGR=very gravelly
- SBK=subangular blocky
- ABK=angular blocky
- RMF = redoximorphic features
- Amount: VF=very few
- Size: VF=very fine
- Shape: T=tubular
- F=few
- C=common
- M=many
- VM=very many
- V=vesicular
- M=medium
- C=coarse
- VC=very coarse

World Geodetic System (WGS 84) coordinates (decimal degrees)
- Latitude: N 37.17078°
- Longitude: W -91.13048°
(b) Medium nutrient status soil.

<table>
<thead>
<tr>
<th>Horizonation</th>
<th>Boundary</th>
<th>Texture</th>
<th>Color</th>
<th>Structure</th>
<th>Soil Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - O</td>
<td>2-0 C/S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2 - A</td>
<td>22 C/S</td>
<td>55% VGR</td>
<td>15</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>3 - E</td>
<td>30 C/S</td>
<td>25% GR</td>
<td>26</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>4 - B t 1</td>
<td>67 C/S</td>
<td>20% CB</td>
<td>37</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5 - B t 2</td>
<td>87 C/W</td>
<td>45% GR</td>
<td>45</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>6 - B t 3</td>
<td>100+ C/W</td>
<td>15% GR</td>
<td>65</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

Abbreviation Code:
A=abrupt
C=clear
G=gradual
S=smooth
W=wavy
GR=gravely
VGR=very gravelly
CB=cobbly
PR=prismatic

---

World Geodetic System (WGS 84)
Latitude: N 37.1806°
Longitude: W -91.1313°

---

Soil pit ID = 1M
MOFEP soil mapping unit = 82F
Slope = 26%
Aspect = 192° SW

Soil nutrient status grouping = medium
Designated MOFEP harvest treatment = NHM
Harvest date for 2011 re-entry period = n.a.
2.3.2 Soil Solution Sampling

Two ZTS were installed per soil pit at depths of 15 and 40 cm using a design similar to Goyne et al. (2000). Samplers were installed in a lateral position by excavating into pit walls (Figure 2.1). A total of 36 ZTS were constructed from high density polyethylene (HDPE) plastic and each ZTS had a sampling area of 0.086 m² (0.27 × 0.32 m). A drainage hole in the ZTS was covered with 53 μm diameter Nitrex® nylon mesh to minimize particle entry into the collection bottles. Each sampler was acid washed and stored in a clean and sealed container prior to installation. To minimize interference between the samplers at 15 and 40 cm depths, ZTS at the 40 cm depth were installed upslope of 15 cm sampler. Each ZTS was filled with acid washed silica sand and placed in contact with the upper surface of laterally excavated holes. Wooden shims were used to lift up the samplers to ensure maximum contact with soil surface and ZTS were regularly monitored throughout the study to ensure good contact with the soil surface. High density polyethylene plastic jugs (25 L) were used as collection bottles, and samplers were connected to the bottles with braided PVC nylon hose. The silica sand which was used in this research was pre-treated in a 0.01M HCl acid bath for 24 hours, followed by 24 hours of soaking in deionized water. The sand was removed from deionized water and was packed in 5.0 cm diameter, 100 cm long polyvinyl chloride (PVC) columns, which were flushed with 7.0 L of deionized water for 1 hour to ensure acid removal. The sand was then oven-dried at 105 °C for 24 hours and stored in clean containers.

Ion exchange resin (IER) samplers were installed at depths of 15 and 40 cm. The construction and design of IER samplers was similar to Susfalk and Johnson (2002). Rexyn 300 (H-OH) ion exchange resin (90 ml volume), acid-washed silica sand, 53 μm diameter Nitrex® nylon mesh, and acid-washed PVC couplings were used in construction of resin bags. Three IER samplers were installed per depth with each IER having sampling area of
83.3 cm² which summed to area of 0.024 m² at each depth increment (six IER samplers per soil pit for a total of 108 IER samplers analyzed per burial period). Two extra resin bags were prepared per collection period and stored at 4°C to serve as check samples during the analysis. The IER samplers were installed for a period of six months with a total of two pre-harvest IER collection periods and two post-harvest IER collection periods.

Throughfall samples were also collected near each sampling site. Eighteen trough-style throughfall samplers each with a sampling area of 0.066 m² (7.5 × 88.75 cm) were constructed from PVC piping and installed approximately 0.75 m above ground level (Kostelnik et al., 1989). A standard rain gauge (10.4 cm diameter x 35.5 cm height) was also installed as an alternative for measuring precipitation.
Figure 2.1. (a) Schematic diagram of instrument placement within soil sampling pits, (b) schematic and photos of zero tension sampler, and (c) schematic and photos of ion exchange resin samplers.
2.3.3 Sample Collection and Description

A total of 18 sets of post-harvest soil solution and throughfall samples were collected over a period of one year and four months and this data was compared to 27 sets of soil solution and throughfall samples collected by Gaddie (2012). The volume of each sample collected in the throughfall and ZTS samplers was measured using graduated cylinders and recorded. A portable electrical conductivity (EC) meter (Accumet® AP75, Fisher Scientific, Singapore) and a portable pH meter (Accumet® AP115, Fisher Scientific, Singapore) were used for determining the EC and pH of stirred and unfiltered field samples. A portion of all solution samples collected in the field was transferred to acid-washed 1L HDPE bottles. Each sample was labeled to ensure proper identification and solution samples were stored in coolers filled with ice or refrigerated after collection. Samples were then transported to laboratory and stored not more than 24 hours at 4°C prior to filtration. Samples were vacuum filtered through 0.45 µm mixed cellulose ester membranes (Millipore Corp., Billerica, MA). Approximately, three subsamples [(a) unacidified, (b) acidified with 85% H₃PO₄ to pH 2, and (c) acidified with concentrated HNO₃ to pH 2] were stored in acid washed 60 ml HDPE bottles at 4°C prior to analysis.

Unacidifed samples were analyzed within 24 to 48 hours of collection for determination of ammonium and anion concentrations. Ammonium was analyzed using a Quikchem Lachat and colorimetric method 10-107-06-1-K (15 March 2001 revision; Lachat Instruments; Hach Company, Loveland, CO), and concentrations of PO₄³⁻, SO₄²⁻, NO₃⁻, NO₂⁻, Cl⁻, F⁻ and Br⁻ were quantified using a Dionex ICS-1000 ion chromatography system equipped with an IonPac® AG14A 4 mm guard column (4 × 50 mm) and an IonPac® AS14A analytical column (4 × 250 mm) (Dionex Corp., Sunnydale, CA). Dionex AS14A eluent (8.0
M sodium carbonate; 1.0 M sodium bicarbonate in deionized water) with flow rate of 1 mL min\(^{-1}\) was utilized in all anion analyses.

Samples acidified to pH 2 with 85% H\(_3\)PO\(_4\) were analyzed for non-purgeable organic carbon (NOPC) also referred as dissolved organic carbon (DOC) and total nitrogen (TN) within 72 hours of collection. These subsamples were analyzed using a Shimadzu TOC-V\(^{TM}\) liquid carbon analyzer equipped with a TNM-1 module, ASI autosampler and sparging needle (Shimadzu Corp.; Kyoto, Japan). Samples were acidified to remove inorganic carbonates.

Samples acidified to pH 2 with concentrated HNO\(_3\) were analyzed within one month of collection. These subsamples were analyzed for base cations (Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), and Na\(^+\)) and total aluminum (Al\(_T\)) using an inductively coupled plasma (ICP) – atomic emission spectrophotometer (AES) (Varian Liberty RL, Australia). Detection limits for all instruments and ions quantified are presented in Table 2.2. In instances where a measured analyte concentration value was > 0 and < the measured detection limit, a value equal to one half the detection limit was substituted for the measured value. However, when analyte concentration value was < 0 (negative), it was replaced by zero.
Table 2.2. Detection limits for instruments used for sample characterization (obtained from Gaddie 2012).

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Analyte</th>
<th>Detection Limit (µmol L⁻¹)</th>
<th>1/2 Detection Limit (µmol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-AES</td>
<td>aluminum (Al⁺⁺)</td>
<td>0.950</td>
<td>0.475</td>
</tr>
<tr>
<td></td>
<td>calcium (Ca²⁺)</td>
<td>0.751</td>
<td>0.375</td>
</tr>
<tr>
<td></td>
<td>magnesium (Mg²⁺)</td>
<td>0.084</td>
<td>0.042</td>
</tr>
<tr>
<td></td>
<td>potassium (K⁺)</td>
<td>37.431</td>
<td>18.716</td>
</tr>
<tr>
<td></td>
<td>sodium (Na⁺)</td>
<td>2.433</td>
<td>1.216</td>
</tr>
<tr>
<td>Dionex ICS-1000</td>
<td>fluoride (F⁻)</td>
<td>2.915</td>
<td>1.457</td>
</tr>
<tr>
<td></td>
<td>bromide (Br⁻)</td>
<td>0.354</td>
<td>0.177</td>
</tr>
<tr>
<td></td>
<td>chloride (Cl⁻)</td>
<td>0.421</td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>nitrite (NO₂⁻)</td>
<td>0.508</td>
<td>0.254</td>
</tr>
<tr>
<td></td>
<td>nitrate (NO₃⁻)</td>
<td>0.386</td>
<td>0.193</td>
</tr>
<tr>
<td></td>
<td>sulfate (SO₄²⁻)</td>
<td>0.328</td>
<td>0.164</td>
</tr>
<tr>
<td></td>
<td>phosphate (PO₄³⁻)</td>
<td>0.785</td>
<td>0.392</td>
</tr>
<tr>
<td>Shimadzu TOC-V</td>
<td>non-purgeable organic carbon (NPOC)</td>
<td>13.436</td>
<td>6.718</td>
</tr>
<tr>
<td></td>
<td>total nitrogen (TN)</td>
<td>7.192</td>
<td>3.596</td>
</tr>
<tr>
<td>Lachat Quikchem</td>
<td>ammonium (NH₄⁺)</td>
<td>1.833</td>
<td>0.917</td>
</tr>
</tbody>
</table>

Ion exchange resin bags were installed for a total of four collection periods: April to October 2010 (pre-harvest #1); October 2010 to July 2011 (pre-harvest #2); January 2012 to July 2012 (post-harvest #1); July 2012 to January 2013 (post-harvest #2). First two collection periods were installed and analyzed by Gaddie (2012). Each resin bag collected in the field was placed in a sealed plastic bag and stored in a cooler filled with ice prior to transportation to the laboratory. At the laboratory, ion exchange resin bags were refrigerated and stored at 4°C until extraction. All the IER bags were opened within acid washed 1L HDPE bottles and extracted using 0.41 L of 1 M KCl. Samples plus extractant solution were agitated for one hour on an end-to-end shaker (Susfalk and Johnson, 2002). Resin extracted solution was vacuum filtered through a 0.45 µm mixed cellulose ester membrane (Millipore Corp.,
Billerica, MA) and further divided in two subsamples: (a) unacidified and (b) acidified with concentrated HNO₃. Subsamples were stored in 60 ml HDPE bottles and stored at 4°C prior to analysis. Extractant solutions were analyzed for NO₃⁻ using a Quikchem Lachat autoanalyzer following colorimetric method 12-107-04-1-B (21 August 2003 revision - Lachat Instruments; Hach Company, Loveland, CO) modified for a 1M KCl background matrix solution (15 March 2001 revision - Lachat Instruments; Hach Company, Loveland, CO), and Ca²⁺, Mg²⁺, Na⁺, and Al concentrations were measured using an ICP–AES (Varian Liberty RL, Australia). Concentrations of other nutrients and elements were not analyzed due to interferences associated with the concentrated extracting solution and relatively high background concentrations of associated ions with the resin.

2.3.4 Data Analysis

Mean concentrations and 95% of confidence intervals around each mean were calculated. Two major setbacks were encountered during soil solution sampling. First, the absence of soil solution samples in 25L HDPE bottles attached to ZTS. The reason for this was a lack of sufficient precipitation needed to generate saturated conditions or macropore flow, subsequently there are a large number of “missing” data points in the dataset. Second, the length of time required to complete harvesting was much longer than initially anticipated (harvesting occurred over an 8 month time period) and due to this challenge many treatments were harvested at different times (Table 2.3).

All data analysis was carried out in SAS™ Statistical Software Version 9.3 (SAS Institute Inc., 2008, Cary, NC, USA). Two separate statistical models were used to compare soil samples collected pre-harvest and one year post-harvest. The first model (Appendix A-I) is a spatially-repeated split-plot model developed in PROC GLIMMIX which created a split by treatment, soil nutrient status and depth, and data were analyzed for treatment effect.
separately for pre-harvest and post-harvest conditions. This model is same as the statistical model developed by Gaddie (2012). The Shapiro-Wilk test for normality was also determined prior to analysis to test the hypothesis that the residuals were normally distributed for all response variables. For all dependent variables PROC UNIVARIATE program in SAS was used for testing normal, log normal, gamma, and exponential sample distributions and visual estimates were used to determine the best-fitted distributions. The Tukey-Kramer least squared differences LSMEANS test was used for determining significant differences (α=0.05) amongst the treatment means. The log normal distribution with the identity link function was selected for all dependent variables within the pre-harvest and post-harvest datasets with exception for exchangeable Mg^{2+} where a gamma distribution was used.

The second model (Appendix A-II) employed is also a spatially-repeated split-plot model developed in PROC GLIMMIX which created a split by treatment, soil nutrient status, harvest and depth, and analyzed the complete pre-harvest and post-harvest dataset simultaneously. The test used to check normality of data was similar to that as described for the first model. The Tukey-Kramer least squared differences LSMEANS test was used for determining significant differences (α=0.05) amongst the treatment means. Contrasts were set up in SAS to check for the effect of treatment and harvest. The lognormal distribution with identity link was selected for all dependent variables in the dataset, with exception of TOC where a gamma distribution was used.
Table 2.3. Block-wise representation of MOFEP sites for treatment, first date of sampling, harvest date (completion) and last date of sampling.

<table>
<thead>
<tr>
<th>Nutrient Status</th>
<th>Site</th>
<th>Treatment</th>
<th>First Date of Sampling</th>
<th>Harvest Date</th>
<th>Last Date of Sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low</strong></td>
<td>1L</td>
<td>No-Harvest Management</td>
<td>4/28/2010</td>
<td>-</td>
<td>3/25/2013</td>
</tr>
</tbody>
</table>
Due to the eight month harvest period and temporal diversity of the data, the ability to make scatter plots combining data from treatments in all three blocks was hindered. Therefore, visual comparisons of soil solution analytes using scatter plots were developed for individual soil pits (Appendix B). Visual comparison of all treatments on basis of pre-harvest and post-harvest was made by calculating the volume weighted mean (VWM) for each analyte:

\[
\text{VWM}_a = \frac{\sum C_{ai} V_i}{\sum V_i}
\]

where, \( C_{ai} \) is the measured concentration of analyte \( a \) in sample \( i \), and \( V_i \) is the volume of the collected soil solution for sample \( i \) (Goyne et al., 2000). Volume weighted means were generated for each event using data obtained from the replicate samples, and the data were used to create boxplots for different sampling time periods (Figure 2.2). In the boxplots, pre-harvest data represents VWM values for all pre-harvest collection events from 04/28/2010 to 12/26/2011 where the latter date represents harvest of all designated treatments. Post-harvest year one represents VWM for all collection events starting from first date after harvest of the first site 03/31/2011 to 4/21/2012 (Table 2.3) and post-harvest year two represents data from 04/22/2012 to 03/25/2013 (Appendix C).
Figure 2.2. Example, boxplot displaying descriptive statistical information (obtained from Gaddie 2012).

Due to complexity of the data set generated by missing data points and occurrence of sampling events during the 8 month period of active harvest (where some treatments were harvested and some were not harvested), we were not able to derive a working model in SAS which could compare pre-harvest sites with post-harvest sites for soil solution samples on an event basis. The only working model which we were able formulate was based on comparing pooled pre-harvest and pooled post-harvest data to one another. A spatially-repeated, split-plot generalized linear mixed model was developed with the split occurring by treatment, soil nutrient status, harvest and depth to analyze throughfall and soil solution collected from all ZTS (Appendix A-III). The Shapiro-Wilk test for normality was also determined prior to analysis to test the hypothesis that the residuals were normally distributed for all response variables. For all dependent variables PROC UNIVARIATE program in SAS was used for testing normal, log normal, gamma, and exponential sample distributions and visual estimates.
were used to determine the best-fitted distributions. The normal distribution with the identity link function was selected for all dependent variables except for Ca\(^{2+}\) and TOC where a gamma distribution was employed. To assess the homogeneity of variance assumption, Levene's test and boxplots were used. The Tukey-Kramer least squared differences LSMEANS test was used to determine significant differences (\(\alpha=0.05\)) amongst the treatment means.

For the IER samplers, mean values were generated for each sampling depth within each pit by averaging extracted analyte values associated with the three subsamples. Ion exchange sampler area, burial time period and mean analyte concentration from IER extracts were then used to calculate total flux in mmol m\(^{-2}\) day\(^{-1}\) for each sampling depth within a sampling pit. Percentage analyte loss per burial period was calculated from the volume of extract and concentration of analyte in an IER extract.

Two separate models were used for statistical analysis of the IER data. The first model is a spatially-repeated, split-plot model developed in PROC GLIMMIX which created a split by treatment, soil nutrient status, collection and depth (Appendix A-IV), and data from the four different collection periods were analyzed separately. Similar tests as described for soil solution analysis were carried in SAS to check normality of data. The lognormal distribution with the identity link function was selected for all dependent variables. To access the homogeneity of variance assumption, Levene's test and boxplots were used. Treatment means were compared for significant differences (\(\alpha=0.05\)) using the Tukey-Kramer least squared differences LSMEANS test. The second model is also a spatially-repeated, split-plot model developed in PROC GLIMMIX which created a split by treatment, soil nutrient status, collection and depth (Appendix A-V). Contrasts were setup for harvest as collection 1 and 2 were from pre-harvest and collection 3 and 4 were from post-harvest data. The lognormal distribution with identity link was selected for all dependent variable for data in second
model with exception of Mg\textsuperscript{2+}, Mg\textsuperscript{2+} flux and Mg\textsuperscript{2+} loss (distribution=\textit{gamma}, link function=\textit{log}).

2.4 Results and Discussions

2.4.1 Soil Characterization and Chemical Properties: Pre- and Post-Harvest

Due to the high variability of Missouri Ozark Highland soils, pre- and post-treatment soil characterization and soil property data first were analyzed independently. This permitted testing of the randomly assigned timber harvest treatment designation (trt) to determine if soil properties were significantly different even prior to harvest (see Appendix A-I for statistical model). For the pre-treatment data, no significant differences were observed for all dependent variables based on treatment designation (trt) alone (Table 2.4a). In contrast, significant differences were observed for TN between treatments one year after harvest (Table 2.4b). Total N was significantly greater in CC plots when compared to NHM but not significantly greater than STS plots (Figure 2.3b). No significant differences were observed for the interaction between treatment and soil nutrient status (trt*sns) or the interaction between treatment and depth (trt*depth) in either the pre- or post-harvest data (Table 2.4a and b).

Interestingly, no significant differences were observed between soils with differing soil nutrient status (sns). However, for pre-treatment data, the interaction between soil nutrient status and depth (sns*depth) showed significance differences for extractable acidity (EA) and effective cation exchange capacity (ECEC) (Table 2.4a). In the case of post-treatment data, the interaction of soil nutrient status and depth was significant for only exchangeable Mg\textsuperscript{2+} (Table 2.4b).

For the pre-treatment data, significant differences on basis of depth were observed for exchangeable Ca\textsuperscript{2+} and Mg\textsuperscript{2+}, EA, ECEC, TOC and TN (Table 2.4a). Mean concentrations ± SE for exchangeable Ca\textsuperscript{2+} (1.6 ± 0.7 cmol\textsubscript{c} kg\textsuperscript{-1}) was greatest for the 0-10 cm depth when
compared to lower depths (Table 2.5a); whereas, mean concentrations ± SE for exchangeable Mg$^{2+}$ (1.5 ± 1.2 cmol·kg$^{-1}$) were greatest for the 30-40 cm depth when compared to other depths (Table 2.5a). Mean EA was significantly greater for the 0-10 cm depth when compared to deeper depths (Table 2.5a). Total OC and TN concentrations significantly decreased with depth to a depth of 30 cm (Table 2.5a).

For the post-treatment data, significant differences on the basis of depth were observed for all dependent variables except extractable Al (Table 2.4b). Mean exchangeable Ca$^{2+}$ concentration (3.2 cmol·kg$^{-1}$) was greatest at the 0-10 cm depth and concentrations were similar for the three deeper depth increments (Table 2.5b). However, exchangeable Mg$^{2+}$ mean concentration (1.2 cmol·kg$^{-1}$) was greatest at the 30-40 cm depth in comparison to more shallow sampling depths. Mean concentrations of exchangeable K$^{+}$, BS, ECEC, EA, TOC and TN were greatest for depth at 0-10 cm and reduced in lower depths (Table 2.5b).
Table 2.4. Type 3 Tests of Fixed Effects, evaluating (a) pre-treatment chemical soil properties and (b) post-treatment chemical soil properties.

Dependent variables include soil pH measured in 0.01 M CaCl₂ (pH salt), the activity of hydrogen ions calculated from soil pH salt, exchangeable concentrations of Ca²⁺, Mg²⁺, and K⁺, effective cation exchange capacity (ECEC), base saturation (Base sat), extractable acidity (EA), extractable aluminum (EAl), aluminum saturation (Al sat), total organic carbon (TOC), and total nitrogen (TN). Statistically significant effects (p-values <0.05) are noted in bold.

(a) Pre-treatment effect on chemical soil properties of MOFEP harvest designations.

<table>
<thead>
<tr>
<th>Source</th>
<th>pH salt</th>
<th>(H⁺) salt</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>K⁺</th>
<th>Base sat</th>
<th>EA</th>
<th>EAl</th>
<th>ECEC</th>
<th>Al sat</th>
<th>TOC</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>trt</td>
<td>0.6846</td>
<td>0.7356</td>
<td>0.8929</td>
<td>0.4546</td>
<td>0.1235</td>
<td>0.5904</td>
<td>0.6823</td>
<td>0.6940</td>
<td>0.8835</td>
<td>0.5824</td>
<td>0.5788</td>
<td>0.1447</td>
</tr>
<tr>
<td>sns</td>
<td>0.3220</td>
<td>0.3508</td>
<td>0.2203</td>
<td>0.1527</td>
<td>0.9730</td>
<td>0.1068</td>
<td>0.2947</td>
<td>0.7544</td>
<td>0.1783</td>
<td>0.1312</td>
<td>0.9065</td>
<td>0.4684</td>
</tr>
<tr>
<td>trt*sns</td>
<td>0.3232</td>
<td>0.3418</td>
<td>0.5611</td>
<td>0.3012</td>
<td>0.1176</td>
<td>0.4494</td>
<td>0.7370</td>
<td>0.9398</td>
<td>0.3272</td>
<td>0.8147</td>
<td>0.9990</td>
<td>0.9528</td>
</tr>
<tr>
<td>depth</td>
<td>0.1849</td>
<td>0.2093</td>
<td><strong>0.0004</strong></td>
<td><strong>0.0292</strong></td>
<td>0.2019</td>
<td>0.0974</td>
<td>&lt;.0001</td>
<td>0.2185</td>
<td><strong>0.0227</strong></td>
<td>0.0815</td>
<td>&lt;.0001</td>
<td>&lt;.0001</td>
</tr>
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<td>0.2044</td>
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<td>0.4212</td>
<td>0.3561</td>
<td>0.4622</td>
<td>0.3330</td>
<td>0.9131</td>
<td>0.9597</td>
<td>0.3280</td>
<td>0.2133</td>
</tr>
<tr>
<td>depth*sns</td>
<td>0.7825</td>
<td>0.7638</td>
<td>0.0808</td>
<td>0.0975</td>
<td>0.1150</td>
<td>0.2317</td>
<td><strong>0.0307</strong></td>
<td>0.0991</td>
<td><strong>0.0322</strong></td>
<td>0.6175</td>
<td>0.1899</td>
<td>0.2008</td>
</tr>
</tbody>
</table>
(b) Post-treatment effect on chemical soil properties of MOFEP harvest designations.

<table>
<thead>
<tr>
<th>Source</th>
<th>pH_{salt}</th>
<th>(H^+)_{salt}</th>
<th>Ca^{2+}</th>
<th>Mg^{2+}</th>
<th>K^+</th>
<th>Base sat</th>
<th>EA</th>
<th>EAl</th>
<th>ECEC</th>
<th>Al sat</th>
<th>TOC</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>trt</td>
<td>0.8121</td>
<td>0.8281</td>
<td>0.7943</td>
<td>0.9736</td>
<td>0.9517</td>
<td>0.9498</td>
<td>0.2578</td>
<td>0.8097</td>
<td>0.7455</td>
<td>0.9947</td>
<td>0.4933</td>
<td>0.0458</td>
</tr>
<tr>
<td>sns</td>
<td>0.6152</td>
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<td>0.1033</td>
<td>0.9684</td>
<td>0.1773</td>
<td>0.7977</td>
<td>0.9670</td>
<td>0.2167</td>
<td>0.3268</td>
<td>0.7849</td>
<td>0.2155</td>
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<tr>
<td>trt*sns</td>
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<td>0.3702</td>
<td>0.5186</td>
<td>0.2276</td>
<td>0.6459</td>
<td>0.3346</td>
<td>0.4676</td>
<td>0.9361</td>
<td>0.3885</td>
<td>0.7012</td>
<td>0.6994</td>
<td>0.7925</td>
</tr>
<tr>
<td>depth</td>
<td><strong>0.0172</strong></td>
<td><strong>0.0129</strong></td>
<td><strong>&lt;.0001</strong></td>
<td><strong>0.0008</strong></td>
<td><strong>&lt;.0001</strong></td>
<td><strong>&lt;.0001</strong></td>
<td>0.6491</td>
<td><strong>0.0002</strong></td>
<td><strong>0.0027</strong></td>
<td><strong>&lt;.0001</strong></td>
<td><strong>&lt;.0001</strong></td>
<td></td>
</tr>
<tr>
<td>depth*trt</td>
<td>0.2638</td>
<td>0.2270</td>
<td>0.8968</td>
<td>0.3541</td>
<td>0.6367</td>
<td>0.5118</td>
<td>0.1978</td>
<td>0.7298</td>
<td>0.5081</td>
<td>0.9766</td>
<td>0.7919</td>
<td>0.9454</td>
</tr>
<tr>
<td>depth*sns</td>
<td>0.7438</td>
<td>0.7314</td>
<td>0.1946</td>
<td><strong>0.0170</strong></td>
<td>0.5435</td>
<td>0.6508</td>
<td>0.5028</td>
<td>0.7260</td>
<td>0.2870</td>
<td>0.6714</td>
<td>0.7907</td>
<td>0.3989</td>
</tr>
</tbody>
</table>
Table 2.5. Mean ± 95% confidence interval (CI) for (a) pre-harvest and (b) post-harvest soil chemical properties of field sampling locations by sampling depth.

(a) Pre-harvest soil chemical properties of field sampling locations by sampling depth.

<table>
<thead>
<tr>
<th>Depth cm</th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>K(^+)</th>
<th>ECEC †</th>
<th>Base sat ‡</th>
<th>EA ¥</th>
<th>Al sat ¶</th>
<th>pH (_{\text{salt}})</th>
<th>(H(^+)) (_{\text{salt}})</th>
<th>TOC</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 10</td>
<td>1.6 ± 0.7</td>
<td>0.6 ± 0.1</td>
<td>0.2 ± 0</td>
<td>5.5 ± 0.8</td>
<td>19 ± 5.7</td>
<td>8.7 ± 1.2</td>
<td>0.7 ± 0.3</td>
<td>4.4 ± 0.2</td>
<td>0.0000551 ± 0.0000142</td>
<td>1.2 ± 0.3</td>
<td>19 ± 4.3</td>
</tr>
<tr>
<td>10 - 20</td>
<td>0.9 ± 0.6</td>
<td>0.7 ± 0.6</td>
<td>0.2 ± 0.1</td>
<td>4.8 ± 1.3</td>
<td>18 ± 6.4</td>
<td>6.1 ± 0.8</td>
<td>1.0 ± 0.4</td>
<td>4.5 ± 0.4</td>
<td>0.0000566 ± 0.0000153</td>
<td>0.5 ± 0.1</td>
<td>8.0 ± 1.2</td>
</tr>
<tr>
<td>20 - 30</td>
<td>1.1 ± 1.1</td>
<td>1.2 ± 1.0</td>
<td>0.2 ± 0</td>
<td>6.2 ± 2.5</td>
<td>19 ± 7.0</td>
<td>5.9 ± 1.3</td>
<td>1.3 ± 0.6</td>
<td>4.2 ± 0.1</td>
<td>0.0000646 ± 0.0000131</td>
<td>0.2 ± 0.1</td>
<td>4.2 ± 0.7</td>
</tr>
<tr>
<td>30 - 40</td>
<td>1.4 ± 1.2</td>
<td>1.5 ± 1.2</td>
<td>0.2 ± 0</td>
<td>6.6 ± 2.6</td>
<td>24 ± 7.5</td>
<td>6.2 ± 1.7</td>
<td>1.6 ± 0.9</td>
<td>4.2 ± 0.1</td>
<td>0.0000734 ± 0.0000163</td>
<td>0.2 ± 0</td>
<td>2.8 ± 0.5</td>
</tr>
</tbody>
</table>

† ECEC, effective cation exchange capacity.
‡ Base sat, percent base saturation.
¥ EA, extractable acidity.
¶ Al sat, percent aluminum saturation.
(b) Post-harvest soil chemical properties of field sampling locations by sampling depth.

<table>
<thead>
<tr>
<th>Depth cm</th>
<th>Soil Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca(^{2+})</td>
</tr>
<tr>
<td>0 - 10</td>
<td>3.2 ± 0.9</td>
</tr>
<tr>
<td>10 - 20</td>
<td>1.7 ± 0.6</td>
</tr>
<tr>
<td>20 - 30</td>
<td>1.5 ± 0.9</td>
</tr>
<tr>
<td>30 - 40</td>
<td>1.7 ± 1.3</td>
</tr>
</tbody>
</table>

† ECEC, effective cation exchange capacity.
‡ Base sat, percent base saturation.
¥ EA, extractable acidity.
¶ Al sat, percent aluminium saturation.
Figure 2.3. Comparisons of mean ± 95% confidence interval (CI) soil TN for (a) pre-harvest and (b) post-harvest data by treatments. Significant differences (p values < 0.05) are noted by differing letters at the top of each bar.
In a separate statistical analysis, the effect of harvest was analyzed by comparing the one year post-harvest data and pre-harvest data using the model found in Appendix A-II. Significant differences associated with harvest were observed for all dependent variables except exchangeable Mg$^{2+}$, ECEC, EA and exchangeable Al (Table 2.6). A significant effect of depth was observed for all dependent variables with exception for EAl. For the interaction between depth and soil nutrient status (depth*sns), significant differences were observed for exchangeable Ca$^{2+}$ and Mg$^{2+}$ and ECEC; whereas, for the interaction between depth and harvest (depth*harvest), significant differences were observed for pH$_{salt}$, H$_{salt}$ ion activity, ECEC, percent base saturation, TOC and TN (Table 2.6).

However, for treatment, only TN showed significant p-values (Table 2.6). For the interaction of treatment and harvest (trt*harvest), no significant differences were observed for all dependent variables with exception for exchangeable K$^+$ (Table 2.6). Exchangeable K$^+$ was significantly greater post-harvest in stands harvested with the STS regeneration method when compared to STS pre-harvest data (Figure 2.4a). Using contrasts developed in SAS examining the interaction between treatment and harvest (trt*harvest) (Appendix A-II), TN in clearcuts post-harvest was observed to be significantly greater when compared to clearcuts pre-harvest (Figure 2.4b). However a similar trend of significantly greater TN was observed for STS and NHM when compared to pre-harvest data (Figure 2.4b). Although TN changed, it was apparently not due to harvest activities but other variations in the system apparently triggered this change.

Albers (2010) observed that overall concentrations of calcium, total organic carbon, total nitrogen and stable and labile nitrogen were diminished in STS plots relative to CC plots at MOFEP ten years after harvest, and these nutrient differences were attributed to differences in slash distribution within the treatments. However, Spratt (2002) was able to correlate changes occurring in a clearcutting plots to decreased organic sulfur, total carbon, total sulfur
and total nitrogen after harvest. Burns and Murdoch (2005) observed greater amounts of potassium chloride (KCl) extractable NO$_3^-$ and NH$_4^+$ in soil horizons for consecutive two year after clearcutting in northern hardwood forest. Johnson and Curtis (2001) observed significant effects of harvest type and species from a meta-analysis, where soil C and N increased (+18%) in sawlog harvesting and decreased (−6%). in WTH. Carmosini et al. (2002) observed more rapid rates of NH$_4$-N production and elevated NO$_3^-$ concentrations in mixed stands of northern Alberta two years after harvesting. Knoepp and Swank (1997) observed significantly greater levels of soil TC and TN in commercial sawlog harvest immediately after cutting and for subsequent three years. Smethurst and Nambiar (1990) found increased concentrations of N mineralization in soil after 12 months of harvesting in clearcutting plots and 64-74 % was estimated to leach below 30 cm of soil depth. There was no significance observed by Johnson and Todd (1998) for effect of sawlog harvesting on soil TN after 15 years of harvesting. The elevated levels of TN in soil after clearcutting in Missouri Ozarks may not be due to harvest activities, but other variations in the system (seasonal changes, precipitation, and sampling error, etc). Further monitoring of soil nutrients after harvest is necessary to identify long-term changes.
Table 2.6. Type 3 Tests of Fixed Effects, evaluating harvest, treatment, soil nutrient status and depth effects on soil chemical properties at MOFEP.

Dependent variables include soil pH measured in 0.01 M CaCl₂ soil slurry (pH salt), the activity of hydrogen ions calculated from soil pH salt, exchangeable concentrations of Ca²⁺, Mg²⁺, and K⁺, effective cation exchange capacity (ECEC), base saturation (Base sat), extractable acidity (EA), extractable aluminum (EAl), aluminum saturation (Al sat), total organic carbon (TOC), and total nitrogen (TN). Statistically significant effects (p-values <0.05) are noted in bold.

Analysis of pre and post-harvest soil sampling data.

<table>
<thead>
<tr>
<th>Source</th>
<th>pH_salt</th>
<th>(H⁺)_salt</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>K⁺</th>
<th>Base sat</th>
<th>EA</th>
<th>EAl</th>
<th>ECEC</th>
<th>Al sat</th>
<th>TOC</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>trt</td>
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<td>0.4514</td>
<td>0.7321</td>
<td>0.2891</td>
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<td>0.7583</td>
<td>0.8596</td>
<td>0.4297</td>
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<tr>
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<td>0.9897</td>
<td>0.0981</td>
<td>0.3309</td>
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<td>0.6859</td>
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<td>0.0202</td>
<td>0.4285</td>
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Figure 2.4. Comparisons of mean (a) exchangeable potassium (K⁺) and (b) total nitrogen (TN) by treatment and harvest mean. Error bars represent the ± 95% confidence interval (CI). Significant differences (p values < 0.05) are noted by differing letters at the top of each bar.
2.4.2 Soil Solution Sampling Data

Aqueous concentrations of ions in soil solution were observed to increase post-harvest for most of the analytes investigated based on scatter plots of data provided in Appendix B. Concentrations of NO₃⁻ at the 15 cm depth in stands harvested via CC increased at all sampling sites when compared to NHM and STS (Appendix B). Similar trends of increase were observed for Ca²⁺ and Mg²⁺. Median VWM analyte concentrations in throughfall decreased in year two post-harvest compared to pre-harvest under CC for low nutrient status soils for throughfall data for pH, EC, PO₄³⁻, Al⁺, Ca²⁺, Mg²⁺, Na⁺, K⁺, TOC and TN. However, median VWM analyte concentrations at the 15 cm depth were typically greater in year two post-harvest compared to pre-harvest under CC for low nutrient status soils for EC, Cl⁻, NO₃⁻, PO₄³⁻, Ca²⁺, Mg²⁺, NH₄⁺ and TN. Whereas, median analytes concentrations at the 40 cm depth for year two post-harvest under CC increased for F⁻, Br⁻, NO₃⁻, Ca²⁺, Mg²⁺ and TN, and decreased for SO₄²⁻ (Appendix C). Throughfall data for medium nutrient status soils indicated decrease in median values of pH, EC, PO₄³⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺, TOC and TN, and an increase in median values of H⁺, Cl⁻, NO₃⁻; and NO₃⁻ after harvest in CC. An increasing trend for median VWM analyte concentrations at the 15 cm depth in year two post-harvest was observed in CC stands on medium nutrient status soils for EC, Br⁻, NO₃⁻, NO₃⁻, Ca²⁺, Mg²⁺, K⁺, NH₄⁺ and TN (Appendix C). Median VWM concentrations were observed to be elevated relative to pre-harvest for medium nutrient status at the 40 cm depth under CC in year two post-harvest for EC, Br⁻, NO₃⁻, Ca²⁺, Mg⁺²⁺, K⁺ and Na⁺ and reduced for SO₄²⁻ (Appendix C).

Statistical analysis of soil solution data determined no significant effect of the following: soil nutrient status (sns); treatment by soil nutrient status (trt*sns); and treatment by soil nutrient status by harvest (trt*sns*harvest) (Table 2.7). The effect of treatment was
significant for EC, Mg^{2+}, Na^+, DOC and TN; whereas, the effect of harvest was significant for all dependent variables except Cl^-, PO_4^{3-}, Mg^{2+}, K^+, and NH_4^+. The interaction between treatment and harvest (trt*harvest) was significant for EC, F^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, DOC, and TN, and the interaction between soil nutrient status and harvest (sns*harvest) was significant for Al_T and Ca^{2+} (Table 2.7). Additionally, the interaction between depth and harvest (depth*harvest) was significant for H^+, EC, F^-, NO_3^-, SO_4^{2-}, Al_T, Ca^{2+}, Mg^{2+}, Na^+, DOC, and TN; whereas interaction between treatment, depth, and harvest (trt*depth*harvest) was significant for H^+, EC, F^-, NO_3^-, Ca^{2+}, Mg^{2+}, DOC, and TN (Table 2.7). The effect of soil nutrient status and depth (sns*depth) was only significant for SO_4^{2-}, Al_T, and Na^+. Lastly, the interactions between treatment, soil nutrient status, and depth (trt*sns*depth) and soil nutrient status, depth, and harvest (sns*depth*harvest) were significant for Al_T, Ca^{2+}, and Na^+ and Al_T and Ca^{2+}, respectively.
Table 2.7. Type 3 Tests of Fixed Effects, evaluating harvest, treatment, soil nutrient status and depth effects on soil solution properties at MOFEP.

Dependent variables include solution pH, hydrogen ion (H+) activity, electrical conductivity (EC), anions (F-, Cl-, Br-, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻), cations (Al⁺, Ca²⁺, Mg²⁺, K⁺, Na⁺), ammonia (NH₄⁺), total organic carbon (TOC), and total nitrogen (TN). Statistically significant effects (p-values <0.05) are noted in bold.

Analysis of pre and post-harvest soil solution data.

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Significant interactions between treatment and harvest (trt*harvest) are plotted in Figure 2.5. Post-harvest EC, NO3\textsuperscript{-}, Mg\textsuperscript{2+}, and TN concentrations were significantly greater in clearcuts when compared to all other treatments (Figure 2.5). Mean Ca\textsuperscript{2+} concentrations were greater in clearcuts post-harvest but not significantly different from all other treatments except STS post-harvest (Figure 2.5f). Additionally, mean SO4\textsuperscript{2-} concentrations in post-harvest clearcuts were significantly diminished relative to pre-harvest data for the same sites (Figure 2.5e) but not significantly different from the other treatments. Dissolved organic carbon concentration was observed to decrease post-harvest in STS and CC sites, where DOC in CC plots was significantly less than all treatments except STS (Figure 2.5h). Fluoride concentrations were greater in all treatments post-harvest when compared to all treatments pre-harvest, thus indicating that there may be an effect of yearly changes not associated with the actual harvest. Nitrite concentrations also increased post-harvest compared to pre-harvest for all treatments but actual NO2\textsuperscript{-} concentrations were very low and significant differences may be due to analytical error (Figure 2.5 b and c).

Significant three way interactions between treatment, depth and harvest (trt*depth*harvest) are shown in Figure 2.6. Mean H\textsuperscript{+} activity increased in clearcuts post-harvest for solutions collected from all depths (throughfall, ZTS-15 cm and ZTS-40 cm), but only throughfall in the CC treatment was significantly greater after harvest relative to before harvest (Figure 2.6a). Electrical conductivity in soil solution at the 15 and 40 cm depths increased in the CC sites relative to pre-harvest concentrations for this treatment, and EC in post-harvest CC sites was significantly greater than STS and NHM post-harvest (Figure 2.6b). Mean concentrations of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} were greater in soil solution collected from ZTS-15 cm and ZTS-40 cm samplers for post-harvest CC sites when compared to pre-harvest data, but the difference was only significant for the concentration of Mg\textsuperscript{2+} at 40 cm depth. Additionally, Ca\textsuperscript{2+} and Mg\textsuperscript{2+} concentrations in soil solution collected from post-harvest CC
sites were also greater than concentrations of these analytes in post-harvest STS and NHM sites (Figure 2.6 c and d). Calcium concentrations were significantly greater for soil solution collected at the ZTS-15 cm depth for CC post-harvest compared to soil solution collected at the ZTS-15 cm depth for STS and NHM post-harvest, whereas soil solution collected at the ZTS 40 cm depth showed significant differences in Ca\(^{2+}\) concentrations among CC post-harvest and STS post-harvest only. Total N and NO\(_3^-\) concentrations increased significantly in post-harvest CC sites for ZTS-15 cm and ZTS-40 cm (Figure 2.6 e and f), relative to pre-harvest data. Additionally, TN and NO\(_3^-\) concentrations in soil solution collected from post-harvest CC sites were greater than concentrations of these analytes in post-harvest STS and NHM sites. Dissolved organic carbon significantly decreased in throughfall solution collected in CC and STS sites post-harvest when compared to pre-harvest data from the same sites (Figure 2.6g). Fluoride concentrations in soil solution at the 15 and 40 cm depths significantly increased in the STS sites relative to pre-harvest concentrations for this treatment, and F\(^-\) in post-harvest STS sites was significantly greater than CC and NHM for ZTS-15 cm (Figure 2.6h). Additionally, there was a significant increase in F\(^-\) concentrations at 40 cm depth for CC post-harvest relative to pre-harvest.
Figure 2.5. Comparisons of mean analyte concentrations by treatments and harvest for soil solution and throughfall. Error bars represent the 95% confidence interval (CI).

(a) electrical conductivity (EC), (b) fluoride (F^-), (c) nitrite (NO_2^-), (d) nitrate (NO_3^-), (e) sulfate (SO_4^{2-}), (f) calcium (Ca^{2+}), (g) magnesium (Mg^{2+}), (h) dissolved organic carbon (DOC), and (i) total nitrogen (TN). Significant differences (p values < 0.05) are noted by differing letters at the top of each bar.
Figure 2.6. Comparisons of mean ± 95% confidence interval (CI) of analytes by treatments, harvest and depth.

(a) hydrogen ion activity (H⁺), (b) electrical conductivity (EC), (c) calcium (Ca²⁺), (d) magnesium (Mg²⁺), (e) total nitrogen (TN), (f) nitrate (NO₃⁻), (g) dissolved organic carbon (DOC), and (h) fluoride (F⁻). Significant differences (p values < 0.05) are noted by differing letters at the top of each bar.
Mean NO$_3^-$ concentrations (Figure 2.6f) from this research were very similar to values obtained by Burns and Murdoch (2005). They studied effects of clearcutting on net rates of nitrification and N mineralization in a northern hardwood forest of New York state. It was reported that mean annual NO$_3^-$ concentrations in soil solution collected from the O and B horizons increased from 20 to 60 µmol L$^{-1}$ before the harvest to approximately 360 to 370 µmol L$^{-1}$ in first year after clearcutting, followed by concentrations decreasing to approximately 170 µmol L$^{-1}$ by the third year post-harvest. A similar trend was observed in data collected from samples collected in the Ozark Highlands following clearcutting (i.e., this work). Mean NO$_3^-$ concentrations in soil solution collected from 15 and 40 cm depth increased from 14.5 ± 5.5 µmol L$^{-1}$ and 12.7 ± 16.1 µmol L$^{-1}$ before clearcut to 282.4 ± 74.4 µmol L$^{-1}$ and 317.2 ± 74.6 µmol L$^{-1}$ respectively, 18 months after harvest (Figure 2.6f). Throughout the three years of sampling at MOFEP, NO$_3^-$ concentrations in soil solution collected from 15 and 40 cm depths in NHM sites remained constant at about 13.6 ± 3.6 µmol L$^{-1}$ and 16.32 ± 5.5 µmol L$^{-1}$, respectively. Clearcutting temporarily decreases uptake of N by plants roots as a result there is excess production of NO$_3^-$ by soil microorganisms. Many studies have attributed increase in NO$_3^-$ leaching after clearcutting to the combined effect of N mineralization and nitrification and decrease N uptake by vegetation (Likens et al., 1969; Vitousek, 1981).

In post-harvest clearcut plots, SO$_4^{2-}$ concentrations decreased (Figure 2.5e). Spratt (2002) correlated changes occurring in clearcut plots to decreased organic sulfur and total sulfur after harvesting. Piirainen et al. (2004) observed annual fluxes of total S and SO$_4^{2-}$ in soil solution collected from O and B horizons to decrease after clearcutting. Decrease in concentration of SO$_4^{2-}$ after clearcutting can be attributed to microbial immobilization and/or reduced mineralization of organic S.
Many previous studies have indicated increased leaching losses for Ca\(^{2+}\) and Mg\(^{2+}\) after harvest (Mann et al., 1988; Johnson et al., 1997; Huntington et al., 2000; Piirainen et al., 2004). Calcium and Mg\(^{2+}\) were reported to increase in forest floor leachates during the second year after clearcutting by Hendrickson et al. (1989). Weis et al. (2006) observed increased nutrient loss of Ca\(^{2+}\) and Mg\(^{2+}\) in soil solution collected at the 40 cm depth one year after clearcutting and reported nutrient loss to decrease in subsequent years. McHale et al. (2007) observed concentrations of 67.1 µmol L\(^{-1}\) of Ca\(^{2+}\) and 33.5 µmol L\(^{-1}\) of Mg\(^{2+}\) being leached through ZTS installed at depth of 25-30 cm after clearcutting in Ca poor soils of southeastern New York, and these values are less than those observing in this study (Figure 2.6 c and d). The increased concentrations of Ca\(^{2+}\) and Mg\(^{2+}\) in solution after harvest are probably due to the decomposition and mineralization of logging residues.

Total N and DOC was observed to significantly decrease for throughfall and increase for ZTS-15 cm and ZTS-40 cm in post-harvest clearcut plots (Figure 2.6 e and g), similar results were reported in many studies (Qualls et al., 2000; Piirainen et al., 2002). The reduced concentrations of TN and DOC in the throughfall after clearcutting, compared to that from NHM, may reflect loss of canopy and decrease in ion release from the foliage. The increased concentrations of TN and DOC in 15 and 40 cm depth below the hardwoods after CC could be due to increased decomposition of slash, given the reduced inputs in throughfall.

2.4.3 Ion Exchange Resin Sampling Data

Analysis of IER flux data determined that soil nutrient status (sns), interaction between treatment and soil nutrient status (trt*sns) were of no significant importance in first collection period (Table 2.8a). A significant difference was observed for NO\(_3^-\) flux amongst the treatments (trt) prior to harvest (Table 2.8a); NO\(_3^-\) flux in NHM (36 ± 22 µmol m\(^{-2}\) day\(^{-1}\)) was significantly greater than STS (2.5 ± 1.7 µmol m\(^{-2}\) day\(^{-1}\)) but was not significantly different
from CC (4.7 ± 3.0 µmol m⁻² day⁻¹). This difference can be attributed to the variable nature of Ozark Highland soils. Additionally, in first collection period, Ca²⁺ flux was significantly greater at the 15 cm depth (39.4 ± 9.87 µmol m⁻² day⁻¹) when compared to 40 cm depth (29.2 ± 6.78 µmol m⁻² day⁻¹). Significant differences were observed for Na⁺ flux (Table 2.8a) for the interaction of depth and treatment (depth*trt) and depth and soil nutrient status (depth*sns).

For the second collection period, limited significant differences were observed for the effects investigated. Depth did have a significant effect on NO₃⁻ flux (Table 2.8b), where flux was observed to be greater at the 40 cm depth (18.1 ± 10.2 µmol m⁻² day⁻¹) compared to 15 cm depth (8.3 ± 3.4 µmol m⁻² day⁻¹). Additionally, the interaction between treatment and soil nutrient status (trt*sns) was observed to be significant for Al⁺ flux.

The pre-harvest treatment designations for the first two collections did not show any significant effect for the analytes except for NO₃⁻ flux from first collection (April to October 2010). This experimental artifact most likely reflects the highly variable nature of Ozark Highland soils and may be related with seasonal shifts of temperature and precipitations.

The third collection period showed no significant values for the effects investigated with exception for the effect of depth and treatment (trt) on NO₃⁻ flux (Table 2.8c). For the effect of treatment, NO₃⁻ flux in the CC treatment (22 ± 11 µmol m⁻² day⁻¹) was significantly greater than NO₃⁻ flux within STS and NHM treatments (3.3 ± 2.8 µmol m⁻² day⁻¹ and 4.5 ± 2.9 µmol m⁻² day⁻¹, respectively). From analysis of flux data from the fourth collection period, the only significant effect was for treatment (trt) on NO₃⁻ flux (Table 2.8d). Again, clearcutting was observed to have significantly greater NO₃⁻ flux (355.3 ± 262.9 µmol m⁻² day⁻¹) than STS and NHM (2.4 ± 0.9 µmol m⁻² day⁻¹ and 16 ± 17 µmol m⁻² day⁻¹, respectively) and these results were similar NO₃⁻ flux during the third IER collection period.
Table 2.8. Type 3 Tests of Fixed Effects evaluating ion exchange resin flux data from (a) April to October 2010, (b) October 2010 to July 2011, (c) January to July 2012, and (d) July 2012 to January 2013 by pre-treatment and post-treatment MOFEP harvest designation (trt), soil nutrient status (sns), and sampler depth. Tukey-Kramer adjusted p-values of nutrient concentrations from split-plot generalized linear mixed model.

Dependent variables include total aluminum (Al\textsubscript{T}), calcium (Ca\textsuperscript{2+}), magnesium (Mg\textsuperscript{2+}), sodium (Na\textsuperscript{+}), and nitrate (NO\textsubscript{3}\textsuperscript{-}). Statistically significant effects (p-values < 0.05) are noted in bold.

(a) Analysis of pre-treatment IER flux data from 1\textsuperscript{st} collection period.

<table>
<thead>
<tr>
<th>Source</th>
<th>Al\textsubscript{T} flux</th>
<th>Ca\textsuperscript{2+} flux</th>
<th>Mg\textsuperscript{2+} flux</th>
<th>Na\textsuperscript{+} flux</th>
<th>NO\textsubscript{3}\textsuperscript{-} flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>trt</td>
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<td>0.1338</td>
<td>0.2522</td>
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</tr>
<tr>
<td>sns</td>
<td>0.8420</td>
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<td>0.2935</td>
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</tr>
<tr>
<td>trt*sns</td>
<td>0.5729</td>
<td>0.8901</td>
<td>0.9363</td>
<td>0.8732</td>
<td>0.8162</td>
</tr>
<tr>
<td>depth</td>
<td>0.0561</td>
<td><strong>0.0250</strong></td>
<td>0.0580</td>
<td>0.0977</td>
<td>0.4196</td>
</tr>
<tr>
<td>depth*trt</td>
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<td>0.2900</td>
<td><strong>0.0403</strong></td>
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</tr>
<tr>
<td>depth*sns</td>
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<td>0.1052</td>
<td><strong>0.0485</strong></td>
<td>0.4762</td>
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</tbody>
</table>

(b) Analysis of pre-treatment IER flux data from 2\textsuperscript{nd} collection period.

<table>
<thead>
<tr>
<th>Source</th>
<th>Al\textsubscript{T} flux</th>
<th>Ca\textsuperscript{2+} flux</th>
<th>Mg\textsuperscript{2+} flux</th>
<th>Na\textsuperscript{+} flux</th>
<th>NO\textsubscript{3}\textsuperscript{-} flux</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1081</td>
</tr>
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<td>sns</td>
<td>0.6951</td>
<td>0.8930</td>
<td>0.9138</td>
<td>0.4382</td>
<td>0.2608</td>
</tr>
<tr>
<td>trt*sns</td>
<td><strong>0.0432</strong></td>
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<td>0.1634</td>
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<td>0.9511</td>
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<td>depth</td>
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<td>0.9220</td>
<td>0.3715</td>
<td><strong>0.0150</strong></td>
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<td>depth*trt</td>
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<td>0.3251</td>
<td>0.4472</td>
<td>0.7837</td>
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</tr>
</tbody>
</table>
(c) Analysis of post-treatment IER flux data from 3rd collection period.

<table>
<thead>
<tr>
<th>Source</th>
<th>Al⁺ flux</th>
<th>Ca²⁺ flux</th>
<th>Mg²⁺ flux</th>
<th>Na⁺ flux</th>
<th>NO₃⁻ flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>trt</td>
<td>0.9025</td>
<td>0.7295</td>
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<td>0.0171</td>
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<td>sns</td>
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<td>0.3952</td>
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<td>trt*sns</td>
<td>0.7602</td>
<td>0.8850</td>
<td>0.8830</td>
<td>0.3506</td>
<td>0.7377</td>
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<td>depth</td>
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<td>0.9907</td>
<td>0.6965</td>
<td>0.7959</td>
<td>0.0303</td>
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<td>depth*trt</td>
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<td>0.6909</td>
<td>0.1446</td>
<td>0.2906</td>
</tr>
<tr>
<td>depth*sns</td>
<td>0.9631</td>
<td>0.8384</td>
<td>0.9902</td>
<td>0.2482</td>
<td>0.9256</td>
</tr>
</tbody>
</table>

(d) Analysis of post-treatment IER flux data from 4th collection period.

<table>
<thead>
<tr>
<th>Source</th>
<th>Al⁺ flux</th>
<th>Ca²⁺ flux</th>
<th>Mg²⁺ flux</th>
<th>Na⁺ flux</th>
<th>NO₃⁻ flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>trt</td>
<td>0.4139</td>
<td>0.1373</td>
<td>0.0840</td>
<td>0.3480</td>
<td>0.0025</td>
</tr>
<tr>
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<td>0.5783</td>
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<tr>
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<td>depth*trt</td>
<td>0.9724</td>
<td>0.7325</td>
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<tr>
<td>depth*sns</td>
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<td>0.2442</td>
<td>0.2011</td>
<td>0.7162</td>
<td>0.3480</td>
</tr>
</tbody>
</table>

Table 2.9. Mean ± 95% confidence interval (CI) for NO₃⁻ flux by treatment and collection.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>NO₃⁻ flux (µmol m⁻² day⁻¹)</th>
<th>Collection 1</th>
<th>Collection 2</th>
<th>Collection 3</th>
<th>Collection 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHM</td>
<td>36 ± 22</td>
<td>23 ± 14</td>
<td>4.5 ± 2.9</td>
<td>16 ± 17</td>
<td></td>
</tr>
<tr>
<td>STS</td>
<td>2.5 ± 1.7</td>
<td>5.9 ± 2.3</td>
<td>3.3 ± 2.8</td>
<td>2.4 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>CC</td>
<td>4.7 ± 3.0</td>
<td>10 ± 5.6</td>
<td>22 ± 11</td>
<td>355.3 ± 262.9</td>
<td></td>
</tr>
</tbody>
</table>
The second statistical model (Appendix A-V) investigating nutrient flux compared all four collection periods by treatment, soil nutrient status and depth. No significant differences were observed amongst the dependent variables for the following main effects and interactions (Table 2.10): soil nutrient status (sns); treatment and soil nutrient status (trt*sns); treatment and depth (trt*depth); soil nutrient status and depth (sns*depth); soil nutrient status and collection (sns*collection); and depth and collection (depth*collection). For the effect of treatment, NO₃⁻ flux in CC (98 ± 76 µmol m⁻² day⁻¹) was significantly different from STS (3.5 ± 1.1 µmol m⁻² day⁻¹) but was not different than the NHM (20 ± 8.4 µmol m⁻² day⁻¹). However for effect of depth, Al₇ and NO₃⁻ flux exhibited significant differences (Table 2.10); where, Al₇ flux was greater at the 15 cm depth than at the 40 cm depth (3.6 ± 1.2 µmol m⁻² day⁻¹ and 2.2 ± 1.3 µmol m⁻² day⁻¹, respectively), and at the 40 cm depth NO₃⁻ flux was greater than at the 15 cm depth (40.3 ± 29.2 µmol m⁻² day⁻¹ and 39.9 ± 45.1 µmol m⁻² day⁻¹, respectively). Collection period was also a significant effect for all dependent variables with exception for Mg²⁺ flux.

An effect of treatment by collection (trt*collection) was also observed in this model (Table 2.10), and significant differences were observed for Ca²⁺, Mg²⁺ and NO₃⁻ flux. Contrasts for interaction of treatment by collection were determined using SAS for all dependent variables on basis of harvest, where collection 1 and 2 represent pre-harvest and collection 3 and 4 represent post-harvest data (Appendix A-V). When pre-harvest NHM and STS were compared to post harvest NHM and STS for all dependent variables, mean flux values were significantly less in the post-harvest NHM and STS sites with an exception for NO₃⁻ flux in STS (Figure 2.7). This decrease in flux values post-harvest is attributed to drought conditions which prevailed in 2012 throughout Missouri (see Appendix N for mean precipitation and temperature). Pre-harvest Al flux in the CC treatment was not significantly different from all three post-harvest treatments (Figure 2.7a). Mean post-harvest Ca²⁺ flux for
the CC sites was nominally greater than all other pre and post-harvest means (Figure 2.7b); whereas, mean post-harvest Mg$^{2+}$ flux in the CC sites was significantly greater when compared to other pre- and post-harvest treatments with exception for post-harvest NHM (Figure 2.7c). Mean Na$^{+}$ flux was significantly less in all post-harvest treatments as compared to the pre-harvest treatments, and Na$^{+}$ flux in post-harvest CC sites was significantly greater than that observed for the post-harvest NHM sites (Figure 2.6d). Post-harvest NO$_3^-$ flux was significantly greater in CC plots than all other pre- and post-harvest treatments (Figure 2.7e).

Mean daily flux in clearcut plots for post-harvest data was greater for Mg$^{2+}$ than Ca$^{2+}$ (Figure 2.7 b and c). Johnson et al. (2008) monitored decadal changes in soils after clearcutting and reported that decreases in exchangeable Ca$^{2+}$ could be attributed to living biomass and detritus, whereas decreases in exchangeable Mg$^{2+}$ could be attributed to leaching. The NO$_3^-$ flux values at 15 cm depth (220 µmol m$^{-2}$ day$^{-1}$) from this research appear to be much greater in post-harvest CC sites than the research conducted by Susfalk and Johnson (2002) where they reported NO$_3^-$ flux values of 0.71 and 0.31 µmol m$^{-2}$ day$^{-1}$ at 15 cm depth in sandy soils of mixed conifer forest located in the Lake Tahoe basin in Nevada. Burns and Murdoch (2005) reported increased mean concentrations of NO$_3^-$ one year after harvest, and concentrations decreased in the second and third years post-harvest. Harvesting decreased the uptake of N by plants and increased NO$_3^-$ production by soil microbes. Likens et al. (1969) and Vitousek (1981) reported increases in NO$_3^-$ leaching after clearcutting which was attributed to the combined effects of increased N mineralization and nitrification and decreased N uptake by vegetation. Many researchers (Stone, 1973; Vitousek, 1981; Lundborg, 1997) have indicated that increases in N-mineralization and nitrification rates after a clearcutting can be due to: (1) an increase in soil temperature from increased solar radiation
reaching forest floor; (2) an increase in soil moisture as a result of decreased transpiration rate; (3) C:N ratio of soil organic matter and slash; (4) the extent of physical disturbance of soils; and (5) an increase in availability of labile organic matter in the soil in the form of slash and roots.
Table 2.10. Type 3 Tests of Fixed Effects evaluating ion exchange resin flux data by collection, MOFEP harvest designation (trt), soil nutrient status (sns), and sampler depth.

Tukey-Kramer adjusted p-values of nutrient concentrations from split-plot generalized linear mixed model.

Dependent variables include total aluminum (Al\text{\textsc{t}}), calcium (Ca\textsuperscript{2+}), magnesium (Mg\textsuperscript{2+}), sodium (Na\textsuperscript{+}), and nitrate (NO\textsubscript{3}\textsuperscript{-}). Statistically significant effects (p-values <0.05) are noted in bold.

Analysis of IER flux data for all collection periods.

<table>
<thead>
<tr>
<th>Source</th>
<th>Al\text{\textsc{t}} flux</th>
<th>Ca\textsuperscript{2+} flux</th>
<th>Mg\textsuperscript{2+} flux</th>
<th>Na\textsuperscript{+} flux</th>
<th>NO\textsubscript{3}\textsuperscript{-} flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>trt</td>
<td>0.3947</td>
<td>0.6243</td>
<td>0.5744</td>
<td>0.2320</td>
<td>0.0226</td>
</tr>
<tr>
<td>sns</td>
<td>0.2382</td>
<td>0.4359</td>
<td>0.4735</td>
<td>0.1974</td>
<td>0.8607</td>
</tr>
<tr>
<td>trt*sns</td>
<td>0.4517</td>
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<td>0.4724</td>
<td>0.5672</td>
<td>0.8320</td>
</tr>
<tr>
<td>depth</td>
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<td>0.5058</td>
<td>0.0172</td>
</tr>
<tr>
<td>trt*depth</td>
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<td>0.9510</td>
<td>0.9689</td>
<td>0.3900</td>
<td>0.6089</td>
</tr>
<tr>
<td>sns*depth</td>
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<td>0.8099</td>
<td>0.7615</td>
<td>0.4214</td>
<td>0.1305</td>
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<td>0.0005</td>
<td>0.1058</td>
<td>&lt;.0001</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>trt*collection</td>
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<td>0.0005</td>
<td>&lt;.0001</td>
<td>0.1356</td>
<td>&lt;.0001</td>
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<tr>
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<td>0.4428</td>
<td>0.8928</td>
<td>0.1767</td>
</tr>
<tr>
<td>depth*collection</td>
<td>0.9035</td>
<td>0.5755</td>
<td>0.4022</td>
<td>0.6680</td>
<td>0.3573</td>
</tr>
</tbody>
</table>
Figure 2.7. Comparisons mean of daily flux of solutes by treatments and harvest (pre-harvest data represented by mean concentrations from collection period 1 and 2, and post-harvest data represented by mean concentrations from collection periods 3 and 4). Error bars represent the 95% confidence interval (CI). Significant differences (p values < 0.05) are noted by differing letters at the top of each bar.

(a) Al\textsubscript{T} flux, (b) Ca\textsuperscript{2+} flux, (c) Mg\textsuperscript{2+} flux, (d) Na\textsuperscript{+} flux, and (e) NO\textsubscript{3} flux.
2.5 Conclusion

Soil sampling data demonstrated significantly greater exchangeable K\(^+\) in post-harvest stands harvested with the STS regeneration method when compared to STS pre-harvest data and this change can be attributed to mineralization of slash after timber harvest. Significant changes were also observed for TN in post-harvest clearcut plots compared to pre-harvest. However a similar trend of significantly greater TN was observed for STS and NHM when compared to pre-harvest data. Apparently, these changes in TN were not due to harvest activities, rather could be due to variations in other systems (precipitation, temperature or sampling error, etc.). To investigate the long-term impact of clearcutting on soil properties, continuous soil sampling and analysis is needed for subsequent years.

The throughfall inputs of Ca\(^{2+}\) and DOC to the forest floor decreased immediately after clearcutting. Increased leaching of Mg\(^{2+}\) and TN was observed in clearcut plots, and the source for these nutrients could be mineralization of slash left behind after timber harvesting. Nitrate losses significantly increased in clearcutting which could be attributed to temporary decrease in uptake of N by plants roots resulting in excess production of NO\(_3^-\) by soil microorganisms or due to increased temperature and moisture conditions associated with canopy loss. Decreased concentration of SO\(_4^{2-}\) after clearcutting may be due to microbial immobilization and/or reduced mineralization. Mean daily flux from IER for NO\(_3^-\) and Mg\(^{2+}\) were significantly greater in post-harvest clearcutting compared to all other pre- and post-harvest treatments which clearly indicate that this increased nutrient flux is due to harvest. When pre-harvest NHM and STS were compared to post harvest NHM and STS for all dependent variables, mean flux values from IER samplers were lower in post-harvest NHM and STS. This decrease in flux values could be related to drought conditions which prevailed in 2012 throughout Missouri.
Overall, concentrations in soil solution and fluxes of Mg\(^{2+}\) and NO\(_3^-\) did increase in post-harvest clearcuts. These potential losses are of great concern for CC and are minimal for STS and NHM. Fluoride concentrations increased in all treatments post-harvest compared to all treatments pre-harvest which indicate that it may be the effect of yearly changes and may not be associated with actual harvest. Due to effect of season, amount of precipitation, harvesting and high variability of Ozark soils further investigation of post-harvest soil solution chemistry and nutrient flux is needed to determine if these nutrients will leach to ground and surface waters, whether these nutrients will continue to be retained on-site, in the soil or in circulation within developing vegetation in long-term.
CHAPTER 3: DETERMINANTS OF TOTAL AND AVAILABLE PHOSPHORUS IN MISSOURI OZARK HIGHLAND FOREST SOILS

3.1 Abstract

Phosphorus is important factor limiting forest growth in many parts of world, and the amount and availability of soil P declines over time with weathering. Soil phosphorus (P) pools are affected by several factors including geomorphic properties (e.g., slope position and parent materials) and chemical and physical properties (e.g., pH, organic carbon content, mineralogy, and clay content). The objective of this study was to identify the importance of geomorphic and soil properties on total and available P concentrations in forested soils of the Missouri Ozark Highlands. Archived soil samples and soil characterization data used in this work were obtained from fifty pedons sampled at the Missouri Ozark Forest Ecosystem Project (MOFEP) located in south-central Missouri. Additionally, soil chemical analyses were conducted to measure total P, available P, and citrate bicarbonate dithionite (CBD) extractable Fe, Al, and Mn in the samples studied. Linear regression and classification and regression tree (CART) analyses were applied to elucidate relationships between P pools and geomorphic and soil chemical properties. Total P and available P in the soils studied ranged from 15.55 to 410.13 mg kg\(^{-1}\) and 3.81 to 30.61 mg kg\(^{-1}\), respectively. Linear regression analyses indicated a moderate correlation of CBD extractable Mn with total P \(r^2 = 0.77\), Bray-1 available P \(r^2 = 0.69\), and Mehlich-3 available P \(r^2 = 0.71\) for soils overlying Eminence bedrock. The CART analysis identified (1) CBD extractable Mn and total organic C as important variables explaining 39% of the cumulative variation in total P; (2) CBD extractable Mn and exchangeable Ca as important variables explaining 49% of the cumulative variation of Bray-1 available P; and (3) CBD extractable Mn and pH as important variables explaining 55% of the cumulative variation of Mehlich-3 available P. This research
aids in understanding and identifying locations in Missouri Ozark forests where of P pools may be relatively small, thus necessitating careful management and monitoring before and after timber harvest.

3.2 Introduction

Missouri is ranked seventh out of twenty northeastern states in forested land area (5.6 million hectares) and the majority of this land, approximately 83%, is privately owned (MDC, 2000). Forested lands of Missouri are economically and ecologically important, particularly in the Ozark Highlands where the vast majority of Missouri’s forests are located. In general, soils underlying Missouri forests are highly weathered and not suitable for agricultural production (Brookshire et al., 1997). These lands are, however, suitable for timber production; average net growth, removals per year of growing stock and forest product consumption for Missouri are 517, 174.3 and 411 million ft³, respectively (adapted from Raeker et al., 2011). Timber harvesting is widespread in Ozark forests and harvesting is used to achieve long-term objectives of the landowner or managing agency. However, few studies have evaluated the influence of forest harvest on soil nutrients in the Missouri Ozarks.

Phosphorus is important limiting factor of forest growth in many parts of world (Fox et al., 2007; May et al., 2009; Trichet et al., 2009). Annually, more than 100 kg of N and 10 kg of P per hectare is needed for pine stands to maintain maximum volume production (Ducey and Allen, 2001; Battaglia et al., 2004). Yanai (1992) estimated the P budget over period of 70 years at the Hubbard Brook Experimental Forest. It was found that 61% of P assimilated each year by trees comes from forest floor and this pool represents only 5% of total P present in the soils studied. Phosphorus turnover rates were also calculated by Yanai (1992) and it was estimated that the forest floor contributed 7% yr⁻¹ and mineral soils contributed 0.3% yr⁻¹. Phosphorus is lost through a number of pathways in a forested ecosystem including biomass
removal by tree harvesting, leaching, soil erosion, and surface runoff. However, leaching of P from soils is expected to be rather limited. For example, Wood et al. (1984) reported that only 0.007 kg ha\(^{-1}\) yr\(^{-1}\) of P is leached northern hardwood forests (Wood et al., 1984).

Phosphorus is a rock-derived nutrient and its availability decreases with time (Creurs et al., 1995; Chadwick et al., 1999; Porder et al., 2006; Vitousek et al., 2010). Phosphorus is universally low in soils and most P is occluded within inorganic and organic substrates with less of availability in subsurface horizons (Brinck, 2009; Brady and Weil, 2010). With increasing soil pH, P bonded to Fe and Al oxides is solubilized and becomes readily available for plants. In contrast, solubility of P bound with Ca-bearing minerals decreases with increasing pH (Hinsinger, 2001). Phosphorus pools can be affected by several factors including landform or slope position, clay content, parent material, depth to bedrock, pH, organic carbon, oxides/hydroxides of Fe, Al, and Mn, calcium and cation exchange capacity.

Missouri Ozark Highland soils are predominantly acidic and highly weathered, and they are derived from variety of parent materials (e.g., residuum, alluvium, loess, and pedisediments) (Hammer, 1997). Therefore, significant potential exists that P concentrations in Ozark Highland soils will, in general, be quite low but also variable. In addition, geologic strata of the Missouri Ozarks consist of sedimentary rocks dominated by cherty limestone and dolomite with small contributions of sandstone and shale which are low in P content (King, 1997). King (1997) indicated that stratified parent material, landscape position, clay content, CEC and organic carbon are important factors affecting distribution and availability of P in the Missouri Ozarks. Hammer (1997) observed available P concentrations to be greater in surface and subsurface horizons for soils developed from residuum associated with lower the Gasconade geologic formation than soils associated with the Roubidoux formation, and most of total P was associated with Fe and Al oxides. The objective of this study was to
further identify the importance of geomorphic and soil properties on total and available P concentrations in forested soils of the Missouri Ozark Highlands.

3.3 Materials and Methods

3.3.1 Study Site and Soil Sampling

The Missouri Ozark Forest Ecosystem Project (MOFEP) is a long term experimental project started by the Missouri Department of Conservation (MDC) in year 1989. This project was started to comprehensively evaluate forest management practices on a wide array of upland ecosystem attributes, and this project is intended to last for three full rotations of 100 to 300 years. The MOFEP sites are located within the Missouri Ozark Highlands, and more specifically within the Current River Forest Breaks and the Current River Oak-Pine Woodland Hills land type associations (Nigh and Schroeder, 2002). The study is located in Shannon, Carter and Reynolds Counties, and these counties primarily consist of forested land (84%) (Hahn, 1991). The forests at MOFEP are predominantly comprised of oaks (Quercus sp.), shortleaf pine (Pinus echinata Mill.), and hickories (Carya sp.) (Kabrick, et al., 2004), and they are managed according to MDC’s Forest Land Management Guidelines (MDC, 1986).

The MOFEP experiment consists of nine sites and each site ranges in size from 314 to 516 ha (Figure 3.1). Geology of the area consists of the Roubidoux, Gasconade, and Eminence sedimentary rock formations, where first two are Ordovician age and third is Cambrian age (Thompson, 1995). Each bedrock unit differs considerably in lithology. The Roubidoux bedrock formation is interstratified with sandstone, dolomite, and silicified stromatolite algal and chert beds. The Gasconade formation is divided into the upper and lower Gasconade formations; the upper Gasconade is comprised of coarsely crystalline dolomite and the lower Gasconade is comprised of finely crystalline dolomite. The upper
Figure 3.1. Location of nine MOFEP sites in three counties and their management treatments (adapted from Kabrick et al., 2011).
portion of this formation is interbedded with chert and layers of silicified stromatolites; the lower portion is interbedded with a few chert nodules and it has a 1 to 3 m thick base of sandstone and quartzose bed. The Eminence formation is dominated by coarse, crystalline dolomite with occasional occurrence of interbedded cherts (Meinert et al., 1997; Kabrick et al., 2011). 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). Soils are highly weathered and formed from a variety of parent materials (e.g., residuum, alluvium, loess and pedisediments) (Hammer, 1997). The most common soil orders at MOFEP are Alfisols and Ultisols (Meinert et al., 1997) with low CEC, low base saturation (BS), and relatively low concentrations of exchangeable calcium and magnesium (Kabrick et al., 2011).

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 according to underlying bedrock, slope position and soil properties (Meinert et al., 1997). A backhoe was used 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. Samples were analyzed for the following parameters and applicable methodology (Burts 2004) is provided in parentheses: particle size distribution (pipette method); exchangeable base cations Ca, Mg, Na, and K (1 mol L⁻¹ NH₄OAc at pH 7); extractable acidity [0.5 mol L⁻¹ BaCl₂/0.2 mol L⁻¹ triethanol-amine (TEA) at pH 8.2 and back-titrated with 0.13 mol L⁻¹ HCl]; cation exchange capacity (calculated by summation of cations exchanged in NH₄OAc at pH 7); organic C [Leco C analyzer (Leco Corp., St. Joseph, MI)]; and soil pH (1:1 solid/solution ratio in water and 1:2 solid/solution ratio in 0.01 mol L⁻¹ CaCl₂). All information for seventy-four pedons is available at Missouri Cooperative Soil
Survey (http://www.soilsurvey.org) and each pedon can be accessed using pedon identifications number provided in Appendix H.

3.3.2 Experimental Protocol and Sample Analysis

Fifty of the 74 originally sampled pedons were used in this research. 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 the archived samples. Sixty-seven of the 74 pedons met the criteria of > 100 cm depth, but only 50 complete pedons could be located. Three soil horizons from each pedon meeting the following criteria were selected for study: (1) first mineral horizon (50 A horizons); (2) first B horizon and where there was no Bt horizon the first Bw was selected (47 Bt and 3 Bw horizons); (3) and the soil horizon encompassing the depth of 100 cm (47 Bt horizons, 2 Bw horizons, and 1 C horizon.

The pedon identification number, horizon, landform, parent material, bedrock, slope position, clay content, CEC, BS, pH and exchangeable Ca and Mg for these 50 pedons (150 horizons) were obtained from Missouri Cooperative Soil Survey (http://www.soilsurvey.org). All samples were analyzed for Bray-1 and Mehlich-3 available P (Bray and Kurtz, 1945; Mehlich, 1984), total P (70% perchloric acid digestion; Kuo 1996), total organic P (extraction with diluted NaOH, concentrated HCl; Mehta, 1954), inorganic P (sequential fractionation scheme for inorganic P; Kuo, 1996) and Fe, Al and Mn oxide content (citrate bicarbonate dithionite method; Loeppert and Inskeep, 1996). Each horizon was analyzed in duplicate and the values were averaged. If results differed by greater than 10% relative to the mean, a third replicate was analyzed; the value exhibiting greater than 10% variability was then excluded from dataset. Analysis results for each horizon, separated on the basis of bedrock formation, are provided in Appendix H.
Procedure for extraction of available phosphorus

Soil samples selected for this research were highly variable in pH ranging from pH 4.4 to 7.2. Therefore, to more accurately quantify the amount of available P, two different available P extraction methods were used: (1) Bray-1 and (2) Melich-3. In brief, Bray-1 was determined by adding 2 g of soil (<2 mm) a 50 mL Erlenmeyer flask. The sample was reacted with 20 ml of Bray-1 extracting solution (0.025 M HCl in 0.03 M NH₄F) for 5 min at 200 rpm on a mechanical shaker (Bray and Kurtz, 1945). The supernatant was filtered through a 0.45 µm Whatman polypropylene syringe filter directly into 50 ml Erlenmeyer flask. For the Mehlich-3 method, 2 grams of well-ground soil (<2 mm) was added to a 50 mL Erlenmeyer flask and extracted with 20 ml of Mehlich-3 extracting solution (0.2 M CH₃COOH, 0.25 M NH₄NO₃, 0.015 M NH₄F, 0.013 M HNO₃, 0.001 M EDTA) for five minutes at 200 rpm on a mechanical shaker (Mehlich, 1984). The supernatant was filtered through a 0.45 µm Whatman polypropylene syringe filter directly into 50 ml Erlenmeyer flask. The concentration of P in solution was measured colorimetrically using the modified ascorbic acid method (Kuo, 1996) described later in this section.

Procedure for extraction of total phosphorus

Total phosphorus content was measured using a rapid digestion with perchloric acid technique (Kuo, 1996). In brief, 2 g of soil (<2 mm) was added to a 200 ml volumetric flask and digested in 30 ml of 12 M perchloric acid (HClO₄) on a hot plate at 130°C in a well-ventilated, perchloric acid hood until the dark color associated with organic matter was no longer visible. Samples were further heated to 203°C for 20 min until heavy white fumes developed above the flask and only white, insoluble material remained in the reaction vessel. When digestion was completed samples were cooled to room temperature and brought to a final volume of 200 ml via addition of Barnstead ultrapure water. The concentration of P in
solution was measured colorimetrically using the modified ascorbic acid method (Kuo, 1996) described later in this section.

**Procedure for sequential extraction of inorganic P**

Sequential extraction of soil to quantify inorganic P fractions was carried out using the procedure described by Kuo (1996). In brief, 0.5 g of soil (<2 mm) was added to a 50 ml centrifuge tube and extracted using the procedure provided in Figure 3.2. At every step in the sequential extraction process, 2 ml of supernatant was analyzed colorimetrically using the modified ascorbic acid method (Kuo, 1996).

**Procedure for extraction of total organic P**

Total organic P in soil was determined using base extraction (extraction with dilute NaOH) followed by acid + base extraction (concentrated HCl, and dilute NaOH) (Kuo, 1996). In brief, 1 gram of soil (<2 mm) was added to a 50 ml polypropylene co-polymer (PPCO) centrifuge tube. Samples were extracted with 35 ml of sodium hydroxide (0.3 M NaOH) for 16 hours on a mechanical shaker and centrifuged to obtain clear supernatant, which was added to a 50 ml volumetric flask. The sample was then extracted with 10 ml of concentrated HCl and heated in water bath to 70°C for 10 minutes. The sample was then cooled at room temperature, and 25 ml of water was added followed by centrifugation. Supernatant was collected in a 100 ml volumetric flask. The same sample was then extracted with 45 ml of sodium hydroxide (0.5 NaOH) and heated for 8 hours in a water bath at 90°C. Following heating, the sample was centrifuged and the supernatant obtained was mixed with supernatant collected from the HCl extraction in a 100 ml volumetric flask. Five milliliter aliquots from the base extraction and acid+base extraction were analyzed using the modified ascorbic acid method (Kuo, 1996).
Figure 3.2. Sequential extraction procedure for extraction of inorganic P in non-calcareous soils.

0.5 g of soil in 50 ml centrifuge tube

25 ml of 1 M NH₄Cl, shake 30 min, centrifuge

25 ml of 0.5 M NH₄F, shake 1 hr, centrifuge, wash with saturated NaCl

25 ml of 0.1 M NaOH, shake 17 hr, centrifuge, wash with saturated NaCl

20 ml of 0.3 M Na₃C₃H₆O₇, 2.5 ml of 1 M NaHCO₃, 1.0 Na₂S₂O₄, heat, stir, centrifuge and wash

25 ml of 0.25 M H₂SO₄, shake 1 hr., centrifuge and wash

Soluble and loosely bound P

Al-P

Fe-P

Reductant Soluble P

Ca-P
Procedure for determining P concentrations in extracts

Phosphorus concentration in extracts obtained from all the procedures described above was measured using a spectrophotometer (Spectronic Genesys 8, SG8074629, England) at 880 nm using the ascorbic acid method described by Kuo (1996). In brief, a 2 ml aliquot of sample was added to a 50 ml volumetric flask along with 30 ml of Barnstead ultrapure water and 8 ml of molybdenum mixed reagent was added to develop blue color. For this method blue color develops in 10 minutes and the color is stable for 24 hours.

Procedure for extraction and determination of oxides of Fe, Al and Mn

Oxides of Fe, Al, and Mn were extracted from soil samples using the citrate-bicarbonate-dithionite (CBD) method (Loeppert and Inskeep, 1996). In brief, 2.5 g of soil (<2 mm) was weighted into a 50 ml polypropylene co-polymer (PPCO) plastic centrifuge tube. Extraction was carried out by adding 25 ml of 0.3 M sodium citrate (C₆H₅Na₃O₄•2H₂O) and 5 ml of 1 M sodium bicarbonate (NaHCO₃). All samples were heated in a water bath at 80°C for 30 minutes and 1 g of sodium dithionite (Na₂S₂O₄) was added in each sample. Samples were removed from the water bath when the soil turned gray in color and samples were cooled at room temperature. After cooling, 5 ml of saturated sodium chloride (32.5 % w/v NaCl) was added to promote flocculation and samples were centrifuged for 15 min at 1200 rpm. Extracts of Fe, Al, and Mn were filtered through a 0.45 µm filter and concentrations were measured using inductively coupled plasma (ICP) – atomic emission spectrophotometer (AES) (Varian Liberty RL, Australia).

3.3.3 Data Analysis

Mean concentrations were calculated as were the 95% of confidence interval around each mean. Linear regression analyses were performed using the PROCREG procedure in SAS™.
Due to high variability in soils of Missouri Ozark Highlands, it was assumed that multiple factors can be associated with P concentrations. This presents a challenge for linear regression which is an approach to model the relationship between a scalar dependent variable and one explanatory variable and the method assumes that the explanatory variable is a fixed factor which lacks multicollinearity (Kutner et al., 2004). To overcome this challenge, a Classification and Regression Tree (CART) analysis was used to analyze the role of soil and geomorphic factors associated with concentrations of various P forms in Ozark Highland soils. Classification and regression tree modeling is a non-parametric, binary recursive partitioning technique that operates through top to bottom recursive partitioning and bottom up pruning, also called the cross-validation procedure (Breiman et al., 1993). Classification and regression tree modeling has been applied to many soil studies to predict nutrient concentrations across the landscape (Bedison and Johnson, 2009; Johnson et al., 2009; Kabrick et al., 2011). The most important merit 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, three forms of soil P were used as continuous response variables for the construction of three different regression trees: total P, Mehlich-3 available P, and Bray-1 available P (mg kg\(^{-1}\)). Predictor variables used for investigating these forms of P included: (1) horizon or depth; (2) parent material; (3) underlying bedrock formation; (4) profile position or slope position; (5) landform type; (6) exchangeable Ca; (7) CEC; (8) soil pH in water; (9)
clay content; (10) total organic carbon content; (11) Fe and Al oxide content; and (12) Mn oxide content (variables are further described in Table 3.1).

The CART analysis consists of four basic steps. First, recursive splitting of nodes occurs during tree development, which includes splitting of data on basis of low and high concentrations of a response variable. Here explanatory variables are used to minimize the variation between the two splits or nodes. To handle continuous data such as available P and total P, splitting was performed to maximize the deviance criteria: \( \text{SST} - (\text{SSL} + \text{SSR}) \), where \( \text{SST} \) is the sum of squares for the data and \( \text{SSR} \) and \( \text{SSL} \) are the sums of squares for the right and left nodes created by splitting the data (Breiman et al., 1984). The second step involves halting the tree building process. During successive partitioning processes each higher node splits into two lower nodes or subsets using explanatory variables which further reduce overall variation in data set. The process of splitting is continued until a terminal node is reached (no further splitting) and residual variation of data is less than 1%. At this point, maximum size of tree has been achieved and information in the data set is likely over-fitted.
Table 3.1. Response and explanatory variable used in CART analysis.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Variable Type</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Response Variables</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total P</td>
<td>Continuous</td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td>Mehlich-3 Available P</td>
<td>Continuous</td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td>Bray-1 Available P</td>
<td>Continuous</td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td><strong>Explanatory Variables</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horizon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; mineral horizon</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; Bt or Bw horizon</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>Horizon at 100 cm depth</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>Parent material</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alluvium</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>Pedisediment</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>Pedisediment over residuum</td>
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<td>-</td>
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<tr>
<td>Bedrock</td>
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<tr>
<td>Eminence</td>
<td>Categorical</td>
<td>-</td>
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<tr>
<td>Roubidoux</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>Upper gasconade</td>
<td>Categorical</td>
<td>-</td>
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<tr>
<td>Lower gasconade</td>
<td>Categorical</td>
<td>-</td>
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<tr>
<td>Slope position</td>
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<tr>
<td>Summit</td>
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<td>-</td>
</tr>
<tr>
<td>Backslope</td>
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<td>Floodplain</td>
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<td>-</td>
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<tr>
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<tr>
<td>Structural bench</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>Ridge</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>Hillslope</td>
<td>Categorical</td>
<td>-</td>
</tr>
<tr>
<td>Floodplain</td>
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<td>-</td>
</tr>
<tr>
<td>ExCa ¥</td>
<td>Continuous</td>
<td>cmolc kg⁻¹</td>
</tr>
<tr>
<td>CEC ¶</td>
<td>Continuous</td>
<td>cmolc kg⁻¹</td>
</tr>
<tr>
<td>pH</td>
<td>Continuous</td>
<td>-</td>
</tr>
<tr>
<td>Clay</td>
<td>Continuous</td>
<td>g kg⁻¹</td>
</tr>
<tr>
<td>TOC ß</td>
<td>Continuous</td>
<td>g kg⁻¹</td>
</tr>
<tr>
<td>CBD Fe+Al €</td>
<td>Continuous</td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td>CBD-Mn Ø</td>
<td>Continuous</td>
<td>mg kg⁻¹</td>
</tr>
</tbody>
</table>

¥ Exchangeable calcium.
¶ Cation exchange capacity.
ß Total organic carbon.
€ Citrate bicarbonate dithionite extractable Iron plus Aluminium (CBD-Fe+Al).
Ø Citrate bicarbonate dithionite extractable Manganese (CBD-Mn).
The third step consists of pruning the tree or removing nodes that explain small variability to create simpler trees. A 10-fold cross validation technique for assessing accuracy of our three models was utilized (see Appendix A-VII for models). During pruning, the maximum size tree or the reference tree developed is partitioned into 10 folds or groups and 10 new subsets of the total data set are created using 9 out of 10 of the folds. The reduced dataset is then used to build 10 test trees containing 10% of the data which is further used to compute classification error for that particular tree. After building 10 test trees, average classification error as a function of tree size is computed and pruning of reference tree is carried to the number of nodes matching the tree size that produces the minimum cross validation error (Breiman et al., 1984). The fourth step involves selection of optimal tree size; trees selected for the three P models had the lowest overall error rate and the dataset was least over-fitted. The CART modeling was performed in R version 2.15.3 (rpart version 4.1-1, The R Foundation for Statistical Computing, Vienna, Austria).

3.4 Results and Discussions

3.4.1 Fractionation of Inorganic and Organic P forms

Sixty horizons were analyzed for organic P and thirty horizons for inorganic P. Although attempts were made to optimize the analysis techniques, phosphorus concentrations for these pools were very low and exhibited relatively high error. Therefore, confidence in these results is minimal and this data has been excluded the remainder of the study.

3.4.2 Mean Concentrations of P pools and Oxides of Fe, Al and Mn

The mean concentration of total P across all 150 soil horizons (three horizons from 50 pedons) was 116.2 mg kg\(^{-1}\) (Table 3.2), which was lower than concentration of total P (163.7 mg kg\(^{-1}\)) reported by King (1997) in Missouri Ozark forest soils. Mean concentrations of Mehlich-3 available P and Bray-1 available P were 7.87 and 5.81 mg kg\(^{-1}\), respectively, and
these values fall in low category ($\leq 11 \text{ mg kg}^{-1}$) of phosphorus levels for soils of this region (Nathan et al., 2007). Also, CBD extractable Fe, Al and Mn mean concentrations were 10.26, 1.45, and 0.53 g kg$^{-1}$ for all horizons (Table 3.2).

Overall, concentrations of P decreased with depth, similar to observations by Brubaker et al. (1993) in soils of eastern Nebraska, where the available P decreased with an increase in calcium carbonates and extractable Ca and Mg. However, carbonates were not present in the soils studied and concentrations of extractable Ca and Mg in forested Ozark Highland soils can be quite low (Kabrick et al., 2011). It is anticipated that over time weathering and leaching of elements occurs and may increase concentrations of CBD extractable Fe, Al and Mn with depth in highly weathered soils. Although mean concentrations of CBD-Fe increased with depth, CBD-Mn decreased with depth and CBD-Al in B horizons was reduced relative to horizons at shallower and deeper depths (Table 3.2).

Mean P concentrations and CBD extractable Fe, Al and Mn were also calculated on basis of parent material, bedrock, and landform. All forms of P and CBD-Mn concentrations were greatest in soils weathered from alluvium parent material, soils overlying the Eminence formation, and soils found on the floodplain landform (Table 3.2). One explanation for greater P concentration in alluvium found on the floodplain is that this material has undergone less weathering relative to soils formed in pedisediments and pedisediments over residuum. The influence of bedrock formation on P concentrations follows observations by Kabrick et al. (2011) regarding calcium concentrations in the same soils studied here. Kabrick et al. (2011) reported that soils overlying the Eminence and lower Gasconade formations contain greater concentrations of Ca. The correlation of greater Ca and P concentrations in soils overlying the Eminence formation may be attributable to the formation of Ca-P complexes in the soil matrix (Walker and Syers, 1976).
Table 3.2. Mean concentrations ± 95% confidence interval of P forms and citrate bicarbonate dithionite extractable iron, aluminum and manganese for all horizons, first mineral horizon, first Bt or Bw horizon, and horizon at 100 cm on the basis of parent material, bedrock and landform in Missouri Ozarks.

<table>
<thead>
<tr>
<th></th>
<th>Total P</th>
<th>Mehlich-3 Available P</th>
<th>Bray-1 Available P</th>
<th>CBD-Fe †</th>
<th>CBD-Al ‡</th>
<th>CBD-Mn ¥</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg kg⁻¹</td>
<td>g kg⁻¹</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td><strong>All Samples</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>All horizons (n=150)</td>
<td>116.19 ± 6.93</td>
<td>7.87 ± 0.41</td>
<td>5.81 ± 0.48</td>
<td>10.26 ± 0.97</td>
<td>1.45 ± 0.08</td>
<td>0.53 ± 0.06</td>
</tr>
<tr>
<td>1st mineral horizon (n=50)</td>
<td>146.32 ± 14.44</td>
<td>10.33 ± 0.79</td>
<td>9.00 ± 0.95</td>
<td>5.38 ± 0.19</td>
<td>1.28 ± 0.07</td>
<td>0.97 ± 0.11</td>
</tr>
<tr>
<td>1st Bt or Bw horizon (n=50)</td>
<td>108.09 ± 8.81</td>
<td>6.92 ± 0.56</td>
<td>4.42 ± 0.59</td>
<td>7.50 ± 0.74</td>
<td>1.19 ± 0.10</td>
<td>0.46 ± 0.08</td>
</tr>
<tr>
<td>Horizon at 100 cm (n=50)</td>
<td>94.16 ± 9.73</td>
<td>6.36 ± 0.51</td>
<td>4.01 ± 0.53</td>
<td>17.90 ± 2.10</td>
<td>1.88 ± 0.19</td>
<td>0.15 ± 0.05</td>
</tr>
<tr>
<td><strong>Parent Material</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Alluvium (n=21)</td>
<td>156.34 ± 28.75</td>
<td>12.57 ± 1.83</td>
<td>9.89 ± 1.78</td>
<td>5.78 ± 0.35</td>
<td>1.07 ± 0.13</td>
<td>0.99 ± 0.19</td>
</tr>
<tr>
<td>Pedisediment (n=66)</td>
<td>106.78 ± 7.54</td>
<td>7.01 ± 0.35</td>
<td>5.14 ± 0.53</td>
<td>10.85 ± 1.36</td>
<td>1.52 ± 0.12</td>
<td>0.47 ± 0.08</td>
</tr>
<tr>
<td>Ped/residuum Ï (n=39)</td>
<td>118.24 ± 11.99</td>
<td>7.23 ± 0.51</td>
<td>5.05 ± 0.70</td>
<td>11.06 ± 1.96</td>
<td>1.41 ± 0.14</td>
<td>0.44 ± 0.10</td>
</tr>
<tr>
<td><strong>Bedrock</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roubidoux (n=30)</td>
<td>109.76 ± 12.68</td>
<td>7.81 ± 0.62</td>
<td>5.67 ± 1.01</td>
<td>9.21 ± 2.30</td>
<td>1.57 ± 0.27</td>
<td>0.42 ± 0.11</td>
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<tr>
<td>Upper Gasconade (n=36)</td>
<td>108.19 ± 9.57</td>
<td>6.80 ± 0.47</td>
<td>5.14 ± 0.81</td>
<td>10.99 ± 2.24</td>
<td>1.43 ± 0.13</td>
<td>0.63 ± 0.13</td>
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<tr>
<td>Lower Gasconade (n=57)</td>
<td>113.25 ± 11.66</td>
<td>7.20 ± 0.57</td>
<td>5.40 ± 0.83</td>
<td>11.27 ± 2.00</td>
<td>1.47 ± 0.15</td>
<td>0.50 ± 0.12</td>
</tr>
<tr>
<td>Eminence (n=24)</td>
<td>147.54 ± 24.19</td>
<td>11.08 ± 1.84</td>
<td>7.86 ± 1.69</td>
<td>7.62 ± 1.35</td>
<td>1.16 ± 0.14</td>
<td>0.63 ± 0.20</td>
</tr>
<tr>
<td><strong>Landform</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Structural Bench (n=48)</td>
<td>98.80 ± 10.59</td>
<td>7.18 ± 0.41</td>
<td>5.47 ± 0.62</td>
<td>10.59 ± 1.58</td>
<td>1.49 ± 0.12</td>
<td>0.53 ± 0.1</td>
</tr>
<tr>
<td>Hillslope (n=36)</td>
<td>131.53 ± 11.91</td>
<td>7.31 ± 0.58</td>
<td>5.52 ± 0.93</td>
<td>10.14 ± 1.75</td>
<td>1.31 ± 0.13</td>
<td>0.39 ± 0.09</td>
</tr>
<tr>
<td>Ridge (n=42)</td>
<td>105.32 ± 9.34</td>
<td>6.75 ± 0.50</td>
<td>4.35 ± 0.63</td>
<td>11.96 ± 2.27</td>
<td>1.64 ± 0.19</td>
<td>0.44 ± 0.11</td>
</tr>
<tr>
<td>Floodplain (n=21)</td>
<td>156.34 ± 28.75</td>
<td>12.57 ± 1.83</td>
<td>9.89 ± 1.78</td>
<td>5.78 ± 0.35</td>
<td>1.07 ± 0.13</td>
<td>0.99 ± 0.19</td>
</tr>
</tbody>
</table>

† Citrate bicarbonate dithionite extractable iron.
‡ Citrate bicarbonate dithionite extractable aluminum.
¥ Citrate bicarbonate dithionite extractable manganese.
Ï Pedisediment over residuum.
Mean concentrations of P forms and CBD Fe, Al and Mn were calculated on the basis of individual horizons for each parent material, bedrock and landform (Figure 3.3 and Appendix I). Parent material had an important effect on concentrations of P forms and CBD-Mn in the horizons studied (Figure 3.3). Mean concentrations of total and available P in all three horizons of the alluvial soils were greater than horizons from pedisediment and pedisediment over residuum derived soils (Figure 3.3a-c). Concentrations of CBD Fe and Al were significantly reduced in alluvial soil horizons occurring at the 100 cm depth relative to the other two parent materials (Figure 3.3d-e). In all three alluvial soil horizons, mean concentrations of CBD-Mn were significantly greater than the other two parent materials (Figure 3.3f). Bedrock and landform also showed some significance in regulating the concentration of P forms and CBD-Mn (Appendix I); whereas, the relationship of CBD Fe and Al with bedrock and landform is unclear (Appendix I). Mean concentrations for all P forms and CBD-Mn were greater in soils found on the Eminence formation and some significant differences were observed when compared to other underlying bedrock formations (Appendix I).

Kabrick et al. (2011) reported that Ca concentrations in soils weathered from alluvium parent material decrease with depth; whereas, Ca and Mg concentrations in soils weathered from pedisediment and pedisediment over residuum parent materials increase with depth. In contrast, available P and total P concentrations decrease with depth in soils weathered from all three parent materials. The overall behavior of P concentrations in these pedons is not clearly explained by trends in Ca and Mg concentrations reported by Kabrick, et al. (2011). Therefore, other factors may be involved in regulating P concentrations in these mineral horizons.

Soil pH is one important factor that may influence P concentrations. Graphs of mean concentrations for P forms and associated pH values are shown in Figure 3.4. Some
significant differences were observed in P concentrations as a function of pH (Appendix M), and mean P concentrations increased concurrently with pH and reached maximum values between the pH 6.25 to 6.75 before decreasing (Fig. 3.4). Our results for P concentrations are in agreement with previous literature citing the relation of P and soil pH (Harrison and Adams, 1987; Sanyal and De Datta, 1991; Brady and Weil, 2010). Comparatively more variation was observed in mean concentrations of available P extracted using the Bray-1 extracting solution than the Mehlich-3 extracting solution (Figure 3.4a-b). Bray-1 estimates of available P are better suited for acidic soils and the method provides less reliable results as soil Ca content increases; whereas, the Mehlich-3 test can estimate P availability on wide range of soils, both acidic and basic in origin (Sims, 2009). Phosphorus content also increased with increasing content of CBD extractable Mn and decreased with increasing content of CBD extractable Fe+Al as a function of pH (Fig. 3.5). Concentrations of CBD-Mn were greatest and concentrations of CBD Fe+Al were least between pH of 6.25 and 6.75. Due to the high variability in soil chemical properties and variance in landscape and geomorphic factors amongst the soils studied, it is difficult to correlate P concentrations with a single factor. Therefore, a robust statistical analysis investigating more than one prediction variable may be required to evaluate soil and geomorphic factors related to P forms.
Figure 3.3. Plots representing mean concentrations of (a) Mehlich-3 available P, (b) Bray-1 available P, (c) total P, (d) CBD-Fe, (e) CBD-Al, (f) CBD-Mn, in three soil horizons by parent material type. Error bars represent ± one standard error.
Figure 3.4. Plots representing mean concentrations of P pools by soil pH.
Comparisons of (a) Mehlich-3 available P (b) Bray-1 available P (c) total P. Error bars represent ± one standard error.
Figure 3.5. Plots representing mean concentrations of P forms, CBD extractable Fe+Al and Mn by soil pH.
Comparisons of (a) Mehlich-3 available P and CBD-Mn-, (b) Bray-1 available P and CBD-Mn-, (c) total P and CBD-Mn (d) CBD-Mn and CBD Fe+Al, (e) Mehlich-3 available P and CBD Fe+Al, (f) Bray-1 available P and CBD Fe+Al, and (g) total P and CBD Fe+Al as a function of pH.
3.4.3 Linear Regression Analysis for P Forms and Predictor Variables

The linear regression coefficients between the three P forms and predictor variables (percent clay, exchangeable Ca, exchangeable Mg, CEC, BS, pH, TOC, and CBD extractable Al, Fe, Mn, Al+Fe and Al+Fe+Mn) are provided in Appendix J. The most important characteristic of Missouri Ozark soils, belonging to orders Alfisols and Ultisols, is the presence of an argillic horizon (USDA-NRCS, 1999). Some weak relationships were observed between the three P forms and clay content (Appendix J-1 to J-3). The strongest r² values between P and clay content were expressed for the hillslope landform in all three horizons (total P). Soils in various landforms were associated with landscape position as: structural bench on either a summit, shoulder or footslope; hillslope on a backslope; ridge either with summit or shoulder; and floodplain with floodplain (Appendix H). Figure 3.6 illustrates the relationship between clay content and mean concentration of total P and available P with depth as a function of landscape position (summit, shoulder, backslope, footslope, and floodplain). As the amount of clay increased, total P decreased with exception for the backslope where total P increased in the horizon found at a 100 cm depth. However, available P fractions did not increase in subsurface horizons and decrease with increasing content of clay with exception in the floodplain where available P and clay both decrease with depth. Day et al. (1987) evaluated the distribution of various forms of soil P in northwest Florida and reported that total P content was directly associated with clay content in soils at lower landscape positions. In the samples studied here, most of the readily available P was concentrated in the surface horizons, perhaps explaining the lack of significant correlation between available P and clay content in deeper soil horizons.

The primary underlying bedrock type in the Missouri Ozarks is dolomite (Keys et al., 1995), which contributes to Ca and Mg content to soils of the region. In samples from all
horizons, the relation between total P and exchangeable Ca was weak ($r^2 = 0.25-0.50$) and in horizon A it was moderate ($r^2 = 0.50-0.75$). Whereas, moderate to strong ($r^2 > 0.75$) relationships between total P and exchangeable Ca in all horizons and in the A horizon were observed for samples overlying the Roubidoux and Eminence bedrock formations. Similar relations between total P and exchangeable Mg were observed in only horizon A for Roubidoux and Eminence bedrocks based on coefficients of determination ($r^2$). Mehlich-3 available P, only, was strongly correlated with exchangeable Ca in A horizon samples from soils overlying the Eminence bedrock formation (Table 3.3 and Appendix J-7 to J-8).

With respect to parent materials, strong correlations were observed for total P in all horizons sampled from alluvial and A horizons in alluvium (Table 3.3a). Weak to moderate relationships were observed between Mehlich-3 available P and exchangeable Ca for all horizons from alluvium and alluvial A horizons (Table 3.3b). However coefficients of correlation were indicated weaker relationships between total P and exchangeable Ca in deeper horizons in pedisediments and pedisediments over residuum parent materials. For landforms, hillslope showed moderate correlation between total P and Ca/Mg for deeper soil horizons; whereas, a strong correlation was observed between Mehlich-3 available P and Ca/Mg in hillslope A horizons (Table 3.3 and Appendix D-7 to D-8). When considering the floodplain landform, moderate relationships were observed for Mehlich-3 available P with exchangeable Ca in the A horizon and Bray-1 available P with exchangeable Ca in the first B horizon.

Clay is important factor regulating exchangeable cation content in a soil profile. As the amount of clay increases in deeper horizons the probability of retaining cations is increased. Most of the regression coefficients were very weak ($r^2 < 0.25$) to weak in lower horizons between the three forms of P and CEC. The strong $r^2$ values which were observed between total P and CEC were: all horizons and A horizon samples from alluvium parent material,
with: bedrock- Roubidoux with horizon A and Eminence with all horizons and horizon A; landform- hillslope with all horizons, horizon B, and horizon at 100 cm and floodplain with all horizons and horizon A (Appendix J-10). When considering Mehlich-3 available P and CEC, strong correlations were observed for A horizon samples overlying the Eminence bedrock and from hillslope landforms. In contrast, Bray-1 available P and CEC were strongly correlated in A horizon samples associated with only the upper Gasconade bedrock formation in horizon A (Appendix J-11 and J-12).

Soil pH has always been considered an important factor regulating the amount of P in soil; however, no significant relationships were observed for total P and pH in horizons located at a depth of 100 cm (Appendix J-16). Moderate and strong relationships between total P and pH were only observed with: parent material- alluvium in A horizon; bedrock- Roubidoux and Eminence in horizon A and B; landform- floodplain with A horizon.

Mehlich-3 available P also showed moderate and strong relations with pH: parent material- alluvium in B horizon; bedrock- Roubidoux in horizon at 100 cm and Eminence in A horizon and B horizon; landform- hillslope in A horizon and floodplain in B horizon. Whereas, Bray-1 available P showed moderate and strong relations with pH: parent material- alluvium in B horizon; bedrock- Roubidoux in horizon at 100 cm and Eminence in B horizon; landform- floodplain in B horizon (Appendix J-17 and J-18). Soil pH for all 150 soil samples ranged from 4.4 to 7.2, making it very difficult to derive important conclusions based on linear regression relations between P forms and soil pH.

Phosphorus forms and their relation with TOC in soil has been studied by many researchers (Harrison, 1982; Ohta and Effendi, 1992; Crews et al., 1995). From regression relations between total P and TOC, moderate relations were observed for: bedrock- upper Gasconade in B horizon and Eminence in all horizons and A horizon; landform- hillslope in B horizon and horizon at 100 cm (Appendix J-19). Mehlich-3 and Bray-1 available P
exhibited weak relations with TOC for all horizons in all formations. King (1997) found that soil organic C was moderately and strongly correlated with TP in soils overlying the Roubidoux, upper Gasconade and Eminence bedrock formations in the Missouri Ozarks having $r^2$ values of 0.65, 0.87, and 0.81 respectively. Additionally, a moderate relationship was observed between Mehlich-3 available P and TOC for all horizons collected from the hillslope landform (Appendix J 19-21).

Oxides of Fe and Al play an important role in regulating inorganic P in acidic soils (Harrison, 1987), and it was reported previously that most of the inorganic P present in Missouri Ozarks is occluded with the Fe and Al fractions (King 1997). Moderate and strong relationships between total P and CBD Fe+Al were observed for: parent material- alluvium in A horizon and horizon at 100 cm depth; bedrock- upper Gasconade in A horizon and horizon at 100 cm and Eminence in A horizon; landform- hillslope in A horizon and horizon at 100 cm and floodplain in A horizon and horizon at 100 cm (Appendix J-31). Some very weak negative relationships were observed between Mehlich-3 available P and CBD Fe+Al in all horizons with exception for samples from alluvium parent material and the floodplain landform (Appendix J-32). Bray-1 available P and CBD Fe+Al also showed very week negative relations in all horizons (Appendix J-33). Concentrations of Fe and Al in most of the soil samples increased with depth and available P decreased with depth which may explain negative relationships observed between available P and CBD Fe+Al. Extractable Mn oxides were very weakly to moderately correlated with all forms of P (Appendix J-28, J-29 and J-30). Some strong relations were observed between total P and CBD-Mn for: parent material- alluvium in all horizons and A horizon; bedrock- Roubidoux in A horizon, upper Gasconade in B horizon, and Eminence in all horizons and A horizon; landform- floodplain in all horizon and A horizon. Mehlich-3 available P and CBD-Mn had strong relationships in B horizon and the horizon at 100 cm for samples overlying Eminence bedrock; whereas, Bray-1
available P and CBD-Mn had strong relation with bedrock; Eminence in B horizon. (Appendix J-29 and J-30).

Linear regression analysis indicated that multiple factors can be used for predicting P in Missouri Ozarks, of which exchangeable Ca, pH, TOC and CBD-Mn exhibited some strong and moderate relations with all three forms of P. But linear regression is an approach to model the relationship between a scalar dependent variable and single explanatory variables and assumes explanatory variable as a fixed factor which lacks multicollinearity (Kutner et al., 2004). To overcome the above challenge classification and regression tree analysis (CART) was selected and results of CART analysis are presented in next section.
Figure 3.6. Mean concentrations of P forms and clay content in g kg\(^{-1}\) for five landscape positions as a function of depth.

Comparisons (a) Total P and clay content (b) Mehlich-3 available P, Bray-1 available P and clay content.
Table 3.3. Linear regression coefficients between exchangeable Ca and P forms in Missouri Ozark soils. Statistically significant effects (p-values <0.05) are noted in bold.

(a) Linear regression relationships between exchangeable Ca and total P concentrations in Missouri Ozark soils.

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(b) Linear regression coefficients between exchangeable Ca and Mehlich-3 available P concentrations in Missouri Ozarks.

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Linear regression coefficients between exchangeable Ca and Bray-1 available P concentrations in Missouri Ozarks.

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Table 3.4. Linear regression coefficients between CBD-Mn and total P concentrations in Missouri Ozarks. Statistically significant effects (p-values <0.05) are noted in bold.

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<tr>
<td>Rouhoudoux</td>
<td>74.46501</td>
<td>0.08367</td>
<td>0.5703</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>Horizon A</td>
<td>51.83702</td>
<td>0.11967</td>
<td>0.8365</td>
<td>0.0002</td>
</tr>
<tr>
<td>Horizon B</td>
<td>96.13003</td>
<td>0.04504</td>
<td>0.2357</td>
<td>0.1549</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>82.1979</td>
<td>-0.03654</td>
<td>0.4917</td>
<td>0.0239</td>
</tr>
<tr>
<td>Upper Gasconade</td>
<td>75.7506</td>
<td>0.05177</td>
<td>0.4846</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>Horizon A</td>
<td>69.05269</td>
<td>0.05443</td>
<td>0.3886</td>
<td>0.0303</td>
</tr>
<tr>
<td>Horizon B</td>
<td>57.32169</td>
<td>0.08429</td>
<td>0.8199</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>88.29608</td>
<td>-0.00218</td>
<td>0.0004</td>
<td>0.9533</td>
</tr>
<tr>
<td>Lower Gasconade</td>
<td>83.40173</td>
<td>0.05996</td>
<td>0.2263</td>
<td>0.0002</td>
</tr>
<tr>
<td>Horizon A</td>
<td>50.45777</td>
<td>0.08385</td>
<td>0.4152</td>
<td>0.0029</td>
</tr>
<tr>
<td>Horizon B</td>
<td>68.50698</td>
<td>0.07992</td>
<td>0.2530</td>
<td>0.0282</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>79.32343</td>
<td>0.35685</td>
<td>0.3378</td>
<td>0.0991</td>
</tr>
<tr>
<td>Eminence</td>
<td>79.13579</td>
<td>0.10777</td>
<td>0.7778</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>Horizon A</td>
<td>91.25684</td>
<td>0.11634</td>
<td>0.8984</td>
<td>0.0003</td>
</tr>
<tr>
<td>Horizon B</td>
<td>87.07509</td>
<td>0.06212</td>
<td>0.5724</td>
<td>0.0298</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>110.46246</td>
<td>-0.00657</td>
<td>0.0101</td>
<td>0.8124</td>
</tr>
<tr>
<td>Landform</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structural Bench</td>
<td>59.99237</td>
<td>0.07272</td>
<td>0.4937</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>Horizon A</td>
<td>32.35421</td>
<td>0.09226</td>
<td>0.5228</td>
<td>0.0016</td>
</tr>
<tr>
<td>Horizon B</td>
<td>30.66415</td>
<td>0.13661</td>
<td>0.6747</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>75.7284</td>
<td>0.01084</td>
<td>0.0075</td>
<td>0.7501</td>
</tr>
<tr>
<td>Hillslope</td>
<td>115.19675</td>
<td>0.04177</td>
<td>0.1090</td>
<td>0.0493</td>
</tr>
<tr>
<td>Horizon A</td>
<td>114.23293</td>
<td>0.0453</td>
<td>0.3644</td>
<td>0.0377</td>
</tr>
<tr>
<td>Horizon B</td>
<td>112.72527</td>
<td>-0.00549</td>
<td>0.0022</td>
<td>0.8852</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>96.00442</td>
<td>0.41063</td>
<td>0.5487</td>
<td>0.0059</td>
</tr>
<tr>
<td>Ridge</td>
<td>81.86816</td>
<td>0.05354</td>
<td>0.3980</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>Horizon A</td>
<td>78.40644</td>
<td>0.05157</td>
<td>0.3188</td>
<td>0.0354</td>
</tr>
<tr>
<td>Horizon B</td>
<td>82.53763</td>
<td>0.06704</td>
<td>0.5743</td>
<td>0.0017</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>86.09653</td>
<td>-0.0501</td>
<td>0.0155</td>
<td>0.6719</td>
</tr>
<tr>
<td>Floodplain</td>
<td>17.5613</td>
<td>0.14057</td>
<td>0.8308</td>
<td>&lt;.0001</td>
</tr>
<tr>
<td>Horizon A</td>
<td>-8.37249</td>
<td>0.16217</td>
<td>0.9410</td>
<td>0.0003</td>
</tr>
<tr>
<td>Horizon B</td>
<td>103.91903</td>
<td>0.03832</td>
<td>0.1137</td>
<td>0.4596</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>76.50968</td>
<td>76.50968</td>
<td>0.0306</td>
<td>0.7074</td>
</tr>
</tbody>
</table>
3.4.4 Classification and Regression Tree Analysis for P pools and Predictor Variables

Due to high variability in soils of the Missouri Ozark highlands, it was assumed that multiple factors may be associated with P concentrations. Linear regression models have a number of assumptions about the explanatory variables which make it questionable to predict multiple factors influencing a predictor variable in soil due to multicollinearity (Kutner et al., 2004). To overcome this challenge, a Classification and Regression Tree (CART) analysis was used to analyze the role of the soil and geomorphic factors associated with concentrations of various P pools in Ozark Highland soils. The CART procedure indicated that CBD extractable Mn (Mn oxides) is the single most important factor explaining variation in all three forms of P studied. This explanatory parameter explained 33%, 27.8 % and 32.2 % of the variability in total P, Mehlich-3 available P, and Bray-1 available P, respectively (Figure. 3.7). Total organic C and CBD-Mn together contributed toward explaining 39.6% of the variation for total P. Soil pH was second most important variable explaining variability for Mehlich-3 available P, which alone explained to 27.3 % of the variability and together with CBD-Mn contributed towards explaining 55.1 % of variability. However, for Bray-1 available P, exchangeable Ca was second most important variable, which explained 16.8% of the variability alone and 49% of the variability when summed with variability explained by CBD-Mn.

For the total P regression tree, soil samples with ≥1183.52 mg kg\(^{-1}\) of CBD-Mn had twice the mean amount of total P (211.55 mg kg\(^{-1}\)) when compared to soil samples containing <1183.52 mg kg\(^{-1}\) of CBD-Mn. No further partitioning of the data occurred for samples with ≥1183.52 mg kg\(^{-1}\) of CBD-Mn. However, for soils containing <1183.52 mg kg\(^{-1}\) of CBD-Mn, total OC accounted an additional of 6.6% of variation in total P concentrations. Where soil samples containing total OC <8.6 g kg\(^{-1}\) had a mean total P of 90.28 mg kg\(^{-1}\). For this
particular node (TOC <8.6 g kg\(^{-1}\)), an additional 2.8% of variation was explained by soil pH and mean total P concentrations were 1.5 times greater at pH > 4.95. For soil samples having total OC ≥8.6 g kg\(^{-1}\), mean total P was 125.03 mg kg\(^{-1}\). Furthermore, additional variation (5.6%) of samples containing total OC ≥8.6 g kg\(^{-1}\) could be explained on basis of landform, where hillslopes had 1.5 times greater total P when compared to floodplains, structural benches and ridges.

As noted previously, CBD-Mn was the single most important variable explaining variability for Mehlich-3 available P (27.8% of variability was explained by this factor alone). Horizon type was the second most important variable, explaining an additional 6.1% of variation, when CBD-Mn was <505.01 mg kg\(^{-1}\). The first mineral horizon contained approximately twice the mean quantity of Mehlich-3 available P compared to first Bt or Bw horizon and horizon at the 100 cm depth. For soil samples having CBD-Mn ≥505.01 mg kg\(^{-1}\) about 27.3% of the variation was explained by soil pH. Mean Mehlich-3 available P concentrations were 2 times greater when soil pH was ≥ 6.25. Additionally, CEC contributed for 5.5% of the variation in Mehlich-3 available P concentrations when soil pH was <6.25. For CEC <14.23 cmolc kg\(^{-1}\) about 2.8% of variation was explained on basis of underlying bedrock formation. Soils overlying the Eminence and Roubidoux bedrock formations showed greater availability of P in contrast to the upper and lower Gasconades. However, when CEC was ≥14.23 cmolc kg\(^{-1}\) about 1.4% of variation was explained on basis of landform where hillslopes and ridges had greater concentrations of Mehlich-3 available P compared to floodplains and structural benches.

For the Bray-1 available P regression tree, CBD-Mn was the single most important variable explaining approximately 32.2% of variability. Additionally, 3.3% of variation was explained by horizon type when CBD-Mn was <511.37 mg kg\(^{-1}\) whereas 16.8% of variation was explained by exchangeable Ca when CBD-Mn was ≥511.37 mg kg\(^{-1}\) (Figure 3.7-II).
Mean Bray-1 available P was 2 times greater when exchangeable Ca was ≥2.75 cmol\textsubscript{c} kg\textsuperscript{-1} and additionally 5.8 % of variation in Bray-1 available P was explained by landform. Hillslopes and floodplains had 1.5 times greater Bray-1 available P concentrations than ridges and structural bench. For exchangeable Ca <2.75 cmol\textsubscript{c} kg\textsuperscript{-1} about 3.5 % of variation was explained by CEC, where mean Bray-1 available P was greater when CEC was ≥13.75 cmol\textsubscript{c} kg\textsuperscript{-1}. However, when CEC was <13.75 cmol\textsubscript{c} kg\textsuperscript{-1}, in addition 3.5 % of variation was explained by underlying bedrock formation. Eminence and Roubidoux bedrock formation had approximately twice the amount of mean Bray-1 available P compared to upper and lower Gasconades. Our analysis also indicated that P in Missouri Ozarks is not related to parent material, profile position, clay and oxides of Fe and Al.
Figure 3.7. Classification and regression tree models.

Regression trees developed from classification and regression tree analysis for (I) total P, (II) Mehlich-3 available P, and (III) Bray-1 available P; concentrations are expressed in mg kg$^{-1}$. Each branch of the regression tree is labeled with the explanatory variable associated with partitioning of the response variable. Boxes represent the nodes including the number of horizons present in each split, the explanatory variable associated with each split, and the mean concentrations of Mehlich-3 available P, Bray-1 available P and total P. Dashed boxes represent the terminal nodes. Model for:

I. Total P

Response variable (total P) $\sim$ Explanatory variables (horizon type +parent material + bedrock + profile position + landform + clay + exchangeable calcium + CEC + pH + sum (CBD Al+Fe) + CBD-Mn + total organic C).

II. Mehlich-3 available P

Response variable (Mehlich-3 available P) $\sim$ Explanatory variables (horizon type +parent material + bedrock + profile position + landform + exchangeable calcium + CEC + pH + sum (CBD Al+Fe) + CBD-Mn + total organic C).

III. Bray-1 available P

Response variable (Bray-1 available P) $\sim$ Explanatory variables (horizon type +parent material + bedrock + profile position + landform + exchangeable calcium + CEC + pH + sum (CBD Al+Fe) + CBD-Mn + total organic C).
I. Classification and regression tree for total P.
II. Classification and regression tree for Mehlich-3 available P.
III. Classification and regression tree Bray-1 available P.

- All Samples
  - Mean AP Bray-1 = 5.81 mg kg⁻¹
  - N = 150

- CBD-Mn
  - (<511.37 mg kg⁻¹)
  - Mean AP Bray-1 = 5.83 mg kg⁻¹
  - N = 90

- Horizon Type
  - First Bt or Bw Horizon, Horizon at 100 cm
  - Mean AP Bray-1 = 3.41 mg kg⁻¹
  - N = 77

- Exchangeable Calcium
  - (<2.75 cmol, kg⁻¹)
  - Mean AP Bray-1 = 6.67 mg kg⁻¹
  - N = 38

- Cation Exchange Capacity
  - (<13.75 cmol, kg⁻¹)
  - Mean AP Bray-1 = 5.97 mg kg⁻¹
  - N = 31

- Landform
  - Ridge, Structural Berg
  - Mean AP Bray-1 = 9.47 mg kg⁻¹
  - N = 10

- Bedrock
  - Upper Gasconade, Lower Gasconade
  - Mean AP Bray-1 = 4.57 mg kg⁻¹
  - N = 20

- Cation Exchange Capacity
  - (≥13.75 cmol, kg⁻¹)
  - Mean AP Bray-1 = 9.60 mg kg⁻¹
  - N = 7

- Exchangeable Calcium
  - (≥2.75 cmol, kg⁻¹)
  - Mean AP Bray-1 = 12.42 mg kg⁻¹
  - N = 22

- Landform
  - Hillside, Floodplain
  - Mean AP Bray-1 = 14.87 mg kg⁻¹
  - N = 12

- Bedrock
  - Eminence, Rouhidaux
  - Mean AP Bray-1 = 8.51 mg kg⁻¹
  - N = 11
Although, many previous studies have demonstrated the importance of iron and aluminum oxides on P sorption and desorption in soil (Brown and Loewenstein, 1978; Jones et al., 1979; Loganathan et al., 1987; Villapando and Graetz, 2001; Agbenin, 2003), the CART analysis identified CBD-Mn as the most important variable explaining the variability of P concentrations in the soils studied. Many modern spectroscopic studies of phosphate adsorption to Fe oxides, indicate that P adsorbs to Fe oxides via an inner-sphere complex (Arai and Sparks, 2001; Lefèvre, 2004; Luengo et al., 2006; Arai and Sparks, 2007; Elzinga and Sparks, 2007; Antelo et al., 2010). However, fewer studies have focused on P sorption to and desorption from manganese oxides (Jugsujinda et al., 1995; Mustafa et al., 2006; Mustafa et al., 2008). Oxides of Mn showed an important effect on P-sorption in acid sulfate soils of Thailand, although the mechanism behind P sorption to Mn oxides was unclear (Jugsujinda, et al., 1995). Lair et al. (2009) also observed a strong correlation between extractable Mn oxides and P sorption in floodplain soils of Austria. Phosphorus sorption to MnO₂ was studied as a function of pH by Mustafa et al. (2006), and P sorption was observed to increase with increased P concentration and decrease with increasing pH. Yao and Millero (1996) found that phosphate adsorption on δMnO₂ is enhanced by addition of Ca²⁺ and Mg²⁺ in 0.7 M NaCl at pH > 4 and it was proposed that this increased adsorption might be due to the changes occurring in surface charge of δMnO₂ and the solution speciation of phosphate. Mustafa et al. (2008) identified that phosphate adsorbs to β-MnO₂ via an outer-sphere complex, which is relatively weak compared to an inner-sphere complex. However, Zaman et al. (2013) suggest that inner-sphere complexes between phosphate and β-MnO₂ can form at lower pH values.
\[ \text{Outer-sphere complex formation} \]
\[ \text{MnOH} + \text{H}^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{MnOH}_2^++\text{H}_2\text{PO}_4^- \]
\[ \text{Mn}_2(\text{OH}_2^+)\text{HPO}_4^{2-} \rightleftharpoons \text{Mn}_2(\text{OH}_2^+)\text{HPO}_4^{2-} \]

\[ \text{Inner-sphere complex formation} \]
\[ \text{MnOH} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{MnH}_2\text{PO}_4 + \text{OH}^- \]
\[ \text{Mn}_2(\text{OH})_2 + \text{HPO}_4^{2-} \rightarrow \text{Mn}_2\text{HPO}_4 + 2\text{OH}^- \]

Although additional research is needed to understand the sorption and desorption of P reacted with oxides of Fe, Al and Mn present in Missouri Ozark soils, sufficient evidence in the literature suggests that Mn oxides can be important sorbents for soil P. Previous work also indicates that Mn oxides may be more soluble than Fe oxides in particular soils resulting in greater mobility and bioavailability of Mn (Narwall and Singh, 2001). If Mn oxides in the Ozarks Highland soils are more soluble than Fe and Al oxides and mineral dissolution results in co-release of P, this may also explain the relationship between Mn and available P pools observed in this research.

Total OC was identified in CART analysis as second most important variable explaining total P for 132 soil samples. A large portion of the P present in forest soils is in organic form associated with organic matter (Condron and Tiessen, 2005). King (1997) found that soil organic C was highly correlated with P forms in soils overlying the Roubidoux, upper Gasconade and Eminence bedrock formations in the Missouri Ozarks. Sharpley (1983) studied the kinetics of P desorption on various soil properties and observed that when organic C was considered alone it explained only 29% of P desorption however when the ratio of extractable Fe and organic C was considered it explained 81% of P desorption. Donald et al. (1993) examined the role of dissolved organic carbon (DOC) in P transport in forested soils and reported that leaching of the hydrophobic neutral fraction of DOC was a possible
mechanism for the redistribution and loss of P. This mechanism may explain that P in Missouri Ozarks is associated with TOC.

The CART analysis procedure indicated that pH explained 2.8% of the variability for total P and 27.8% of the variability for Mehlich-3 available P. Soil pH was reported by many researchers as an important factor regulating the dissolution of P-bearing minerals (Pierzynski and McDowell, 2005; Oelkers and Valsami-Jones, 2008). With increasing pH, P bounded with metal oxides maybe solubilized and becomes readily available for plants; whereas, P solubility decreases with increasing pH when P is bonded to Ca, (Hinsinger, 2001). The above findings suggest that P in Missouri Ozarks can be correlated to soil pH where average concentrations of total P and Mehlich-3 available P increases as soil pH increases (Figure 3.4).

It is interesting to note that the CART analysis suggested landform type (eg. structural bench, ridge, hillslope, and floodplain) has minor role, explaining less than 6% of variation for all three forms of P (Figure 3.5). Landform and slope position largely govern the redistribution of water and cations in soil (Trettin et al., 1999). Phosphorus movement in landscape was studied by Smeck (1985) and it was concluded that highest content of P was at lower end of the hydraulic gradient. Smeck and Runge (1971) indicated that pedons on upper landscape positions tend to lose P and, in contrast, pedons on lower landscape position tend to accumulate P. From all three CART models hillslope was associated with higher mean P values and structural bench was associated with lower mean P values whereas role of ridge and floodplain with P is still ambiguous.

Cation exchange capacity and bedrock were also of minor importance and explained less than 6% of variation in CART models for Mehlich-3 available P and Bray-1 available P (Figure 3.7). Soils formed in parent material derived from underlying Roubidoux and Eminence formations had greater concentrations of available P than the soils formed in
parent material derived from underlying upper and lower Gasconade formations. The Roubidoux bedrock formation in the study area is interstratified with sandstone, dolomite, and silicified stromatolite algal and chert beds which do not contribute to CEC (Bailey, 2000); whereas, Eminence formation is dominated by coarse crystalline dolomite with occasional occurrence of interbedded cherts. However, the upper Gasconade is comprised of coarsely crystalline dolomite, interbedded with chert and layers of silicified stromatolites and the lower Gasconade is comprised of finely crystalline dolomite, interbedded with a few chert nodules and the base of this formation is a 1 to 3 m bed of sandstone and quartzose (Meinert et al., 1997; Kabrick et al., 2011). Richards et al. (1997) investigated differences in P on the basis of parent material and bedrock and reported that soils derived from limestone parent material had the greatest values of P when compared to soils derived from sandstone parent material. Safford and Harrison (2004) observed contrasting results while comparing soil P in burned versus unburned plots, and reported that soils derived from sandstone parent material had higher levels of P than soils derived from limestone parent material. Thus, the influence of underlying bedrock on available P is still unclear in the Missouri Ozarks and more research is needed regarding the chemical composition of underlying bedrocks.

Findings from the CART analysis associated CBD-Mn with concentrations of all P forms as the primary variable and total C, pH, and Ca as secondary variables for total P, Mehlich-3 available P, and Bray-1 available P, respectively. Presently, we are unaware of any published research explaining sorption and desorption of P from oxides of Mn and comparing it with sorption and desorption of P from oxides of Fe and Al. We anticipate that Mn oxides may act as important sorbents of phosphates and, when their dissolution is greater than Fe and Al oxides, P may be released into solution more readily than P bound to Fe and Al oxides. Additional studies are required to test this hypothesis to fully elucidate the role played by oxides of Mn in regulating P concentrations in Missouri Ozark Highland soils.
This research can further help to derive relations between forest vegetation and soils of the Missouri Ozarks based on P forms and concentrations. For example, the type of tree species present at particular landscape position or on particular type of bedrock can be associated with amount of P present in soil. Results from this research can be used by forest managers and soil scientists as a tool to identify sites which contain greater or lesser amounts of P or sites at risk for P depletion. Thus, this research can also act tool for recommending implementation of harvesting operations on particular portions of the landscape. For instance, if a site for proposed harvest has a total organic C content <8.6 g kg\(^{-1}\) and pH <4.95 or proposed harvest site is present on the upper and lower Gasconades with soil pH <6.25 then it is important to implement harvest regimens that conserve P onsite.

### 3.5 Conclusion

Concentration of available P and total P are highly variable in Missouri Ozark Highland soils. Mean concentrations of Mehlich-3 available P was 7.87 mg kg\(^{-1}\), Bray-1 available P was 5.81 mg kg\(^{-1}\) and total P was 116.19 mg kg\(^{-1}\). Phosphorus concentrations were greater in first mineral horizon and availability of P decreased with depth. Linear regressions indicated a strong correlation of CBD extractable Mn with total P (77 %), Bray-1 available P (69 %), and Mehlich-3 available P (71 %) for soils overlying the Eminence formation. Due to the high variability in soil samples and geological strata it was not possible to associate a single factor explaining concentrations of P forms in Ozark Highlands. Instead, multiple factors were necessary for explaining the P in this complex landscape. The CART analysis indicated that, from all the geomorphic and soil properties investigated, extractable Mn was the single most important variable explaining variation in concentrations of P forms. Other secondary variables that were also identified as important were total organic C, pH, and exchangeable Ca. Further research is needed to elucidate the role of Mn oxides in regulating concentrations...
of P forms in Ozark Highland soils, and research described here can be used to formulate
future research. This research will also help in identifying sites which are potentially
vulnerable to nutrient depletions and can serve as aid for recommending harvesting
operations.
CHAPTER 4: CONCLUSIONS

4.1 Summary

The primary objective of this study was to enhance understanding of nutrient dynamics and pools in forested soils of the Missouri Ozark Highlands. The study was divided into two specific research objectives: first was to quantify the influence of clearcutting and single tree selection forest regeneration on soil solution chemistry and nutrient flux in low and medium nutrient status soils at MOFEP; and the second was to identify the importance of geomorphic and soil properties on total and available P concentrations in Ozark Highland soils. To complete the first objective, *in situ* measurements of soil solution and nutrient flux obtained taken with zero tension samplers and ion exchange resin samplers in low and medium nutrient status soils at two depths 15 cm and 40 cm; throughfall samples were also collected. All samples were collected at the Missouri Ozark Forest Ecosystem Project (MOFEP) before and after clearcut and single-tree selection harvests. To complete the second objective, fifty out seventy-four of the pedons sampled during the initiation of MOFEP were analyzed for Bray-1 and Mehlich available P, total P, total organic P, inorganic P (sequential fractionation scheme for inorganic P) and Fe, Al and Mn oxide content (citrate bicarbonate dithionite method).

The influence of regeneration methods on soil solution chemistry and nutrient flux was observed by collecting soil solution from clearcut, single tree selection, and no-harvest management sites. Samples collected were then analyzed for pH and electrical conductivity, and anions (Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻), cations (K⁺, Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, and total aluminum), DOC, and total N. Ion exchange resin samples were used for determining cumulative ion flux at 15 and 40 cm depths.
Seasonal fluctuations were observed in most of the analytes. Significant increases in nutrient concentrations in solutions collected with ZTS samplers (15 and 40 cm depths) were observed for EC, NO$_3^-$, Mg$^{2+}$, and TN. Mean SO$_4^{2-}$ concentrations in clearcuts post-harvest were significantly less than pre-harvest conditions at the same sites. Mean concentrations of Ca$^{2+}$ and Mg$^{2+}$ were greater in soil solution collected from ZTS-15 cm and ZTS-40 cm samplers for post-harvest CC sites when compared to pre-harvest data. Total N and NO$_3^-$ concentrations were significantly increased in post-harvest clearcuts for ZTS-15 cm and ZTS-40 cm compared to pre-harvest, and DOC significantly decreased in throughfall solution in post-harvest clearcuts when compared to pre-harvest conditions at the same sites.

Mean daily flux for NO$_3^-$ and Mg$^{2+}$ determined from IER samplers was significantly greater in post-harvest clearcuts relative to pre-harvest. When pre-harvest NHM and STS were compared to post-harvest NHM and STS for all dependent variables, mean flux values from IER samplers were significantly lower in post-harvest NHM and STS with an exception of NO$_3^-$ flux in STS (the mean NO$_3^-$ flux was less but not significantly different). This decrease in flux values was attributed to drought conditions which prevailed in 2012 throughout Missouri.

Overall, loss of base cations is of concern for Ca$^{2+}$ and especially for Mg$^{2+}$. There are potential losses of TN and NO$_3^-$ immediately after clearcutting which are of great concern and these losses are minimal for STS harvest. Fluoride and NO$_2^-$ concentrations increased in all treatments post-harvest compared to all treatments pre-harvest which indicate that it may be the effect of yearly changes and may not be associated with actual harvest. Due to the effect of season, amount of precipitation, harvesting and high variability of Ozark soils further investigation of post-harvest soil solution chemistry and nutrient flux is needed to determine if these nutrients will leach to ground and surface waters, whether these nutrients
will continue to be retained on-site, in the soil or in circulation within developing vegetation in the long-term.

Analysis of total P, Mehlich-3 available P and Bray-1 available P revealed that overall concentration of available P and total P are highly variable in Missouri Ozark Highland soils. Mean concentrations of Mehlich-3 available P was 7.87 mg kg\(^{-1}\), Bray-1 available P was 5.81 mg kg\(^{-1}\) and total P was 116.19 mg kg\(^{-1}\). Phosphorus concentrations were greater in the first mineral horizon and availability of P decreased with depth. Linear regression analyses indicated a strong correlation of CBD extractable Mn with total P (77 %), Bray-1 available P (69 %), and Mehlich-3 available P (71 %) for soils overlying the Eminence bedrock. Due to high variability in soil samples and geological strata it was not possible to associate a single factor which could explain all of the P in these highlands. Thus, multiple factors needed to explain P distribution.

A CART analysis including multiple geomorphic and soil property explanatory variables indicated that extractable Mn was the most important variable explaining variation in P forms. Secondary variables of importance were total organic C (total P regression tree), pH (Mehlich-3 available P regression tree), and exchangeable Ca (Bray-1 available P regression tree). The combination of first two variables resulted in the CART analyses explaining 39, 55, and 49 % of variation for total P, Mehlich-3 available P, and Bray-1 available P, respectively. Other factors which contributed toward explaining variability in total P were pH and bedrock; whereas, horizon type, CEC, landform and bedrock aided in explaining limited amounts of variability for Bray-1 available P and Mehlich-3 available P. These all factors were of minor importance and explained < 6% of P form variation.

Although further study is needed to elucidate the role of oxides of Mn in regulating most of P concentrations, this research can help in identifying sites which are potentially vulnerable to P depletions and can serve as aid for regulating harvesting operations. This
research can further help to derive relations between forest vegetation and soils of the Missouri Ozarks based on P forms and concentrations. For example, the type of tree species present at particular landscape position or on particular type of bedrock can be associated with amount of P present in soil. Results from this research can help forest managers and soil scientists as tool to identify sites which are greater or lesser amounts of P or sites at risk for P depletion. Thus, this research can also act tool for recommending implementation of harvesting operations on particular portions of the landscape. For instance, if a site for proposed harvest has a total organic C content <8.6 g kg\(^{-1}\) and pH <4.95 or proposed harvest site is present on the upper and lower Gasconades with soil pH <6.25 then it is important to implement harvest regimens that conserve P onsite.
4.2 Future Research

Future research investigating post-harvest soil solution chemistry is needed to see the trend of change anticipated for nutrients by designated forest regeneration methods (Figure 4.1). Sampling in this research represents 3 years of data which includes approximately 1.5 years of pre-harvest data and 1.5 years of post-harvest data. Clearcutting and STS regeneration methods showed significant changes in nutrient flux for most of the analytes where clearcutting had higher mean nutrient loss when compared to STS. But long term research is needed to clearly differentiate the certain impact of harvesting on loss and replenishment of nutrients over the period of time. We hypothesize that increased NO$_3^-$ concentrations post-harvest in clearcutting plots may drop in 3 to 5 years to pre-harvest levels (Burns and Murdoch, 2005). Similar trend of drop to pre-harvest levels could be anticipated for other nutrients (Johnson et al., 2008). Additionally, effect of season and amount of precipitation do influence the amount of nutrients being leached so, this aspect also needs to be further included in future research.
Figure 4.1. Hypothetical relationships between nutrient availability and forest regeneration methods (clearcutting and single tree selection). In this example, some nutrients for clearcutting are anticipated to come back at a faster rate to initial levels, when first harvesting event was introduced (J. Kabrick, unpublished).
Future research examining the chemical processes involved in adsorption and desorption of P with Mn can help in elucidating the role of oxides of Mn at MOFEP. We hypothesize that citrate dithionite extractable and oxalate extractable Fe, Al and Mn can effect P sorption in MOFEP soils and P can be readily desorbed from Mn when compared to Fe and Al. Further it is also hypothesized that higher desorption of P from Mn could be because P is adsorbed to Mn oxide surfaces via outer-sphere complexes, which are relatively weak compared to inner-sphere complexes (Mustafa et al., 2008). Additionally, P is adsorbed to inner-sphere complexes of Fe and Al which absorb P more strongly by forming binuclear bridge (Figure 4.2).

**Outer-sphere complex formation**

\[ \text{Fe(OH)}_2 + H^+ + H_2PO_4^- \xrightarrow{\text{Complexation}} \text{Fe(OH)}_2^+ \cdot \cdot \cdot \cdot \cdot H_2PO_4^- \]

**Inner-sphere complex formation**

\[ \text{Fe(OH)}_2 + \text{HPO}_4^{2-} \xrightarrow{\text{Complexation}} \text{Fe(OH)}_2 \cdot \cdot \cdot \cdot \cdot \text{HPO}_4^{2-} \]

![Figure 4.2. Adsorption of phosphates to outer sphere complexes of Mn and inner sphere complexes of Fe.](image-url)

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REFERENCES


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Thompson, T.L. 1995. The stratigraphic succession in Missouri. Rolla: Missouri Department of Natural Resources-Geology and Land Survey.


APPENDIX

A. Statistical Models

A-I  Code for spatially-repeated split-plot generalized linear mixed model in SAS software for analysis of soil characterization data collected from sampling sites; each block split by treatment (trt), soil nutrient status (sns) and is repeated by depth.

```
proc glimmix data=DATASET maxopt=2000 pconv=1e-4 plots=studentpanel;
   class depth trt SNS block depth1;
   model DEPENDENT VARIABLE = trt|SNS|depth @2/ dist=lognormal link=identity;
*distribution codes must be changed in above statement for each dependent variable*
   Random int sns trt|sns /subject = block;
   random depth/ type=sp(pow)(depth1) subject=trt*SNS(block) residual;
   lsmeans trt sns depth trt*depth /pdiffadjust=tukeylinesilink cl;
run;
```

A-II  Code for spatially-repeated split-plot generalized linear mixed model in SAS software for analysis of soil characterization data collected from sampling sites; each block split by treatment (trt), soil nutrient status (sns), harvest and is repeated by depth.

```
proc glimmix data=DATASET maxopt=2000 pconv=1e-4 plots=studentpanel;
   class depth trt SNS block depth1;
   model DEPENDENT VARIABLE = trt|SNS|depth|harvest @2/ dist=lognormal link=identity;
*distribution codes must be changed in above statement for each dependent variable*
   Random int sns trt|sns*trt /subject = block;
   random depth/ type=sp(pow)(depth1) subject=trt*SNS*harvest(block) residual;
   lsmeans trt sns depth trt*harvest /pdiffadjust=tukeylinesilink cl;
   contrast 'preharvest nhm vs postharvest nhm' harvest 1 -1 trt*harvest 0 0 1 -1 0 0;
   contrast 'preharvest uam vs postharvest uam' harvest 1 -1 trt*harvest 1 -1 0 0 0 0;
   contrast 'preharvest eam vs postharvest eam' harvest 1 -1 trt*harvest 0 0 0 0 1 -1;
run;
```

A-III  Code for spatially-repeated split-plot generalized linear mixed model in SAS software for analysis of soil solution data; each block split by treatment (trt), soil nutrient status (sns), harvest and is repeated by depth.

```
proc glimmix data=ds2 maxopt=2000 pconv=1e-4 plots=studentpanel;
   class block trt SNS depth depth1 harvest;
   model DEPENDENT VARIABLE = trt|harvest|sns|depth @3/ dist=normal link=identity;
*distribution codes must be changed in above statement for each dependent variable*
   random int sns trt sns*trt /subject=rep;
   random depth/ type=sp(pow)(depth1) subject=trt*SNS*harvest(block) ;
   output out=pred pearson(blup)=resid pred=pred;
```
lsmeans trt*harvest trt*harvest*sns trt*harvest*depth /pdiff adjust=tukey lines cl ilink; run;

A-IV Code for spatially-repeated split-plot generalized linear mixed model in SAS software for analysis of ion exchange resin data; each block split by treatment (trt), soil nutrient status (sns), collection and is repeated by depth.

Proc GLIMMIX data=DATASET maxopt=2000 pconv=1e-4 plots=studentpanel;
where collection = 1;
class depth trt SNS block depth1;
model DEPENDENT VARIABLE = trt|SNS|depth @2/ dist=lognormal link=identity;
*distribution codes must be changed in above statement for each dependent variable*
Random intsns/subject = block;
random depth/ type=sp(pow)(depth1) subject=trt*SNS*collection(block) residual;
lsmeans trt sns trt*sns depth depth*sns depth*trt /pdiffadjust=tukey lines cl ilink;
run;

A-V Code for spatially-repeated split-plot generalized linear mixed model in SAS software for analysis of ion exchange resin data; each block split by treatment (trt), soil nutrient status (sns), collection and is repeated by depth.

Proc GLIMMIX data=DATASET maxopt=2000 pconv=1e-4 plots=studentpanel;
class depth trt SNS block depth1;
model DEPENDENT VARIABLE = trt|SNS|depth|collection @2/ dist=lognormal link=identity;
*distribution codes must be changed in above statement for each dependent variable*
random intsns/subject = block;
random depth/ type=sp(pow)(depth1) subject=trt*SNS*collection(block) residual;
lsmeans trt sns collection trt*sns depth depth*sns depth*trt trt*collection*trt /pdiffadjust=tukey lines cl ilink;
contrast 'collection 1 2 verse collection 3 4' collection 1 1 -1 -1;
contrast 'collection 1 2 verse coll 3 4 all trt' collection 3 3 -3 -3 trt*collection 1 1 -1 1 1 1 -1 -1 1 1 -1 -1;
contrast 'collection 1 2 trt nhn verse collection 3 4 trt nhn' collection 1 1 -1 -1 trt*collection 0 0 0 1 1 -1 -1 0 0 0 0 0 0;
contrast 'collection 1 2 trt eam verse collection 3 4 trt eam' collection 1 1 -1 -1 trt*collection 1 1 -1 -1 0 0 0 0 0 0 0 0;
contrast 'collection 1 2 trt UAM verse collection 3 4 trt uam' collection 1 1 -1 -1 trt*collection 0 0 0 0 0 0 0 1 1 -1 -1;
contrast 'collection 1 2 trt eam verse collection 3 4 trt uam' collection 1 1 -1 -1 trt*collection 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 -1;
contrast 'collection 1 2 trt eam verse collection 3 4 trt nhm' collection 1 1 -1 -1 trt 2 -2 trt*collection 1 1 0 0 0 0 0 0 -1 -1 0 0 0 0 0 0;
contrast 'collection 1 2 trt nhm verse collection 3 4 trt uam' collection 1 1 -1 -1 trt 0 2 -2 trt*collection 0 0 0 0 1 1 0 0 0 0 0 -1 -1;
contrast 'collection 1 2 trt nhm verse coll 1 2 trt uam' trt 0 2 -2 trt*collection 0 0 0 0 1 1 0 0 -1 -1 0 0;
contrast 'collection 1 2 trt nhm verse coll 1 2 trt eam' trt 2 -2 0 trt*collection 1 1 0 0 0 0 0 0 -1 -1 0 0;
contrast 'collection 1 2 trt eam verse coll 1 2 trt uam' trt 2 0 -2 trt*collection 1 1 0 0 0 0 0 0 -1 -1 0 0;
contrast 'collection 3 4 trt nhm verse coll 3 4 trt uam' trt 0 2 -2 trt*collection 0 0 0 0 0 0 1 0 0 1 -1 1 -1 1 -1 0 0 0 0;
contrast 'collection 3 4 trt nhm verse coll 3 4 trt eam' trt 2 -2 0 trt*collection 0 0 1 1 0 0 1 -1 1 0 0 0 0;
contrast 'collection 3 4 trt eam verse coll 3 4 trt uam' trt 2 0 -2 trt*collection 0 0 1 1 0 0 0 0 0 0 0 0 0 -1 -1 1 0 0 0 0;
run

A-VI Code used for calculating linear regression in SAS for total P, Mehlich-3 available P, and Bray-1 available P.

\textbf{ProcReg} data=\texttt{DATASET}\ maxopt=\texttt{2000}\ pconv=\texttt{1e-4}\ plots=studentpanel;
Class clay ca mg cec bs ph tc tp apm apb al fe mn alfe alfemn;
Model DEPENDENT VARIABLE = INDEPENDENT VARIABLE;
Run;

A-VII Code used in generating classification and regression trees for total P, Mehlich-3 available P, and Bray-1 available P in R statistical software.

(a) Mehlich-3 available P

library(rpart)
s1=read.table (file="\texttt{DATASET}\",sep="\",header=\texttt{TRUE})
attach(s1)
head(s1)
apmehlich.tree=rpart(apmehlich
~Horizontype+parentmaterial+bedrock+landform+profposition+clay+Ca+Sumcec+Water
pH+ Mn.CBD+sum.al.fe+tcarbon, data=s1,method="anova")
plot(apmehlich.tree)
text(apmehlich.tree)
plotcp apmehlich.tree)
rsq.rpart(apmehlich.tree)
summary(tp.tree)
prune (tp.tree, cp=0.01)
(b) Bray-1 available P

library(rpart)
s1=read.table (file="DATASET",sep=" ",header=TRUE)
attach(s1)
head(s1)
tp.tree=rpart(tp~Horizontype+parentmaterial+bedrock+landform+profposition+clay+Ca+
Sumcec+WaterpH+ Mn.CBD+sum.al.fe+tcarbon, data=s1, method="anova")
plot(tp.tree)
text(tp.tree)
plotcp (tp.tree)
rsq.rpart(tp.tree)
summary(tp.tree)
prune (tp.tree, cp=0.01)

(c) Total P

library(rpart)
s1=read.table (file="DATASET",sep=" ",header=TRUE)
attach(s1)
head(s1)
tp.tree=rpart(tp~Horizontype+parentmaterial+bedrock+landform+profposition+clay+Ca+
Sumcec+WaterpH+ Mn.CBD+sum.al.fe+tcarbon, data=s1, method="anova")
plot(tp.tree)
text(tp.tree)
plotcp (tp.tree)
rsq.rpart(tp.tree)
summary(tp.tree)
prune (tp.tree, cp=0.0)
B. Block wise scatter plots representing nutrient leaching from low and medium nutrient status soils at MOFEP indicating all 45 collection events. Dashed line represents date of harvest for single tree selection (STS) and solid line represents date of harvest for clearcutting (CC).

Block 1
I. Low nutrient status
I-1. Throughfall
I-2. Depth 15 cm

The diagrams depict changes in pH, EC, and (EC) across the pre-harvest and post-harvest periods for different sampling dates from 2009 to 2013. The data are classified into NHM, STS, and CC categories.
I-3. Depth 40 cm
II. Medium status soils
II-1. Throughfall
II-2. Depth 15 cm
II-3. Depth 40 cm

[Graphs showing pH, soil pH, and EC at pre-harvest and post-harvest stages for NHM, STS, and CC treatments.]

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Block 2
I. Low nutrient status
I-1. Throughfall
I-2.   Depth 15 cm

[Graphs showing pH, EC (μS cm⁻¹), and other data over time for NHM, STS, and CC categories before and after harvest.]
I-3. Depth 40 cm

[Graphs showing pH, electrical conductivity (EC), and another unspecified parameter at different dates pre- and post-harvest for NHM, STS, and CC treatments.]

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II. Medium nutrient status

II-1. Throughfall

[Graphs showing pH, (H+), and EC over pre-harvest and post-harvest periods with data points for NHM, STS, and CC]
II-2. Depth 15 cm
II-3. Depth 40 cm
I. Low nutrient status
I-1. Throughfall
I-2. Depth 15 cm

![Graph showing pH values over time for different sampling periods](image)

![Graph showing EC values over time for different sampling periods](image)
I-3. Depth 40 cm
The diagrams illustrate the concentrations of different chemicals over time, categorized by pre-harvest and post-harvest periods. Each diagram shows the date of sampling along the x-axis and the chemical concentration (in μmol L⁻¹) along the y-axis. The concentrations vary across different treatments labeled as NHM, STS, and CC.
II. Medium nutrient status

II-1. Throughfall
II-2. Depth 15 cm
III-3. Depth 40 cm
C. Volume weighted mean boxplots for low and medium status soils for soil solution data collected at MOFEP.

1. Low nutrient status soils
   1.1. Throughfall
1.2. Depth 15 cm
1.3. Depth 40 cm
2. Medium nutrient status soils
2.1. Throughfall
2.2. Depth 15 cm
2.3. Depth 40 cm

![Box plots showing data for VWM pH, VWM EC, and VWM H']
D. Mean ± 95% confidence interval (CI) for (a) pre-harvest and (b) post-harvest soil chemical properties of field sampling locations by sampling depth.

### (a) Pre-harvest Soil Chemical Properties

<table>
<thead>
<tr>
<th>Depth cm</th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>K(^+)</th>
<th>ECEC †</th>
<th>Base sat ‡</th>
<th>EA ¥</th>
<th>Al sat ¶</th>
<th>pH (_{\text{salt}})</th>
<th>(H(^{+})) (_{\text{salt}})</th>
<th>TOC</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 10</td>
<td>1.6 ± 0.7</td>
<td>0.6 ± 0.1</td>
<td>0.2 ± 0</td>
<td>5.5 ± 0.8</td>
<td>19 ± 5.7</td>
<td>8.7 ± 1.2</td>
<td>0.7 ± 0.3</td>
<td>4.4 ± 0.2</td>
<td>0.0000551 ± 0.0000142</td>
<td>1.2 ± 0.3</td>
<td>19 ± 4.3</td>
</tr>
<tr>
<td>10 - 20</td>
<td>0.9 ± 0.6</td>
<td>0.7 ± 0.6</td>
<td>0.2 ± 0.1</td>
<td>4.8 ± 1.3</td>
<td>18 ± 6.4</td>
<td>6.1 ± 0.8</td>
<td>1.0 ± 0.4</td>
<td>4.5 ± 0.4</td>
<td>0.0000566 ± 0.0000153</td>
<td>0.5 ± 0.1</td>
<td>8.0 ± 1.2</td>
</tr>
<tr>
<td>20 - 30</td>
<td>1.1 ± 1.1</td>
<td>1.2 ± 1.0</td>
<td>0.2 ± 0</td>
<td>6.2 ± 2.5</td>
<td>19 ± 7.0</td>
<td>5.9 ± 1.3</td>
<td>1.3 ± 0.6</td>
<td>4.2 ± 0.1</td>
<td>0.0000646 ± 0.0000131</td>
<td>0.2 ± 0.1</td>
<td>4.2 ± 0.7</td>
</tr>
<tr>
<td>30 - 40</td>
<td>1.4 ± 1.2</td>
<td>1.5 ± 1.2</td>
<td>0.2 ± 0</td>
<td>6.6 ± 2.6</td>
<td>24 ± 7.5</td>
<td>6.2 ± 1.7</td>
<td>1.6 ± 0.9</td>
<td>4.2 ± 0.1</td>
<td>0.0000734 ± 0.0000163</td>
<td>0.2 ± 0</td>
<td>2.8 ± 0.5</td>
</tr>
</tbody>
</table>

† ECEC, effective cation exchange capacity.
‡ Base sat, percent base saturation.
¥ EA, extractable acidity.
¶ Al sat, percent aluminum saturation.

### (b) Post-harvest Soil Chemical Properties

<table>
<thead>
<tr>
<th>Depth cm</th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>K(^+)</th>
<th>ECEC †</th>
<th>Base sat ‡</th>
<th>EA ¥</th>
<th>Al sat ¶</th>
<th>pH (_{\text{salt}})</th>
<th>(H(^{+})) (_{\text{salt}})</th>
<th>TOC</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 10</td>
<td>3.2 ± 0.9</td>
<td>0.8 ± 0.2</td>
<td>0.3 ± 0</td>
<td>7.5 ± 0.8</td>
<td>31 ± 6.9</td>
<td>9.1 ± 1</td>
<td>0.9 ± 0.7</td>
<td>4.7 ± 0.2</td>
<td>0.0000303 ± 0.0000136</td>
<td>1.5 ± 0.1</td>
<td>27 ± 2.1</td>
</tr>
<tr>
<td>10 - 20</td>
<td>1.7 ± 0.6</td>
<td>0.7 ± 0.3</td>
<td>0.2 ± 0</td>
<td>5.5 ± 0.8</td>
<td>25 ± 6.1</td>
<td>7.0 ± 0.5</td>
<td>1.4 ± 1.2</td>
<td>4.6 ± 0.1</td>
<td>0.0000309 ± 0.0000106</td>
<td>0.8 ± 0.1</td>
<td>15 ± 1.6</td>
</tr>
<tr>
<td>20 - 30</td>
<td>1.5 ± 0.9</td>
<td>1 ± 0.7</td>
<td>0.2 ± 0</td>
<td>5.7 ± 1.6</td>
<td>25 ± 7.0</td>
<td>6.0 ± 0.6</td>
<td>0.8 ± 0.2</td>
<td>4.6 ± 0.1</td>
<td>0.0000328 ± 0.000008</td>
<td>0.6 ± 0.1</td>
<td>10 ± 1.7</td>
</tr>
<tr>
<td>30 - 40</td>
<td>1.7 ± 1.3</td>
<td>1.2 ± 1.2</td>
<td>0.2 ± 0</td>
<td>5.6 ± 2.0</td>
<td>26 ± 9.5</td>
<td>5.4 ± 0.9</td>
<td>0.9 ± 0.3</td>
<td>4.8 ± 0.2</td>
<td>0.0000278 ± 0.0000117</td>
<td>0.4 ± 0.1</td>
<td>7.9 ± 1.0</td>
</tr>
</tbody>
</table>

† ECEC, effective cation exchange capacity.
‡ Base sat, percent base saturation.
¥ EA, extractable acidity.
¶ Al sat, percent aluminum saturation.
E. Mean ± 95% confidence interval (CI) for pre-harvest and post-harvest soil chemical properties of field sampling locations for (a) low and (b) medium nutrient status soils by treatment and sample depth.

(a) Low nutrient status soils.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Depth cm</th>
<th>Harvest Status</th>
<th>Soil Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca²⁺ Mg²⁺ K⁺</td>
</tr>
<tr>
<td>NHM</td>
<td>0 - 10</td>
<td>Pre-harvest</td>
<td>1.2 ± 1.5 0.3 ± 0.2 0.2 ± 0.1 9.8 ± 6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Post-harvest</td>
<td>1.5 ± 0.9 0.4 ± 0.2 0.2 ± 0.1 9.8 ± 6.1</td>
</tr>
<tr>
<td></td>
<td>10 - 20</td>
<td>Pre-harvest</td>
<td>0.2 ± 0.2 0.1 ± 0.1 0.1 ± 0.1 4.2 ± 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Post-harvest</td>
<td>0.9 ± 0.8 0.3 ± 0.1 0.2 ± 0.1 4.0 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>20 - 30</td>
<td>Pre-harvest</td>
<td>0.6 ± 0.5 0.2 ± 0.1 0.2 ± 0.1 4.3 ± 2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Post-harvest</td>
<td>0.2 ± 0.1 0.2 ± 0.1 0.1 ± 0.1 3.6 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>30 - 40</td>
<td>Pre-harvest</td>
<td>0.5 ± 0.5 0.2 ± 0.1 0.2 ± 0.1 3.0 ± 0.5</td>
</tr>
</tbody>
</table>

STS 0 - 10 Pre-harvest 0.5 ± 0.3 0.4 ± 0.5 0.1 ± 0.1 7.3 ± 0.2 9.7 ± 8.1 9.0 ± 0.5 53 ± 38 4.1 ± 0.2 0.0000790 ± 0.00000394 14 ± 3.6 0.9 ± 0.0

10 - 20 Pre-harvest 0.3 ± 0.3 0.4 ± 0.5 0.1 ± 0.1 5.2 ± 1.8 11 ± 9.8 5.5 ± 0.6 58 ± 33 4.1 ± 0.3 0.0000817 ± 0.0000048 7.3 ± 0.7 0.4 ± 0.2

Post-harvest 1.0 ± 1.0 0.4 ± 0.5 0.2 ± 0.1 4.2 ± 1.1 19 ± 12 6.5 ± 0.7 38 ± 29 4.5 ± 0.3 0.0000361 ± 0.00000267 13 ± 1.7 0.8 ± 0.2

20 - 30 Pre-harvest 0.6 ± 0.6 0.3 ± 0.3 0.1 ± 0.1 5.1 ± 2.0 12 ± 2.9 4.8 ± 1.9 63 ± 6.6 4.1 ± 0.0 0.0000794 ± 0.0000027 9.3 ± 0.7 0.2 ± 0.1

Post-harvest 0.7 ± 0.6 0.4 ± 0.5 0.2 ± 0.1 3.9 ± 1.4 18 ± 12 5.4 ± 0.6 39 ± 32 4.4 ± 0.1 0.0000376 ± 0.0000021 9.7 ± 3.5 0.5 ± 0.2

30 - 40 Pre-harvest 0.5 ± 0.2 0.6 ± 0.3 0.1 ± 0.1 5.8 ± 1.8 20 ± 6.0 5.0 ± 2.0 51 ± 3.1 4.1 ± 0.0 0.0000794 ± 0.0000027 2.7 ± 0.7 0.2 ± 0.1

Post-harvest 0.7 ± 0.6 0.5 ± 0.6 0.2 ± 0.1 5.1 ± 0.8 17 ± 10 5.9 ± 0.7 45 ± 28 4.7 ± 0.0 0.0000279 ± 0.00000346 8.3 ± 4.5 0.5 ± 0.0

CC 0 - 10 Pre-harvest 3.0 ± 3.2 0.7 ± 0.5 0.3 ± 0.1 9.9 ± 2.4 30 ± 22 8.7 ± 2.3 13 ± 13 48.8 ± 0.7 0.0000249 ± 0.00000217 21 ± 8.4 1.5 ± 0.5

Post-harvest 4.1 ± 3.6 0.7 ± 0.3 0.3 ± 0.1 8.6 ± 2.4 35 ± 23 8.4 ± 1.9 19 ± 24 48.8 ± 0.6 0.0000237 ± 0.00000266 28 ± 6.8 1.6 ± 0.2

10 - 20 Pre-harvest 1.2 ± 1.1 0.6 ± 0.5 0.3 ± 0.1 6.4 ± 0.3 25 ± 17 5.9 ± 1.1 23 ± 24 47.6 ± 0.6 0.0000260 ± 0.00000218 9.3 ± 0.7 0.6 ± 0.0

Post-harvest 2.2 ± 2.3 0.5 ± 0.2 0.2 ± 0.1 7.2 ± 2.6 28 ± 21 7.1 ± 1.6 36 ± 36 48.8 ± 0.5 0.0000212 ± 0.00000148 15 ± 4.5 0.9 ± 0.1

20 - 30 Pre-harvest 0.6 ± 0.5 0.5 ± 0.5 0.2 ± 0.2 6.3 ± 0.9 17 ± 12 5.5 ± 0.8 44 ± 40 43 ± 0.2 0.0000377 ± 0.00000273 4.0 ± 0.0 0.3 ± 0.1

Post-harvest 1.2 ± 0.9 0.5 ± 0.3 0.2 ± 0.1 4.5 ± 0.3 24 ± 15 6.0 ± 1.6 39 ± 23 47.6 ± 0.6 0.0000272 ± 0.00000249 11 ± 5.3 0.6 ± 0.1

30 - 40 Pre-harvest 0.3 ± 0.2 0.7 ± 0.7 0.2 ± 0.2 6.6 ± 1.9 15 ± 10 5.8 ± 1.0 58 ± 21 42 ± 0.1 0.0000690 ± 0.00000191 2.7 ± 0.7 0.2 ± 0.1

Post-harvest 1.1 ± 1.0 0.5 ± 0.5 0.2 ± 0.1 4.2 ± 0.6 25 ± 20 5.6 ± 1.8 49 ± 15 47.0 ± 0.5 0.0000259 ± 0.00000194 9.0 ± 1.9 0.5 ± 0.2

† ECEC, effective cation exchange capacity.
‡ Base sat, percent base saturation.
¥ EA, extractable acidity.
¶ Al sat, percent aluminum saturation.

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### (b) Medium nutrient status soils.

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<td>Post-harvest</td>
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</table>

† ECEC, effective cation exchange capacity.
‡ Base sat, percent base saturation.
¥ EA, extractable acidity.
¶ Al sat, percent aluminum saturation.
F. Ion exchange resin mean ± 95% confidence interval (CI) for nutrient flux data pre and post-harvest by treatment (TRT) and sample depth for (a) low and (b) medium nutrient status soils.

(a) Low nutrient status soils.

<table>
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<th>Pre-harvest</th>
<th>TRT</th>
<th>Depth</th>
<th>Al&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Ca&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Mg&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Na&lt;sup&gt;+&lt;/sup&gt;</th>
<th>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</th>
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<td>30.0 ± 6.23</td>
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<td>45.3 ± 46.5</td>
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<td>48.6 ± 29.1</td>
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<td>9.27 ± 6.46</td>
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<td>5.95 ± 10.9</td>
<td>27.8 ± 31.7</td>
<td>31.6 ± 31.4</td>
<td>97.2 ± 63.7</td>
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Collection 1 April to Oct 2010
Collection 2 Oct to July 2011
Collection 3 Jan to July 2012
Collection 4 July to Jan 2013
(b) Medium nutrient status soils.

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Collection 1 April to Oct 2010
Collection 2 Oct to July 2011
Collection 3 Jan to July 2012
Collection 4 July to Jan 2013
G. Ion exchange resin mean ± 95 % confidence interval (CI) for nutrient loss data pre- and post-harvest by treatment (TRT) and sample depth for (a) low and (b) medium nutrient status soils.

(a) Low nutrient status soils.

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<th>Pre-harvest</th>
<th>TRT</th>
<th>Depth</th>
<th>Al&lt;sub&gt;r&lt;/sub&gt; (µmol)</th>
<th>Ca&lt;sup&gt;2+&lt;/sup&gt; (µmol)</th>
<th>Mg&lt;sup&gt;2+&lt;/sup&gt; (µmol)</th>
<th>Na&lt;sup&gt;+&lt;/sup&gt; (µmol)</th>
<th>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt; (µmol)</th>
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Collection 2 Oct to July 2011
Collection 3 Jan to July 2012
Collection 4 July to Jan 2013
(b) Medium nutrient status soils.

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Collection 1 April to Oct 2010
Collection 2 Oct to July 2011
Collection 3 Jan to July 2012
Collection 4 July to Jan 2013
H. Soil characterization associated with each horizon by geological formation in Missouri Ozarks.

H-I. Soil characterization associated with each horizon for Eminence geological formation in Missouri Ozarks.

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† Pedon identification in Missouri Cooperative Soil Survey database (http://www.soilsurvey.org).
¶ Exchangeable calcium.
‡ Cation exchange capacity.
† Citrate bicarbonate dithionite extractable aluminum.
ü Citrate bicarbonate dithionite extractable iron.
þ Citrate bicarbonate dithionite extractable manganese.
H-II. Soil characterization associated with each horizon for Roubidoux geological formation in Missouri Ozarks.

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<th>CEC ‡</th>
<th>ExCa ¶</th>
<th>pH</th>
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<th>Mehlich-3 Available P</th>
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<th>CBD Iron Ġ</th>
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† Pedon identification in Missouri Cooperative Soil Survey database (http://www.soilsurvey.org).
‡ Exchangeable calcium.
¶ Cation exchange capacity.
€ Total organic carbon.
† Citrate bicarbonate dithionite extractable aluminum.
Ġ Citrate bicarbonate dithionite extractable iron.
þ Citrate bicarbonate dithionite extractable managanese.
H-III. Soil characterization associated with each horizon for Upper Gasconade geological formation in Missouri Ozarks.

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<th>CBD Aluminum</th>
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291
H-IV. Soil characterization associated with each horizon for Lower Gasconade geological formation in Missouri Ozarks.

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† Pedon identification in Missouri Cooperative Soil Survey database (http://www.soilsurvey.org).
¶ Exchangeable calcium.
‡ Cation exchange capacity.
€ Total organic carbon.
Ĩ Citrate bicarbonate dithionite extractable aluminum.
ù Citrate bicarbonate dithionite extractable iron.
þ Citrate bicarbonate dithionite extractable manganese.
I. Mean concentrations of P forms and citrate bicarbonate dithionite extractable iron, aluminum and manganese on the basis of parent material, bedrock and landform in Missouri Ozarks.

I-I. Mean concentrations of P forms and citrate bicarbonate dithionite extractable iron, aluminum and manganese for all horizons on the basis of parent material, bedrock and landform in Missouri Ozarks (n=X).

<table>
<thead>
<tr>
<th></th>
<th>Total P</th>
<th>Mehllich-3 Available P</th>
<th>Bray-1 Available P</th>
<th>CBD-Fe †</th>
<th>CBD-Al ‡</th>
<th>CBD-Mn ¥</th>
</tr>
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<td></td>
<td>mg kg⁻¹</td>
<td>g kg⁻¹</td>
<td>mg kg⁻¹</td>
<td>mg kg⁻¹</td>
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<td>mg kg⁻¹</td>
</tr>
<tr>
<td>All Samples</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All horizons (n=150)</td>
<td>116.19 ± 6.93</td>
<td>7.87 ± 0.41</td>
<td>5.81 ± 0.48</td>
<td>10.26 ± 0.97</td>
<td>1.45 ± 0.08</td>
<td>0.53 ± 0.06</td>
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<tr>
<td>1st mineral horizon (n=50)</td>
<td>146.32 ± 14.44</td>
<td>10.33 ± 0.79</td>
<td>9.00 ± 0.95</td>
<td>5.38 ± 0.19</td>
<td>1.28 ± 0.07</td>
<td>0.97 ± 0.11</td>
</tr>
<tr>
<td>1st Bt or Bw horizon (n=50)</td>
<td>108.09 ± 8.81</td>
<td>6.92 ± 0.56</td>
<td>4.42 ± 0.59</td>
<td>7.50 ± 0.74</td>
<td>1.19 ± 0.10</td>
<td>0.46 ± 0.08</td>
</tr>
<tr>
<td>Horizon at 100 cm (n=50)</td>
<td>94.16 ± 9.73</td>
<td>6.36 ± 0.51</td>
<td>4.01 ± 0.53</td>
<td>17.90 ± 2.10</td>
<td>1.88 ± 0.19</td>
<td>0.15 ± 0.05</td>
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<tr>
<td>Parent Material</td>
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<td></td>
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</tr>
<tr>
<td>Alluvium (n=21)</td>
<td>156.34 ± 28.75</td>
<td>12.57 ± 1.83</td>
<td>9.89 ± 1.78</td>
<td>5.78 ± 0.35</td>
<td>1.07 ± 0.13</td>
<td>0.99 ± 0.19</td>
</tr>
<tr>
<td>Pedisediment (n=66)</td>
<td>106.78 ± 7.54</td>
<td>7.01 ± 0.35</td>
<td>5.14 ± 0.53</td>
<td>10.85 ± 1.36</td>
<td>1.52 ± 0.12</td>
<td>0.47 ± 0.08</td>
</tr>
<tr>
<td>Ped/residuum (n=39)</td>
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<td>7.23 ± 0.51</td>
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<td>11.06 ± 1.96</td>
<td>1.41 ± 0.14</td>
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<td>Bedrock</td>
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<tr>
<td>Roubidoux (n=30)</td>
<td>109.76 ± 12.68</td>
<td>7.81 ± 0.62</td>
<td>5.67 ± 1.01</td>
<td>9.21 ± 2.30</td>
<td>1.57 ± 0.27</td>
<td>0.42 ± 0.11</td>
</tr>
<tr>
<td>Upper Gasconade (n=36)</td>
<td>108.19 ± 9.57</td>
<td>6.80 ± 0.47</td>
<td>5.14 ± 0.81</td>
<td>10.99 ± 2.24</td>
<td>1.43 ± 0.13</td>
<td>0.63 ± 0.13</td>
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<tr>
<td>Lower Gasconade (n=57)</td>
<td>113.25 ± 11.66</td>
<td>7.20 ± 0.57</td>
<td>5.40 ± 0.83</td>
<td>11.27 ± 2.00</td>
<td>1.47 ± 0.15</td>
<td>0.50 ± 0.12</td>
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<td>Eminence (n=24)</td>
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<td>7.86 ± 1.69</td>
<td>7.62 ± 1.35</td>
<td>1.16 ± 0.14</td>
<td>0.63 ± 0.20</td>
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<td>Landform</td>
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<td>Structural Bench (n=48)</td>
<td>98.80 ± 10.59</td>
<td>7.18 ± 0.41</td>
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<td>10.59 ± 1.58</td>
<td>1.49 ± 0.12</td>
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<td>Hillslope (n=36)</td>
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<td>7.31 ± 0.58</td>
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<td>1.31 ± 0.13</td>
<td>0.39 ± 0.09</td>
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<tr>
<td>Ridge (n=42)</td>
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<td>6.75 ± 0.50</td>
<td>4.35 ± 0.63</td>
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<td>1.64 ± 0.19</td>
<td>0.44 ± 0.11</td>
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<td>Floodplain (n=21)</td>
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<td>12.57 ± 1.83</td>
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<td>5.78 ± 0.35</td>
<td>1.07 ± 0.13</td>
<td>0.99 ± 0.19</td>
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† Citrate bicarbonate dithionite extractable iron.
‡ Citrate bicarbonate dithionite extractable aluminum.
¥ Citrate bicarbonate dithionite extractable manganese.
Ĭ Pedisediment over residuum.
I-II. Mean concentrations of P forms and citrate bicarbonate dithionite extractable iron, aluminum and manganese on the basis of parent material in Missouri Ozarks.

<table>
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<tr>
<th>Total P</th>
<th>Mehlich-3 Available P</th>
<th>Available P</th>
<th>CBD-Fe †</th>
<th>CBD-Al ‡</th>
<th>CBD-Mn ¥</th>
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<tr>
<td></td>
<td>g kg⁻¹</td>
<td>µg kg⁻¹</td>
<td>mg kg⁻¹</td>
<td>mg kg⁻¹</td>
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<tr>
<td>1st mineral horizon</td>
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<tr>
<td>Alluvium</td>
<td>244.46 ± 59.46</td>
<td>14.79 ± 4.34</td>
<td>13.73 ± 3.70</td>
<td>5.56 ± 0.68</td>
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<tr>
<td>Ped/bedrock</td>
<td>126.75 ± 42.96</td>
<td>9.40 ± 1.77</td>
<td>8.19 ± 2.94</td>
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<td>1.25 ± 0.11</td>
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<tr>
<td>Ped/residuum</td>
<td>140.85 ± 24.66</td>
<td>9.74 ± 1.38</td>
<td>7.67 ± 2.68</td>
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<tr>
<td>Alluvium</td>
<td>137.24 ± 19.27</td>
<td>11.73 ± 2.8</td>
<td>9.23 ± 2.31</td>
<td>5.54 ± 0.58</td>
<td>0.98 ± 0.13</td>
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<tr>
<td>Ped/bedrock</td>
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<td>6.10 ± 0.76</td>
<td>3.71 ± 1.46</td>
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<td>Ped/residuum</td>
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<td>19.79 ± 4.93</td>
<td>1.11 ± 0.29</td>
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<tr>
<td>Horizon at 100 cm depth</td>
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<td>Alluvium</td>
<td>137.24 ± 19.27</td>
<td>11.73 ± 2.8</td>
<td>9.23 ± 2.31</td>
<td>5.54 ± 0.58</td>
<td>0.98 ± 0.13</td>
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<tr>
<td>Ped/bedrock</td>
<td>102.11 ± 34.37</td>
<td>6.10 ± 0.76</td>
<td>3.71 ± 1.46</td>
<td>7.36 ± 0.82</td>
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<td>Ped/residuum</td>
<td>108.2 ± 32.20</td>
<td>6.21 ± 0.76</td>
<td>3.66 ± 1.13</td>
<td>19.79 ± 4.93</td>
<td>1.11 ± 0.29</td>
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† Citrate bicarbonate dithionite extractable iron.
‡ Citrate bicarbonate dithionite extractable aluminum.
¥ Citrate bicarbonate dithionite extractable manganese.

I-III. Mean concentrations of P forms and citrate bicarbonate dithionite extractable iron, aluminum and manganese on the basis of bedrock in Missouri Ozarks.

<table>
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<tr>
<th>Total P</th>
<th>Mehlich-3 Available P</th>
<th>Available P</th>
<th>CBD-Fe †</th>
<th>CBD-Al ‡</th>
<th>CBD-Mn ¥</th>
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<td>g kg⁻¹</td>
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<td>mg kg⁻¹</td>
<td>mg kg⁻¹</td>
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<tr>
<td>Roubidoux</td>
<td>140.52 ± 28.67</td>
<td>10.06 ± 0.91</td>
<td>9.38 ± 1.74</td>
<td>4.79 ± 0.41</td>
<td>1.19 ± 0.10</td>
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<td>Upper Gasconade</td>
<td>129.30 ± 17.44</td>
<td>8.49 ± 0.89</td>
<td>7.77 ± 1.64</td>
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<td>1.25 ± 0.10</td>
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<td>5.55 ± 0.24</td>
<td>1.32 ± 0.12</td>
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<tr>
<td>Eminence</td>
<td>215.80 ± 57.94</td>
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<td>9.95 ± 3.94</td>
<td>5.30 ± 0.69</td>
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<tr>
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</tr>
<tr>
<td>Roubidoux</td>
<td>112.46 ± 16.08</td>
<td>6.77 ± 0.79</td>
<td>4.70 ± 1.26</td>
<td>6.83 ± 1.10</td>
<td>1.40 ± 0.32</td>
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<tr>
<td>Upper Gasconade</td>
<td>107.37 ± 16.59</td>
<td>6.28 ± 0.47</td>
<td>3.64 ± 0.95</td>
<td>7.18 ± 1.13</td>
<td>1.11 ± 0.13</td>
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<tr>
<td>Lower Gasconade</td>
<td>103.54 ± 17.55</td>
<td>6.17 ± 0.32</td>
<td>3.83 ± 0.46</td>
<td>8.23 ± 1.52</td>
<td>1.17 ± 0.14</td>
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<tr>
<td>Eminence</td>
<td>118.52 ± 19.19</td>
<td>9.95 ± 2.92</td>
<td>7.03 ± 2.58</td>
<td>5.86 ± 0.81</td>
<td>0.90 ± 0.14</td>
</tr>
<tr>
<td>Horizon at 100 cm depth</td>
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<tr>
<td>Roubidoux</td>
<td>76.29 ± 5.61</td>
<td>6.58 ± 0.76</td>
<td>2.92 ± 0.75</td>
<td>16.00 ± 5.87</td>
<td>2.13 ± 0.71</td>
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<td>Upper Gasconade</td>
<td>87.91 ± 12.05</td>
<td>5.62 ± 0.52</td>
<td>4.02 ± 0.97</td>
<td>20.05 ± 4.97</td>
<td>1.94 ± 0.25</td>
</tr>
<tr>
<td>Lower Gasconade</td>
<td>102.80 ± 23.56</td>
<td>5.49 ± 0.35</td>
<td>3.61 ± 0.67</td>
<td>20.03 ± 2.94</td>
<td>1.91 ± 0.24</td>
</tr>
<tr>
<td>Eminence</td>
<td>108.31 ± 10.58</td>
<td>9.39 ± 2.41</td>
<td>6.60 ± 2.00</td>
<td>11.70 ± 3.16</td>
<td>1.27 ± 0.31</td>
</tr>
</tbody>
</table>

† Citrate bicarbonate dithionite extractable iron.
‡ Citrate bicarbonate dithionite extractable aluminum.
¥ Citrate bicarbonate dithionite extractable manganese.
I-IV. Mean concentrations of P forms and citrate bicarbonate dithionite extractable iron, aluminum and manganese on the basis of landform in Missouri Ozarks.

<table>
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<tr>
<th></th>
<th>Total P</th>
<th>Mehlich-3 Available P</th>
<th>Bray-1 Available P</th>
<th>CBD-Fe †</th>
<th>CBD-Al ‡</th>
<th>CBD-Mn ¥</th>
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<td></td>
<td>ng kg⁻¹</td>
<td>g kg⁻¹</td>
<td>ng kg⁻¹</td>
<td>g kg⁻¹</td>
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<tr>
<td>Structural Bench</td>
<td>126.19 ± 21.05</td>
<td>9.27 ± 0.64</td>
<td>8.04 ± 1.13</td>
<td>5.62 ± 0.27</td>
<td>1.29 ± 0.10</td>
<td>1.02 ± 0.17</td>
</tr>
<tr>
<td>Hillslope</td>
<td>148.35 ± 12.85</td>
<td>10.29 ± 0.77</td>
<td>9.20 ± 1.91</td>
<td>5.02 ± 0.46</td>
<td>1.12 ± 0.16</td>
<td>0.75 ± 0.17</td>
</tr>
<tr>
<td>Ridge</td>
<td>121.97 ± 19.86</td>
<td>9.10 ± 1.02</td>
<td>7.01 ± 1.30</td>
<td>5.40 ± 0.33</td>
<td>1.28 ± 0.09</td>
<td>0.84 ± 0.22</td>
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<tr>
<td>Floodplain</td>
<td>244.46 ± 59.46</td>
<td>14.79 ± 4.34</td>
<td>13.73 ± 3.70</td>
<td>5.56 ± 0.68</td>
<td>1.48 ± 0.23</td>
<td>1.56 ± 0.36</td>
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<tr>
<td><strong>1st Bt or Bw horizon</strong></td>
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<td>Hillslope</td>
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<td>6.15 ± 0.29</td>
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<td>1.14 ± 0.24</td>
<td>0.32 ± 0.12</td>
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<tr>
<td>Ridge</td>
<td>110.50 ± 16.19</td>
<td>5.98 ± 0.45</td>
<td>3.01 ± 0.71</td>
<td>6.72 ± 0.75</td>
<td>1.25 ± 0.24</td>
<td>0.42 ± 0.18</td>
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<tr>
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<td>11.73 ± 2.8</td>
<td>9.23 ± 2.31</td>
<td>5.54 ± 0.58</td>
<td>0.98 ± 0.13</td>
<td>0.87 ± 0.17</td>
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<td><strong>Horizon at 100 cm depth</strong></td>
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<td>4.19 ± 0.85</td>
<td>18.37 ± 3.30</td>
<td>2.01 ± 0.27</td>
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<td>5.47 ± 0.34</td>
<td>3.55 ± 0.85</td>
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<td>11.18 ± 2.07</td>
<td>6.72 ± 2.18</td>
<td>6.24 ± 0.54</td>
<td>0.75 ± 0.04</td>
<td>0.53 ± 0.13</td>
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† Citrate bicarbonate dithionite extractable iron.
‡ Citrate bicarbonate dithionite extractable aluminum.
¥ Citrate bicarbonate dithionite extractable manganese.
J. Linear regression coefficients for total P, available P (Mehlich-3) and available P (Bray-1) concentrations in Missouri Ozarks.

J.1. Linear regression coefficients between clay and total P concentrations in Missouri Ozarks.

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<tr>
<td>All horizons</td>
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<td>0.3090</td>
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<td>0.0176</td>
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$\beta_1$: Intercept  
$\beta_2$: Slope  
$\beta_3$: $r^2$  
$\beta_4$: p-value
J.2. Linear regression coefficients between clay and Mehlich-3 available P concentrations in Missouri Ozark.

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<td>Roubidoux</td>
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$\beta_0$ Intercept
$\beta_2$ Slope
$\beta_3$ $r^2$
$\beta_4$ p-value
J.3. Linear regression coefficients between clay and Bray-1 available P concentrations in Missouri Ozarks.

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$\beta_1$ Intercept  
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$\beta_3$ $r^2$  
$\beta_4$ p-value
J.4. Linear regression coefficients between Ca and total P concentrations in Missouri Ozarks.

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β₁ Intercept
β₂ Slope
β₃ r²
β₄ p-value
### J.5. Linear regression coefficients between Ca and Mehlich-3 available P concentrations in Missouri Ozarks.

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$\beta_1$: Intercept  
$\beta_2$: Slope  
$\beta_3$: $r^2$  
$\beta_4$: p-value
J.6. Linear regression coefficients between Ca and Bray-1 available P concentrations in Missouri Ozarks.

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| β₁ Intercept         | β₂ Slope | β₃ r² | β₄ p-value |
J.7. Linear regression coefficients between Mg and total P concentrations in Missouri Ozarks.

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$\beta_1$: Intercept  
$\beta_2$: Slope  
$\beta_3$: $r^2$  
$\beta_4$: p-value
### J.8. Linear regression coefficients between Mg and Mehlich-3 available P available P concentrations in Missouri Ozarks.

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- \( \beta_1 \) Intercept
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- \( \beta_4 \) p-value
J.9. Linear regression coefficients between Mg and Bray-1 available P concentrations in Missouri Ozarks.

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β₃ r²  
β₄ p-value
### J.10. Linear regression coefficients between CEC and total P concentrations in Missouri Ozarks.

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\( \beta_4 \): p-value
J.11. Linear regression coefficients between CEC and Mehlich-3 available P concentrations in Missouri Ozarks.

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- \( \beta_1 \): Intercept
- \( \beta_2 \): Slope
- \( \beta_3 \): \( r^2 \)
- \( \beta_4 \): p-value
J.12. Linear regression coefficients between CEC and Bray-1 available P concentrations in Missouri Ozarks.

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- β₁ Intercept
- β₂ Slope
- β₃ r²
- β₄ p-value
J.13. Linear regression coefficients between BS and total P concentrations in Missouri Ozarks.

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| β3 | r²        |
| β4 | p-value   |
J.14. Linear regression coefficients between BS and Mehlich-3 available P concentrations in Missouri Ozarks.

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β₁ Intercepts
β₂ Slope
β₃ r²
β₄ p-value
J.15. Linear regression coefficients between BS and Bray-1 available P concentrations in Missouri Ozarks.

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$\beta_1$: Intercept  
$\beta_2$: Slope  
$\beta_3$: $r^2$  
$\beta_4$: p-value
J.16. Linear regression coefficients between pH and total P concentrations in Missouri Ozarks.

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J.17. Linear regression coefficients between pH and Mehlich-3 available P concentrations in Missouri Ozarks.

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$\beta_2$: Slope
$\beta_3$: $r^2$
$\beta_4$: p-value

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J.18. Linear regression coefficients between pH and Bray-1 available P concentrations in Missouri Ozarks.

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$\beta_1$ Intercept
$\beta_2$ Slope
$\beta_3$ $r^2$
$\beta_4$ p-value
J.19. Linear regression coefficients between TOC and total P concentrations in Missouri Ozarks.

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\( \beta_1 \) Intercept
\( \beta_2 \) Slope
\( \beta_3 \) \( r^2 \)
\( \beta_4 \) p-value
J.20. Linear regression coefficients between TOC and Mehlich-3 available P concentrations in Missouri Ozarks.

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β₀ Intercept
β₁ Slope
β₂ r²
β₃ p-value
J.21. Linear regression coefficients between TOC and Bray-1 available P concentrations in Missouri Ozarks.

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\( \beta_1 \) Intercept
\( \beta_2 \) Slope
\( \beta_3 \) \( \bar{r}^2 \)
\( \beta_4 \) p-value
J.22. Linear regression coefficients between CBD extractable Al and total P concentrations in Missouri Ozarks.

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$\beta_1$: Intercept  
$\beta_2$: Slope  
$\beta_3$: $r^2$  
$\beta_4$: p-value  

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J.23. Linear regression coefficients between CBD extricable Al and Mehlich-3 available P concentrations in Missouri Ozarks.

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$\beta_1$: Intercept
$\beta_2$: Slope
$\beta_3$: $r^2$
$\beta_4$: $p$-value
J.24. Linear regression coefficients between CBD extricable Al and Bray-1 available P concentrations in Missouri Ozarks.

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- \( \beta_1 \) Intercept
- \( \beta_2 \) Slope
- \( \beta_3 \) \( r^2 \)
- \( \beta_4 \) p-value
J.25. Linear regression coefficients between CBD extricable Fe and total P concentrations in Missouri Ozarks.

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β₁: Intercept  
β₂: Slope  
β₃: r²  
β₄: p-value
J.26. Linear regression coefficients between CBD extricable Fe and Mehlich-3 available P concentrations in Missouri Ozarks.

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\( \beta_1 \) Intercept
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\( \beta_3 \) r²
\( \beta_4 \) p-value
J.27. Linear regression coefficients between CBD extractable Fe and Bray-1 available P concentrations in Missouri Ozarks.

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$\beta_1$ Intercept  
$\beta_2$ Slope  
$\beta_3$ $r^2$  
$\beta_4$ p-value
J.28. Linear regression coefficients between CBD extricable Mn and total P concentrations in Missouri Ozarks.

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$\beta_1$ Intercept  
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$\beta_3$ $r^2$  
$\beta_4$ p-value
J.29. Linear regression coefficients between CBD extricable Mn and Mehlich-3 available P concentrations in Missouri Ozarks.

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$\beta_1$ Intercept
$\beta_2$ Slope
$\beta_3$ $r^2$
$\beta_4$ p-value
J.30. Linear regression coefficients between CBD extricable Mn and Bray-1 available P concentrations in Missouri Ozarks.

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β₀ Intercept
β₁ Slope
β² r²
β₄ p-value
J.31. Linear regression coefficients between CBD extractable Al+Fe and total P concentrations in Missouri Ozarks.

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$\beta_1$ Intercept
$\beta_2$ Slope
$\beta_3$ $r^2$
$\beta_4$ p-value
J.32. Linear regression coefficients between CBD extricable Al+Fe and Mehlich-3 available P concentrations in Missouri Ozarks.

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<th>Slope</th>
<th>r²</th>
<th>p-value</th>
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| **Parent Material**     |           |        |        |         |
| Alluvium                | -4.49994  | 0.00249 | 0.2645 | 0.0171  |
| Horizon A               | -6.0122   | 0.00295 | 0.3088 | 0.1952  |
| Horizon B               | -3.37784  | 0.00232 | 0.2913 | 0.2112  |
| Horizon at 100 cm       | 0.41724   | 0.00154 | 0.1531 | 0.3855  |

| Pedisement              |           |        |        |         |
| All horizons            | 7.90777   | -0.00007308 | 0.0938 | 0.0039  |
| Horizon A               | 9.1607    | -0.00007759 | 0.0014 | 0.8486  |
| Horizon B               | 5.07632   | 0.00011994  | 0.0961 | 0.1017  |
| Horizon at 100 cm       | 5.06345   | 0.00020474  | 0.0601 | 0.1998  |

| Ped/residuum            |           |        |        |         |
| All horizons            | 8.39761   | -0.00009364 | 0.1469 | 0.0160  |
| Horizon A               | 9.58696   | 0.00023735  | 0.0002 | 0.9658  |
| Horizon B               | 6.2739    | -0.0000665  | 0.0017 | 0.8935  |
| Horizon at 100 cm       | 5.3158    | 0.0001925   | 0.0195 | 0.6490  |

| **Bedrock**             |           |        |        |         |
| Roubidoux               | 8.80886   | -0.00009309 | 0.1474 | 0.0362  |
| Horizon A               | 5.57609   | 0.00075031  | 0.1577 | 0.2558  |
| Horizon B               | 8.827     | -0.00024966 | 0.1971 | 0.1987  |
| Horizon at 100 cm       | 7.35823   | -0.00004284 | 0.1344 | 0.2975  |

| Upper Gasconade         |           |        |        |         |
| All horizons            | 7.39364   | -0.00004797 | 0.0587 | 0.1545  |
| Horizon A               | 9.4268    | -0.00013358 | 0.0035 | 0.8553  |
| Horizon B               | 4.85603   | 0.00017167  | 0.2004 | 0.1445  |
| Horizon at 100 cm       | 5.26869   | 0.0001592   | 0.0256 | 0.6195  |

| Lower Gasconade         |           |        |        |         |
| All horizons            | 8.53653   | -0.00010481 | 0.1518 | 0.0027  |
| Horizon A               | 12.07668  | -0.00030978 | 0.0191 | 0.5725  |
| Horizon B               | 6.10527   | 0.0000676   | 0.0012 | 0.8871  |
| Horizon at 100 cm       | 4.94449   | 0.00002431  | 0.0470 | 0.3726  |

| Eminence                |           |        |        |         |
| All horizons            | 13.32888  | -0.00025619 | 0.0409 | 0.3435  |
| Horizon A               | -5.75802  | 0.00298     | 0.3924 | 0.0965  |
| Horizon B               | 4.38567   | 0.00082311  | 0.0693 | 0.5289  |
| Horizon at 100 cm       | 14.9441   | -0.00042779 | 0.3775 | 0.1051  |

| **Landform**            |           |        |        |         |
| Structural Bench        | 8.05451   | -0.00007206 | 0.0881 | 0.0404  |
| Horizon A               | 13.00756  | -0.00054119 | 0.0828 | 0.2797  |
| Horizon B               | 5.25834   | 0.0001124   | 0.0684 | 0.3280  |
| Horizon at 100 cm       | 5.53764   | 0.00002341  | 0.0347 | 0.4895  |

| Hillslope               | 8.76672   | -0.00012756 | 0.1686 | 0.0129  |
| Horizon A               | 6.16521   | 0.00067191   | 0.1918 | 0.1544  |
| Horizon B               | 6.22088   | -0.0000077   | 0.0047 | 0.8332  |
| Horizon at 100 cm       | 4.76595   | 0.00003781   | 0.1243 | 0.2609  |

| Ridge                   | 7.58413   | -0.00006121 | 0.0887 | 0.0554  |
| Horizon A               | 9.56895   | -0.00007044 | 0.0007 | 0.9301  |
| Horizon B               | 4.87889   | 0.00013869   | 0.0896 | 0.2985  |
| Horizon at 100 cm       | 4.42498   | 0.00002866   | 0.1785 | 0.1324  |

| Floodplain              | -4.49994  | 0.00249     | 0.2645 | 0.0171  |
| Horizon A               | -6.0122   | 0.00295     | 0.3088 | 0.1952  |
| Horizon B               | -3.37784  | 0.00232     | 0.2913 | 0.2112  |
| Horizon at 100 cm       | 0.41724   | 0.00154     | 0.1531 | 0.3855  |

| β_i Intercept           |   |   |   |         |
| β_2 Slope               |   |   |   |         |
| β_3 r²                  |   |   |   |         |
| β_4 p-value             |   |   |   |         |
J.33. Linear regression coefficients between CBD extricable Al+Fe and Bray-1 available P concentrations in Missouri Ozarks.

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\( \beta_1 \) Intercept  \\
\( \beta_2 \) Slope  \\
\( \beta_3 \) \( r^2 \)  \\
\( \beta_4 \) p-value
J.34. Linear regression coefficients between CBD extractable Al+Fe+Mn and total P concentrations in Missouri Ozarks.

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<tr>
<td>All horizons</td>
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<td><strong>Floodplain</strong></td>
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<td>All horizons</td>
<td>-154.90643</td>
<td>0.03971</td>
<td>0.4563</td>
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<td>Horizon B</td>
<td>138.07564</td>
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<tr>
<td>Horizon at 100 cm</td>
<td>-99.73352</td>
<td>0.02486</td>
<td>0.8233</td>
<td>0.0048</td>
</tr>
</tbody>
</table>

$\beta_1$ Intercept
$\beta_2$ Slope
$\beta_3$ $r^2$
$\beta_4$ p-value
J.35. Linear regression coefficients between CBD extractable Al+Fe+Mn and Mehlich-3 available P concentrations in Missouri Ozarks.

<table>
<thead>
<tr>
<th></th>
<th>Intercept</th>
<th>Slope</th>
<th>$r^2$</th>
<th>p-value</th>
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<td><strong>All samples</strong></td>
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<tr>
<td>All horizons</td>
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<td>Alluvium</td>
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<td>All horizons</td>
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<tr>
<td>Horizon A</td>
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<td>0.00259</td>
<td>0.4515</td>
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<tr>
<td>Horizon B</td>
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<td>Horizon at 100 cm</td>
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<td>0.3029</td>
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<td>Horizon at 100 cm</td>
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<td>0.0608</td>
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<tr>
<td>Horizon at 100 cm</td>
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<td><strong>Bedrock</strong></td>
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<td>Roubidoux</td>
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<td>Horizon A</td>
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<td>Structural Bench</td>
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<td><strong>Hillslope</strong></td>
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<tr>
<td>All horizons</td>
<td>-7.05194</td>
<td>0.0025</td>
<td>0.4485</td>
<td>0.0009</td>
</tr>
<tr>
<td>Horizon A</td>
<td>-7.47264</td>
<td>0.00259</td>
<td>0.4515</td>
<td>0.0983</td>
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<tr>
<td>Horizon B</td>
<td>-5.84531</td>
<td>0.00238</td>
<td>0.3831</td>
<td>0.1383</td>
</tr>
<tr>
<td>Horizon at 100 cm</td>
<td>-4.3031</td>
<td>0.00206</td>
<td>0.3029</td>
<td>0.2005</td>
</tr>
</tbody>
</table>

$\beta_1$ Intercept
$\beta_2$ Slope
$\beta_3$ $r^2$
$\beta_4$ p-value
J.36. Linear regression coefficients between CBD extractable Al+Fe+Mn and Bray-1 available P concentrations in Missouri Ozarks.

| All samples | \( \beta_1 \) & \( \beta_2 \) & \( \beta_3 \) & \( \beta_4 \) |
|-------------|--------|--------|--------|--------|
| All samples | \( 7.30752 \) & -0.00012224 & 0.0651 & 0.0016 |
| Horizon A   | \( 2.70359 \) & 0.00082544 & 0.0743 & 0.0555 |
| Horizon B   | 5.02906 & -0.00006698 & 0.0085 & 0.5247 |
| Horizon at 100 cm | 4.92216 & -0.00004557 & 0.0373 & 0.1792 |

| Parent Material | \( \beta_1 \) & \( \beta_2 \) & \( \beta_3 \) & \( \beta_4 \) |
|-----------------|--------|--------|--------|--------|
| Alluvium        | All horizons | -1.32552 & 0.00143 & 0.1539 & 0.0786 |
|                 | Horizon A   | 3.4602  & 0.00119 & 0.1323 & 0.4225 |
|                 | Horizon B   | 4.90309 & 0.0005853 & 0.0340 & 0.6924 |
|                 | Horizon at 100 cm | 0.6934 & 0.00080125 & 0.0416 & 0.6611 |
| Pedisediment    | All horizons | \( 6.53427 \) & -0.00010859 & 0.0866 & 0.0057 |
|                 | Horizon A   | 6.95607 & 0.00016298 & 0.0042 & 0.7397 |
|                 | Horizon B   | 2.23416 & 0.00016388 & 0.0494 & 0.2463 |
|                 | Horizon at 100 cm | 4.45761 & -0.00004288 & 0.0570 & 0.2121 |
| Ped/residuum    | All horizons | 5.42806 & -0.00002917 & 0.0072 & 0.6063 |
|                 | Horizon A   | -2.14314 & 0.00134 & 0.2383 & 0.0906 |
|                 | Horizon B   | 3.66173 & -6.80E-08 & 0.0000 & 0.9993 |
|                 | Horizon at 100 cm | 0.88562 & 0.00013461 & 0.3313 & 0.0396 |
| Bedrock         | All horizons | 7.48216 & -0.00016225 & 0.1587 & 0.0292 |
|                 | Horizon A   | 6.96077 & 0.00035957 & 0.0154 & 0.7329 |
|                 | Horizon B   | \( 10.09532 \) & -0.00062828 & 0.4219 & 0.0421 |
|                 | Horizon at 100 cm | 3.63657 & -0.00003932 & 0.1136 & 0.3408 |
| Upper Gasconade | All horizons | 6.35412 & -0.00009272 & 0.0689 & 0.1220 |
|                 | Horizon A   | 2.49707 & 0.00065189 & 0.0492 & 0.4886 |
|                 | Horizon B   | 0.81282 & 0.00031842 & 0.1816 & 0.1672 |
|                 | Horizon at 100 cm | 6.03944 & -0.00009098 & 0.2387 & 0.1070 |
| Lower Gasconade | All horizons | 6.3803 & -0.00007371 & 0.0338 & 0.1707 |
|                 | Horizon A   | 9.24255 & -0.00005938 & 0.0004 & 0.9392 |
|                 | Horizon B   | 3.78059 & 0.00000525 & 0.0004 & 0.9393 |
|                 | Horizon at 100 cm | 1.07042 & 0.00011521 & 0.3020 & 0.0148 |
| Eminence       | All horizons | 8.32053 & -0.00004911 & 0.0017 & 0.8471 |
|                 | Horizon A   | \( -7.07238 \) & 0.00222 & 0.5077 & 0.0473 |
|                 | Horizon B   | -2.15051 & 0.00126 & 0.2424 & 0.2152 |
|                 | Horizon at 100 cm | 11.29631 & -0.00035316 & 0.3486 & 0.1233 |
| Landform       | Structural Bench | All horizons | 5.84712 & -0.00002956 & 0.0061 & 0.5973 |
|                 | Horizon A   | 8.97269 & -0.00011831 & 0.0025 & 0.8543 |
|                 | Horizon B   | 3.39727 & 0.00008532 & 0.0134 & 0.6695 |
|                 | Horizon at 100 cm | \( 1.71074 \) & 0.00012075 & 0.2522 & 0.0474 |
| Hillslope      | All horizons | 7.17452 & -0.00013952 & 0.0745 & 0.1072 |
|                 | Horizon A   | \( -1.59255 \) & 0.00157 & 0.2895 & 0.0711 |
|                 | Horizon B   | 3.80178 & 0.00000134 & 0.0000 & 0.9856 |
|                 | Horizon at 100 cm | 3.75686 & -0.00001125 & 0.0018 & 0.8948 |
| Ridge          | All horizons | \( 5.58488 \) & -0.00008822 & 0.1112 & 0.0309 |
|                 | Horizon A   | 5.12232 & 0.00025132 & 0.0100 & 0.7340 |
|                 | Horizon B   | 1.77173 & 0.00014833 & 0.0413 & 0.4862 |
|                 | Horizon at 100 cm | 4.68966 & -0.00006401 & 0.2418 & 0.0741 |
| Floodplain     | All horizons | -1.32552 & 0.00143 & 0.1539 & 0.0786 |
|                 | Horizon A   | 3.4602  & 0.00119 & 0.1323 & 0.4225 |
|                 | Horizon B   | 4.90309 & 0.0005853 & 0.0340 & 0.6924 |
|                 | Horizon at 100 cm | 0.6934 & 0.00080125 & 0.0416 & 0.6611 |

\( \beta_1 \) Intercept  \\
\( \beta_2 \) Slope  \\
\( \beta_3 \) \( r^2 \)  \\
\( \beta_4 \) p-value
K. Plots representing mean concentrations of Mehlich-3 available P, Bray-1 available P and total P.

K-I. Plots representing mean concentrations of (a) Mehlich-3 available P, (b) Bray-1 available P, (c) total P, (d) CBD-Fe, (e) CBD-Al, (f) CBD-Mn, (g) CBD Fe+Al, and (h) CBD Fe+Al+Mn in three soil horizons by parent material type. Error bars represent ± one standard error.
K-II. Plots representing mean concentrations of P pools by soil pH.
Comparisons of (a) Mehlich-3 available P (b) Bray-1 available P (c) total P. Error bars represent ± one standard error.
K-III. Plots representing mean concentrations of P forms, CBD extractable Fe+Al and Mn by soil pH.

Comparisons of (a) Mehlich-3 available P and CBD-Mn-, (b) Bray-1 available P and CBD-Mn-, (c) total P and CBD-Mn (d) CBD-Mn and CBD Fe+Al, (e) Mehlich-3 available P and CBD Fe+Al, (f) Bray-1 available P and CBD Fe+Al, and (g) total P and CBD Fe+Al as a function of pH.
L. Classification and Regression Trees

Regression trees developed from classification and regression tree analysis for (I) total P, (II) Mehlich-3 available P, and (III) Bray-1 available P; concentrations are expressed in mg kg⁻¹. Each branch of the regression tree is labeled with the explanatory variable associated with partitioning of the response variable. Boxes represent the nodes including the number of horizons present in each split, the explanatory variable associated with each split, and the mean concentrations of Mehlich-3 available P, Bray-1 available P and total P. Dashed boxes represent the terminal nodes. Model for:

I. Total P

Response variable (total P) ~ Explanatory variables (horizon type + parent material + bedrock + profile position + landform + clay + exchangeable calcium + CEC + pH + sum (CBD Al+Fe) + CBD-Mn + total organic C).

II. Mehlich-3 available P

Response variable (Mehlich-3 available P) ~ Explanatory variables (horizon type + parent material + bedrock + profile position + landform + exchangeable calcium + CEC + pH + sum (CBD Al+Fe) + CBD-Mn + total organic C).

III. Model for Bray-1 available P

Response variable (Bray-1 available P) ~ Explanatory variables (horizon type + parent material + bedrock + profile position + landform + exchangeable calcium + CEC + pH + sum (CBD Al+Fe) + CBD-Mn + total organic C).
I. Classification and regression tree for total P.
II. Classification and regression tree for Mehlich-3 available P.

- **CBD-Mn (<505.01 mg kg⁻¹)**
  - Mean AP Mehlich-3 = 6.28 mg kg⁻¹
  - N = 89
  - (27.8 %)

- **Horizon Type First Bt or Bw Horizon, Horizon at 100 cm**
  - Mean AP Mehlich-3 = 5.81 mg kg⁻¹
  - N = 77
  - (6.1 %)

- **Horizon Type First Mineral Horizon (A)**
  - Mean AP Mehlich-3 = 9.26 mg kg⁻¹
  - N = 12

- **Cation Exchange Capacity (<14.23 cmol, kg⁻¹)**
  - Mean AP Mehlich-3 = 7.97 mg kg⁻¹
  - N = 33
  - (5.5 %)

- **Bedrock Upper Gasconade, Lower Gasconade**
  - Mean AP Mehlich-3 = 7.10 mg kg⁻¹
  - N = 23
  - (2.8 %)

- **Bedrock Eminence, Roubidoux**
  - Mean AP Mehlich-3 = 9.98 mg kg⁻¹
  - N = 10

- **Landform Floodplain, Structural Bench**
  - Mean AP Mehlich-3 = 9.79 mg kg⁻¹
  - N = 11
  - (1.4 %)

- **Landform Hillslope, Ridge**
  - Mean AP Mehlich-3 = 12.15 mg kg⁻¹
  - N = 10

- **CBD-Mn (≥505.01 mg kg⁻¹)**
  - Mean AP Mehlich-3 = 10.19 mg kg⁻¹
  - N = 61
  - (27.3 %)

- **pH < 6.25**
  - Mean AP Mehlich-3 = 9.12 mg kg⁻¹
  - N = 54

- **pH ≥ 6.25**
  - Mean AP Mehlich-3 = 18.5 mg kg⁻¹
  - N = 7

- **All Samples**
  - Mean AP Mehlich-3 = 7.87 mg kg⁻¹
  - N = 150
III. Classification and regression tree Bray-1 available P.
M. Mean concentrations for forms of P ± 95% confidence intervals.

Mean concentrations were calculated by adding P concentrations present at specific point of pH (eg. If at pH 4.4 there were seven soil horizons, then mean total P and confidence interval for these seven horizons is represented as 99.4 ± 11.0 for total P, 8.4 ± 1.2 for Mehlich-3 available P, and 4.9 ± 1.2 for Bray-1 available P).

<table>
<thead>
<tr>
<th>Soil pH</th>
<th>Total P</th>
<th>Mehlich-3 Available P</th>
<th>Bray-1 Available P</th>
</tr>
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<tbody>
<tr>
<td>4.4</td>
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<td>8.4 ± 1.2</td>
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N. Mean precipitation, air, and soil temperature for three years of MOFEP research (April/2010 to March/2013).

(a) Mean monthly precipitation (inches) from Carr Creek Missouri weather station, (b) Mean precipitation (inches) from 45 collection events as recorded from rain gauge installed at each soil pit (one collection event represent mean precipitation from 18 soil pits), (c) Mean monthly air temperature (degree Fahrenheit) from Carr Creek Missouri weather station, and (d) Mean monthly soil temperature from Carr Creek Missouri weather station.