Influence of Residue Management on Soil Chemical Properties and Nutrient Flux in Forests Harvested for Woody Biomass

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ASHLEY SCHROEDER

Dr. Keith W. Goyne, Thesis Supervisor

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The undersigned, appointed by the Dean of the Graduate School,

have examined the Thesis entitled

Influence of Residue Management on Soil Chemical Properties and

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Presented by Ashley Schroeder

A candidate for the degree of

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

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Dr. Keith W. Goyne

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Dr. John M. Kabrick

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Dr. Robert J. Kremer

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ABSTRACT

Altered soil solution chemistry and nutrient flux within forests harvested for woody biomass may result from disturbance, slash removals, slash decomposition, and mineralization. Because of the potential adverse effects of woody biomass harvest to soil nutrient pools and overall soil quality, the Missouri Department of Conservation (MDC) has developed Best Management Practices (BMPs) to retain coarse woody residues associated with biomass harvesting to retain nutrient capital and sustain forest productivity. However, these BMPs remain untested. To investigate the potential impacts of woody biomass harvest and use of BMPs to mitigate deleterious effects, this study examined soil nutrient concentrations and nutrient flux in Missouri Ozark forest soils immediately following harvest to 1.5 years post-harvest. The eight treatments investigated were Missouri's 1/3 harvest residue retention BMP for thinning and commercial biomass harvests and alternative harvest scenarios. Chemical properties of soils within the harvest treatments were quantified immediately after harvest and one year post-harvest, and analysis of variance results are presented. Total organic carbon (TOC) was the only dependent variable that was affected by harvest treatment (p-value = 0.0467); where TOC content for clearcut A (Missouri's BMP) and clearcut B (removal of all biomass) were significantly greater than for clearcut C (alternative BMP). Changes in nutrient flux were monitored using Plant Root Simulator (PRS^{TM}) ion exchange membrane probes provided by Western Ag Innovations. Nutrient flux dynamics differed for the nutrients measured within harvest treatments and at two different depths. Results indicate greater nutrient flux in the clearcut treatments compared to the intermediate

thinning and control treatments for specific ionic species measured (NH_4^+, NO_3^-, P, K, S, Ca, Mg, Mn, Al, Fe, Cu, Zn, and B).

Litter decomposition plays a major role in the cycling of energy and nutrients in woodland ecosystems. The influence of woody biomass harvest scenarios were investigated during a one year litterbag experiment in an oak-hickory forest of the Missouri Ozarks. Total nitrogen (TN), total organic carbon (TOC), C:N ratio, and percent mass loss of leaf litter material were analyzed and compared amongst eight harvest treatments. Percent mass loss was positively correlated to total nitrogen. Treatment type and decomposition time had a significant effect on TN ($p = 0.0474$ and $p < 0.0001$ respectively). When comparing the effect of treatment on TN, clearcut B (removal of all biomass) was significantly lower than the control, intermediate A, clearcut A, (current 1/3 BMP) and clearcut C (alternative BMP). To semi-quantitatively assess how decomposition processes vary in leaf litter material across different harvesting treatments, solid-state ^{13}C nuclear magnetic resonance spectroscopy with cross-polarization and magic-angle spinning (CPMAS-NMR) technique was applied to analyze the organic C dynamics of mixed leaf litter. The type of harvest treatment had a significant effect on the alkyl-C concentration ($p = 0.0411$), and on the aromatic-C concentration ($p = 0.0071$). Significant decreases were seen in the total aliphatic C functional groups amongst clearcut treatments compared to intermediate and control treatments. A significant interactive effect of treatment type and decomposition time was found for the concentrations of the alkyl-C, O-alkyl-C, and aromatic-C functional groups, indicating that the change in concentration of these functional groups with decomposition time was significantly different among the different harvest treatments.

This research will enhance our understanding of nutrient cycling in a forested ecosystem following a woody biomass harvest, which will aid in maintaining sustainable nutrient concentrations and long-term site productivity. To ensure long-term sustainability and forest productivity, it is recommended to use the current Missouri BMPs or the alternative BMP (retain tops of all cut trees ≥ 20 cm dbh; remove boles, tops and limbs of all cut trees ≤ 20 cm dbh). Overall, the biomass guidelines supplement existing forestry rules and guidelines, encourage forest health and productivity, and enhance the full suite for ecological values. The current BMP and alternative BMP provide an opportunity to suggest alternative harvesting techniques, besides the traditional sawlog harvest, to high grading and damaging practices on the long-term health of the forest ecosystem.

Chapter 1: Introduction, Objectives and Literature Review

1.1 Introduction

While the need for wood products is perpetually at odds with environmental interests, including the conservation of soil health, there is a growing effort to reconcile the best interests of both, especially here in Missouri. As the demand for energy increases, renewable sources are being investigated as a viable alternative energy source. An example of this is woody biomass for bioenergy. The forest products industry is a significant contributor to Missouri's revenue, and bioenergy from woody biomass could expand this industry and generate additional revenue. There are, however, significant concerns that whole tree harvesting for woody biomass could adversely affect soil nutrient pools and overall soil quality. To address these concerns and enhance sustainability in forests harvested for woody biomass, the Missouri Department of Conservation (MDC) developed Best Management Practices (BMPs) for managers and landowners to follow; however, these BMPs remain untested. The objectives of this study are to: investigate changes in soil nutrient flux and soil nutrient concentrations under conditions representative of various types of woody biomass harvest and, subsequently, different residue retention levels, and evaluate the efficacy of current Best Management Practices (BMPs) for woody biomass harvest to determine if they adequately protect soil nutrients and the sustainability of forest growth in the Ozark Highlands.

The study site for this project is located within the Missouri Department of Conservation's Indian Trail Conservation Area in the Ozark Highlands region of Missouri. The study site consists of a randomized complete block design with three blocks. The three blocks (i.e. full replications) contain each of the eight treatments being

investigated. Subsequently, there are 24 total plots each approximately 4 acres in areal extent. The eight treatments being investigated include Missouri's 1/3 harvest residue retention BMP for thinning and commercial biomass harvests (Missouri Woody Biomass Harvesting BMP Manual, 2009) and other alternative harvest scenarios suggested by the Missouri Forest Products Association, practitioners, state and federal agency scientists, and university scientists. Harvest scenarios for the plots are **(a)** thinning with one of three residue retention scenarios **(i-iii)** and **(b)** clearcutting with one of four residue retention scenarios **(i-iv)**: **(i)** retain in place the tops of one in three harvested trees ≥ 25 cm diameter breast height (dbh) and one in three cut trees < 25 cm in their entirety (i.e., follow Missouri BMP guidelines); **(ii)** retain tops of all harvested trees ≥ 25cm dbh while removing all biomass for trees between 7.5 and 25 cm dbh; **(iii)** remove all woody biomass for trees > 7.5 cm dbh, including tops; and **(iv)** harvest of trees ≥ 25 cm dbh with only sawlogs removed from the forest (current harvesting practice for the region). The eighth treatment will be a no harvest (control) plot.

Changes in plant available nutrients were monitored in each plot at depth of 10cm and 30cm every other month for a one year duration using ion exchange membrane probes. Treatment effects on bulk soil chemical properties were assessed through measurement of cation exchange capacity, pH, exchangeable base cations, and total carbon and nitrogen content. Decomposition of mixed hardwood leaf litter under the imposed harvest and control sites was evaluated over a one year time period using a buried bag technique.

Overall this research will enhance our understanding of the efficacy of the established BMPs for woody biomass harvests to ensure the sustainability of such harvests.

1.2 Objectives and Hypotheses

Primary Research Objective

To evaluate the efficacy of the current Best Management Practices for woody biomass harvest to determine if they adequately protect soil nutrients and the sustainability of forest growth in the Ozark Highlands.

Specific Research Objectives

1. To monitor changes in soil nutrient flux and soil solid phase nutrient concentrations under conditions representative of various types of woody biomass harvest or traditional harvest and, subsequently, different residue retention levels.

2. To quantify the influence of woody biomass harvests on changes in carbon and nitrogen pools and fractions, exchangeable base cations, and pH.

3. To evaluate the rate of leaf-litter decomposition and nutrient release (nitrogen and carbon) on the forest floor following woody biomass harvesting practices.

Specific Research Hypotheses

1. The overall soil nutrient availability through the soil profile will increase at first due to a flush of nutrients from the harvesting of trees, but will eventually decrease over time due to leaching. As harvest intensity increases, we expect that overall nutrient flux through the soil profile will increase due to increased solute concentrations.

2. Total organic carbon and total nitrogen will decrease with time due to the labile pools of carbon and nitrogen being utilized; however, such changes will not be

observed in the timeframe of this study (1.5 years post-harvest). Exchangeable base cations and pH will decrease over time as harvest intensity increases.

3. As harvest intensity increases, leaf-litter decomposition and nutrient release will increase. As harvest intensity increases, soil moisture and soil temperature will increase due to less uptake of water by plants and more radiant energy associated with opening of the canopy, thus increasing microbial activity and leaf-litter decomposition.

1.3 Literature Review

The desire to decrease energy costs and greenhouse gas emissions has sparked interest for using woody biomass as an energy resource (Janowiak and Webster, 2010). The term biomass is generally defined as any organic material that can be converted into energy. Woody biomass refers to vegetation removed from the forest, usually logging slash, small-diameter trees, tops, limbs, or trees not considered merchantable in traditional markets (Evans, 2008). Biomass has long been used as an energy source but is undergoing widespread reevaluation as a viable resource for the large scale production of bioenergy. Even though the overall contribution of wood to the nation's energy portfolio is small, national efforts to increase alternative energy use, such as the Energy Policy Act of 2005 and the Energy Independence and Security Act of 2007, aim to increase woody biomass use for energy.

The United States is currently the largest producer of electricity from biomass. Biomass represents 1.5% of the total electricity supply compared to 0.1% for wind and solar combined (Alternative Energy, 2008). Woody biomass has long been a useful but underutilized byproduct of forest management activities (Evens, 2008). Biomass may be used for energy production at different scales, including large-scale power generation or small-scale thermal heating projects at governmental, educational, or other institutions. The biomass resource supply cycle includes important elements such as harvesting biomass crops, collecting biomass residues, and storing and transporting biomass resources. It is believed that U.S. forests currently yield 129 million dry tons of biomass per year, and could potentially increase yield to 226 million dry tons per year by 2030 (Downing et al., 2011). No woody biomass in Missouri is currently used to produce biofuels. Utilization of woody biomass for electricity generation is minuscule because it utilizes less than 1 percent of the annual woody biomass growth. However, woody biomass can feed a wide range of bioenergy production technologies in Missouri including liquid biofuels such as biobutanol, co-combustion with coal for electricity, and biomass fueled combined heat and power facilities.

Concerns about greenhouse gas emissions associated with fossil fuel combustion have resulted in legislation that requires Missouri to increase current renewable energy production to 15 percent by 2021 (Janowiak and Webster, 2009). Wood-based bioenergy often compares favorably with fossil fuels and several renewable energies because of a relatively low amount of fossil fuel inputs and a smaller “carbon footprint.” Therefore, woody biomass used for renewable energy production has the potential to reduce net greenhouse gas emissions, support renewable energy mandates, and increase energy

dependence while meeting other forest resource management goals. In order for that to occur, woody biomass energy must be produced in a way that is socially, economically, and ecologically sustainable.

The impact that these new initiatives will have on wood supply is unknown, but it is certainly possible that competition for raw material between wood-using facilities will increase. Increased competition may impact harvest levels through shorter rotations, intensification of harvesting through increased residue removal, or increased use of small diameter and poor quality stems. Regardless of the outcome, there is concern that forests harvested for woody biomass will put more pressure on our forests. Wood supply is a concern for traditional wood processing sectors and the emerging bioenergy industry, and the general public has raised concerns regarding long-term sustainability of biomass harvesting (Benjamin et al. 2009, Marciano et al. 2009). Because the forests from which biomass is harvested for energy are likely to represent a continuum of production systems, it is crucial to analyze the effects this will have on soil quality and forest productivity.

1.3.1 Potential Effects of Forest Biomass Harvests – Environmental Concerns

Forest management activities directly and indirectly remove nutrients from a site, and the resulting effect on site quality has been a concern for several decades (Leaf, 1979). The initial nutrient status of the site and the balance between natural inputs and losses within the forest ecosystem may have concerning effects on whether biomass removal is deleterious to sustain productivity (Grigal, 2000). Forest composition and structure at individual sites will change because of the woody biomass harvesting. Thus, any

disturbance occurring within the forest ecosystem will lead to changes in soil properties, including the disruption of nutrient cycling.

Forest biomass thinnings, to promote forest health or for energy production, can potentially impact the soil resource by altering soil physical, chemical, and biological properties. Although the impacts of stand removal on soil properties in the western U.S. have been documented, much less is known on periodic removals of biomass by thinnings or other partial cutting practices (Page-Dumroese et al., 2010). According to P.M. Hazlett et al. (2011), soil and other environmental data related to sawlog only harvest (SOH) and whole-tree harvest (WTH) are generally known. However, little information exists for woody biomass harvests that fall between SOH and WTH in terms of biomass removed from or retained within the forests. Harvesting techniques, like WTH, that remove logging slash from forest stands for biomass production, rather than leaving the harvest residues onsite, can have large impacts on nutrient availability (Sinclair, 1992).

Concerns have been raised about the intensive harvesting of woody biomass on forested sites for energy, including the increased removal of dead wood, threats to wildlife and biodiversity, and the loss of nutrients and soil productivity (Evans and Pershel, 2009). In response to these concerns, various US states have either adopted woody biomass harvesting guidelines or are in the process of developing them. States have amended their existing forestry best management practices (BMPs) or developed new biomass harvesting guidelines for reasons similar to why forestry has become regulated: public anxiety over environmental protection; correction of misapplied forestry practices; the need for greater accountability; the growth of local ordinances; landscape-

level concerns; and following the lead of others (Ellefson et al., 2004, Evans et al., 2010). Most forestry best management practices were not written at a time when energy from forests was being considered and, therefore, does not address how much woody biomass can be sustainably harvested from forests. More specifically, biomass harvesting guidelines are designed to fill the gaps where existing BMPs and forest practice regulations may not be sufficient to protect forest resources under new biomass harvesting regimes (Evans et al., 2010).

According to Angima and Terry (2011), BMPs are defined as "effective and practical site-specific methods or techniques generally recommended for maintaining soil productivity and achieving related forestland stewardship objectives." Biomass harvesting guidelines in general recognize the potential that woody biomass harvests have to meet a variety of silvicultural goals, including site preparation, salvage operations, fuel reduction, and the maintenance of forest health and aesthetics. Therefore, Missouri's coarse woody biomass guidelines for state that in thinning and commercial harvest, harvesters should retain at least one-third of the tops and small trees fallen during biomass harvesting operations (Missouri Woody Biomass Harvesting BMP Manual, 2009). The BMPs for woody biomass harvest often focus on practices that are intended to maintain or improve nutrient and carbon levels in harvested soils.

1.3.2 Soil Organic Carbon

Organic carbon is an important soil component that imparts benefits to soil biological, chemical and physical properties. Life in the soil is carried out largely using soil organic matter (SOM) as an energy source. Most soil organisms are heterotrophic

and gain their energy by decomposing SOM. The activities of these organisms drive the majority of the transformations that take place in the soil (Fisher and Binkley, 2000).

Soil organic matter is also an important contributor to the soil's chemical characteristics. The chemical reactivity of SOM is directly related to the quantities and types of organic functional groups and structural components that are present (Essington, 2004). For example, humic substances can have a net negative charge resulting from the dissociation of H^+ from hydroxyl (-OH), carboxylic (-COOH), or phenolic (C_6H_{12}-OH) groups (Fisher and Binkley, 2000). However, the extent of H^+ dissociation is pH dependent, resulting in variable cation exchange capacity.

Soil organic matter associated with the clay fraction is considered to be the most stable fraction, with physical constriction and the formation of complexes with mineral elements contributing to its stabilization (Eusterhues et al., 2003; Paul, 1984; Sollins et al., 1996). A useful indicator of soil organic carbon (SOC) cycling is bulk SOM composition. The most common indicator of SOM composition is the C/N ratio, which reflects differences in carbon and nitrogen net accumulation rates. The bulk of logging slash typically consists of coarse woody material that also has a low nitrogen content. During the initial decomposition stage, the C/N ratio of fresh organic inputs decreases as carbon is lost to the atmosphere (Baldock and Skjemstad, 2000; Johnson, 1995). Also, the reduction of C/N ratios can be thought of as an indicator of SOM humification (John et al., 2005).

In coarse-textured, acid soils, a large portion of the CEC is provided by organic functional groups (Federer and Hornbeck, 1985). The ratio between CEC and SOC

(CEC/C ratio) is an indicator of the large amounts of organic matter functional groups. A high CEC/C ratio represents the high sorptive capacity of SOM for cations (Miralles et al., 2009), which may help reduce nutrient loss after logging, minimize environmental impacts, and improve forest regeneration (Johnson et al., 1997).

Organic carbon storage in forest soils has attracted attention recently due to its potential as a substantial carbon sink (Brown, 2002). Soil organic carbon is an important indicator of soil quality due to its effects on many soil properties and plant growth factors. Soil organic carbon is composed of several fractions including labile or active carbon that is responsible for much of the biological activity in soil and has the greatest influence on soil quality (Lal, 2005). Water extractable carbon represents a potentially mobile and labile fraction of SOM that freely dissolves in water, thus it is the most easily utilized by soil organisms (Chantigny, 2003). Labile soil carbon pools are especially important because they are more vulnerable to disturbances and play vital roles in nutrient cycling (Hu et al., 1997). Labile pools could also be most affected by altered temperature and soil moisture regimes resulting from climate change (Zak et al., 1993) or shortly after forest harvest.

1.3.3 Forest Harvest Effects on Soil Organic Carbon

The most common forest management activities are harvesting and site preparation. Since soil is a major carbon pool in many forest ecosystems, SOM loss from stand disturbance can have a large impact on forest ecosystem function, and possibly affect long-term site productivity (Johnson et al., 1995; Grigal, 2000; Johnson and Curtis, 2001). After harvest, the forest floor is exposed to more light and heat, and deprived of plants which draw water from the soil, overall increasing soil temperature and moisture

(Vitousek et al., 1979). Harvesting operations often cause drastic soil disturbance due to mixing of the forest floor into mineral horizons (Nyland, 2001). A post-harvest decline in SOC is generally due to the mixing and movement of the organic material or litter layer into the mineral soil (Yanai et al., 2003), and due to the leaching of dissolved organic carbon (Kalbitz et al., 2000). According to Li et al. (2007) and Lal (2005), these changes to the soil environment can increase decomposition of the more labile carbon fractions. Understanding the actively cycling carbon fraction in a given forest is important in determining management regimes (Ellert and Gregorich, 1995). Any decline in biomass input may be compensated by the large amount of harvest residues left behind (Post, 2003; Yanai et al., 2003).

Forest harvesting is generally thought to lead to a reduction of soil carbon stocks for a few decades, followed by a partial or complete recovery period during which soil carbon stocks increase (Aber et al., 1979; Covington, 1981; Jiang et al., 2002). Extensive research of timber harvesting effects on soil properties has shown that traditional clear-cut harvesting can have a negative, short-term impact on SOM content, primarily through reduced litter inputs and increased decomposition of forest slash (Alban et al., 1994; Powers et al., 1998; Stone and Kanzems, 2002; Powers et al., 2005). However, long-term studies generally have shown that SOM eventually recovers to preharvest levels on most sites during the first rotation (Johnson and Curtis, 2001; Nave et al., 2010). Thus, it is clear that management can alter carbon storage in forests and their soils; however, it has yet to be determined how to best manage forests to optimize carbon storage.

1.3.4 Soil Nitrogen

Nitrogen is a vital nutrient to forest systems and is frequently a limiting factor in forest productivity (Miegroet et al., 2007). Disturbances, including forest harvesting, causes increased nitrogen mineralization in forest soils (Vitousek et al., 1985). Nitrogen is only available to plants in specific forms, inorganic ammonium (NH_4^+) and nitrate (NO_3^-) and changes in environmental conditions can influence microbial processes which in turn influences the form of soil nitrogen and soil productivity (Qualls et al., 2000). Nitrogen is often tightly cycled through a forest system, as seen in Figure 1.1. Biochemical transformations of N, such as nitrification, denitrification, mineralization, immobilization (assimilation), and N-fixation, are performed by a variety of soil-inhabiting organisms. Physical transformations of N include several forms that are gases, which move freely between soil and atmosphere (Kleinman, 2011). Nitrogen is cycled in forest systems, and once nitrogen is removed from the soil, by the removal of biomass during harvest, this vital nutrient may be rapidly depleted from the system.

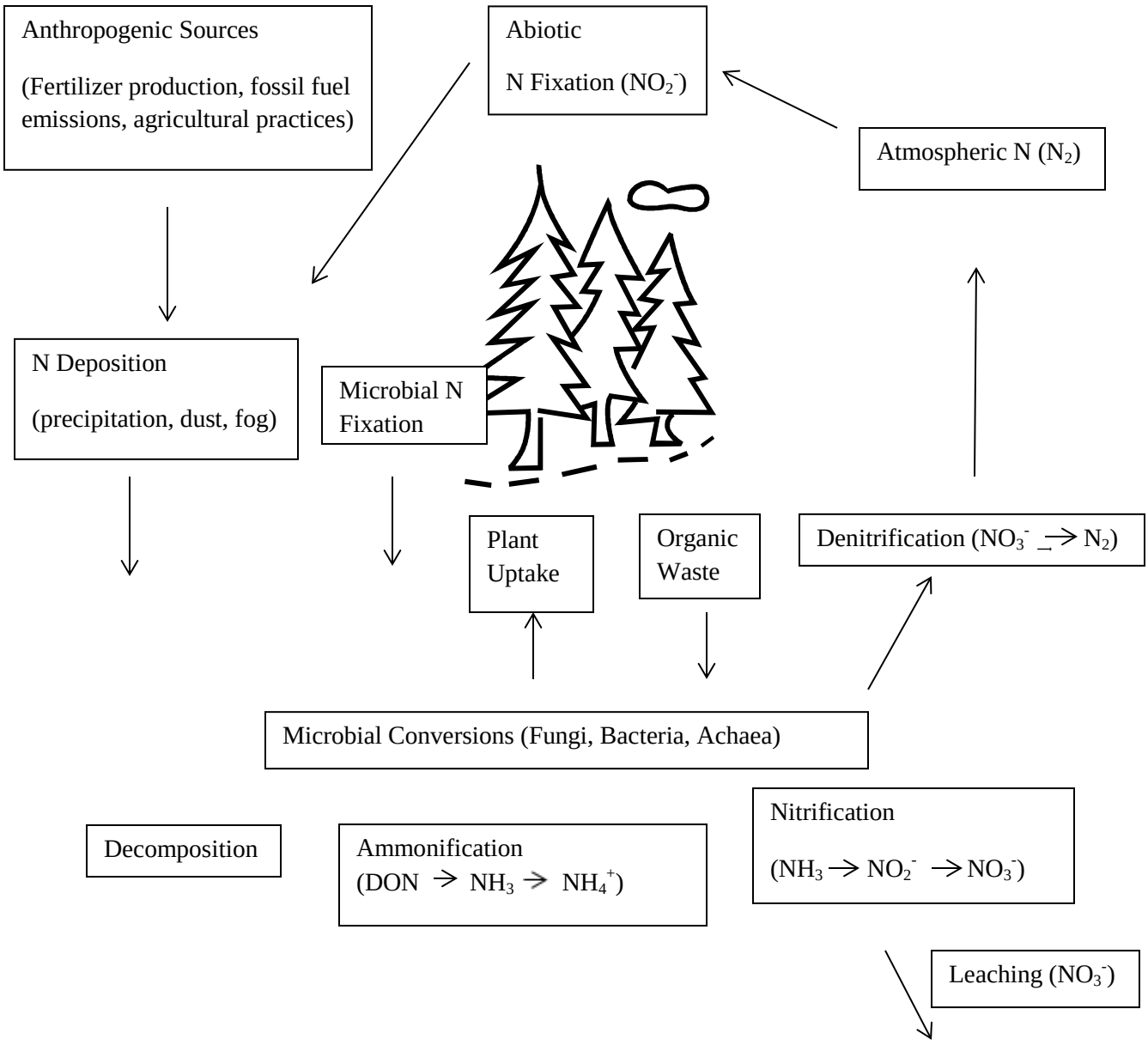

Figure 1.1. Nitrogen cycling in forest systems

1.3.5 Forest Harvest Effects on Soil Nitrogen

The fact that most nitrogen in soils associated with organic matter has led many forest soil scientists to assume that nitrogen retention in forest ecosystems is controlled almost exclusively by biological processes (Johnson et al., 2000). It is commonly assumed that competition among plant roots, heterotrophs, and nitrifiers for NH_4^+ dominates the fate of nitrogen in ecosystems (Vitousek et al., 1979; Johnson and Edwards, 1979; Johnson, 1992). Nitrogen depletion is a major concern, not only because timber harvest and leaching removes nitrogen availability from the soil, but also because nitrogen often limits forest growth (Federer et al., 1989). Changes in the soil environment and plant biochemistry influence nitrogen forms which make the prediction of soil nitrogen content and forest productivity difficult. While we expect active carbon to decrease in concentration it is also likely that nitrogen will diminish as well and be lost from the system. The organic residue produced in nitrogen-rich sites has a lower C:N ratio and microbial immobilization is less. Vitousek et al. (1982) observed that nitrate can accumulate rapidly following disturbances in nitrogen-rich sites. Wiklander (1982) observed large but brief nitrate losses in high quality sites that had been clearcut, and smaller, delayed losses following a clearcut in low quality sites. The processes that regulate nitrogen losses from disturbed forests are strongly affected by nitrogen availability prior to disturbance, but they can also be altered substantially by the type of disturbance or by forest management practices (Hart et al., 1981).

1.3.6 Importance of Soil Chemical Properties

Due to the inherently low nutrient availability at the study locations in the Missouri Ozarks, the soil will be a good indicator of any potential problems from nutrient

removals associated with biomass harvesting. Biomass removal associated with forest harvest can potentially alter the forest ecosystem through loss of nutrients via increased rates of nutrient leaching (Johnson and Todd, 1990; Belleau et at., 2006). Soil nutrients are essential for plant growth and development; thus, greater removals of wood biomass for bioenergy or other uses frequently raises concerns about whether adequate levels of nutrients can be maintained to protect site productivity (Janowiak and Webster, 2010). Soil organic matter is important in forest ecosystems because it influences many biogeochemical processes, and improves retention of soil nutrients so that they will eventually be available for plant growth (Grand and Lavkulich, 2012). For example, soils with higher organic matter levels may have better cation exchange capacity (CEC), which means that these soils can retain cation or positively charged nutrients such as ammonium so that the ammonium can be used for plant growth. SOM also serves as the food source for many soil organisms, and serves as a tremendous reservoir or pool of terrestrial carbon that would otherwise be released to the atmosphere.

Many chemical reactions that influence nutrient availability are influenced by the soil chemical environment and soil pH in particular (Schoenholtz et al., 2000). Some research has indicated the pH-soil quality relationship to be consistent with tree response under more acid forest soil conditions, which has included defining an ideal pH range and describing the relative decline in tree productivity below and above that specific range (e.g. Gale et al., 1991; Burger et al., 1994). However, it was concluded that in forest soils, higher pH values are not necessarily better and can negatively affect nutrient availability.

Although we mechanistically understand many relationships that bring about the soil chemical-nutrient supplying aspect of soil quality, we are still faced with a number of

challenges, including the identification of critical relationships that affect forest productivity at any given site and reference conditions against which to judge the relative level at which a given soil is functioning.

1.3.7 Forest Harvest Effects on Soil Chemical Properties

Since the soil is the major source of exchangeable nutrient cations (e.g., Ca, Mg, and K), it is important to examine the effects of clear-cut logging on these nutrients. Most of the research on the effect of nutrient removal from increased woody biomass harvesting comes from studies comparing whole-tree harvesting to stem-only harvesting (Saarsalmi et al., 2010). In stem-only harvesting, significant woody material is left on-site and only the tree bole is removed. Studies show that stem-only harvests have minimal impact on soil nutrient loss, as material left on-site allows for soils to replenish nutrient supplies (Clinton et al., 1996; Kimmins, 1996; Belleau et al., 2006; Thiffault et al., 2006). Whole-tree harvesting removes more nutrients, but this depends on the nutrient content and type of material removed, as well as the tree species and the season in which the harvest occurs. Foliage has the greatest above-ground nutrient content, followed by small twigs, branches, and stems (Kimmins, 1977). The removal of even a large amount of nutrients from a site, however, may also only be a fraction of the total amount of nutrients on a site (Van hook et al., 1982). Depending on the type of material and decomposition rates, woody biomass nutrients may either be taken up by trees or leach from the site.

Logging disrupts nutrient availability and productivity due to nutrient leaching. Short-term effects would be caused by the removal of trees due to the fact that mineral nutrients are held within tree biomass. Regrowth of vegetation at the site could be influenced in the long -term due to the downward movement of nutrients in the soil

(Johnson et al. 1997). However, residues left on site after timber harvesting may cause a long-term increase of exchangeable nutrient cations. For example, Johnson and Todd (1998) observed this result in soil exchangeable Ca^{2+} after 15 years post-harvest due to decomposing residues. However, Olsson (1999) found that pools of exchangeable K, Mg, and Ca were reduced after whole tree harvest (WTH). It was concluded that the effect of WTH on soil pools would be more noticeable for Ca^{2+} in the long run, but soil pools of K and Mg would experience short-term effects. According to Thiffault et al. (2006), harvest intensity influenced soil CEC, which was most likely due to effects on pH and organic matter. Staaf and Olsson (1991) observed a significant reduction in soil pH after WTH compared to SOH. Therefore, studies investigating harvest effects on soil nutrients are often conflicting and difficult to compare due to differences in soils, topography, climate, tree species, etc. Furthermore, Ozark Highland soils may be susceptible to nutrient depletion following a woody biomass harvest due to the soil's strongly acidic pH, small CEC, and minimal exchangeable base cation content.

1.3.8 Soil Solution Sampling

Ion exchange resin-based techniques are becoming popular in many types of research studies. They have a wide potential for applications in agriculture, forestry, and soil science. The majority of ion exchange resin studies have been used as a sink for nutrient ions due to the fact that they are used to exchange counter ions for nutrient ions in the soil (Cortini and Comeau, 2008; Meason and Idol, 2008; Qian and Schoenau, 2001; Drohan et al., 2005; Hangs et al., 2003). A common, commercially available ion exchange resin (IER) device known as Plant Root Stimulator^{TM} (PRS^{TM}) probe (Western Ag Innovations, Saskatoon, Saskatchewan, Canada) is used for measuring soil nutrient available ions.

There are several advantages to using IER devices in membrane form for soil testing. Not only are they cost effective and cause minimal disturbance, but they also can allow re-measurement of certain points in the soil over time and the majority of elements can be extracted from the membrane simultaneously with one extraction (Drohan et al., 2005). Western Ag Innovations claims that the use of resin extraction in soil testing reduces laboratory cost by 50-70% and improves testing accuracy.

The PRS^{TM} probes consist of a cation or anion ion exchange membrane imbedded into plastic probe (Fig. 1.2; Western Ag Innovations Inc. 2010) and inserted into the soil. The dimensions of the probe are 15cm in length and 3cm wide, with both sides of the membrane being 17.5cm^2. The membrane is chemically pre-treated so that it exhibits surface characteristics and nutrient sorption phenomena that resemble a plant root surface. When buried in the soil, the probe can assess nutrient supply rates by continuously adsorbing charged ionic species over the burial period. In order to allow nutrient ions in the soil solution to be readily available to adsorb onto the probe, it is important to use counter-ions with the lowest affinity. Thus, the cation and anion exchange probes use Na^+ and HCO_3^- as the counter-ion, respectively (Western Ag Innovations Inc., 2010).

Figure 1.2. PRS Probe (Western Ag Innovations Inc., 2010)

There have been many studies conducted to investigate factors affecting the absorption of soil nutrients onto PRS^{TM} probes. The time period in which the probes are buried in the soil has been an issue and has been addressed by many studies. The burial period recommendation given in several studies varies greatly, but also depends on the type of research (agricultural vs. forest soil research). In a study by Johnson et al. (2007), nutrient availability was measured in a greenhouse study where the PRS^{TM} probes were buried in pots filled with soil. The probes were inserted at two different depths. The probes at the shallowest depth were removed after 30 days and replaced with new ones. The second sets of top probes, along with the probes at the other two depths, were removed after 57 days. In a study conducted by Drohan et al. (2005), nutrient sorption was monitored at two different depths and was collected at the end of one month and three months. Results showed that there were significant differences between one and three month burial periods regardless of the depth or season. Some ions absorbed onto the membrane continuously over the three months, however, other ions seemed to fluctuate

and decrease. The conclusion that the burial time should be one month or less due to acquiring relative differences in ion absorption was supported by their results.

When the probes are left in the soil for an extended duration (multiple weeks), nutrient ions adjacent to the probe that are already in the available form, along with nutrients that are converted to the available form, will be adsorbed onto the membrane surface. The amount of nutrient ions adsorbed onto the probe at the end of the burial period represents the potential nutrient supply rate to a plant for the duration of the burial. This is expressed in units of micrograms of nutrient adsorbed per 10 cm^2 of membrane surface over the burial time (Western Ag Innovations Inc., 2010).

1.3.9 Leaf-litter Decomposition

Decomposition of leaf litter is vital to nutrient cycling and the productivity of forests (Vitousek, 1982; Didham, 1998). Leaf tissue can account for 70% or more of aboveground litterfall in forests, with the remainder composed of stems and small twigs (Robertson and Paul, 1999). As leaves are broken down by insect and microbial decomposers, organically-bound nutrients are released as free ions to the soil solution which are then available for uptake by plants. In most forest systems, litter decomposition is the major source of nutrients for trees. Decomposition refers to the processes that convert dead organic matter into smaller and simpler compounds. Decomposition is mainly a biological process carried out by insects, worms, bacteria, and fungi both on the soil surface and in the soil (Fisher and Binkley, 2000).

The rate of decomposition is influenced by three main factors: temperature, soil moisture, and litter quality. Generally decomposition increases exponentially with

temperature; that is, for every 10 degree rise in temperature, decomposition increases by a factor of 2 (Kirschbaum, 1995). Nevertheless, leaf decomposition does occur at a low rate during the winter months even under deep snow (Taylor and Jones, 1990). As temperatures increase, soil moisture assumes an increasingly important role in litter decomposition. Although, decomposition can be slow in very wet soils because anaerobic conditions develop in saturated soils. However, in general, rates of fresh litter decomposition increase with increasing temperature and precipitation (Karberg et al., 2008). This general pattern of decomposition can also be influenced by the quality of the litter. Substrate quality has been defined in many different ways, – such as nitrogen content, lignin content, and the C:N ratio of the litter (Moorhead et al., 1999). Researchers have found that decomposition of leaf litter can be predicted by the C:N ratio (Taylor et al., 1989), by the lignin content (Meentemeyer, 1978), or by the lignin:nitrogen ratio (Melillo et al., 1982). Basically, high quality leaves (e.g., nutrient-rich alder leaves) will decompose faster than low quality leaves (e.g., nutrient-poor conifer needles). Many studies have shown striking differences in decomposition rates among species (Adams and Angradi, 1996; Cornelissen, 1996). Substrate quality can even vary within a leaf. Berg and co-workers (Berg and Staaf, 1980; McClaugherty and Berg, 1987) have shown that in the initial stages (0 to 3 months) of leaf breakdown small soluble carbon molecules, such as starches and amino acids, are lost first, leaving behind the more recalcitrant molecules like lignin. Decomposition during this first phase is rapid because these molecules are easy to break down and energy rich. The second stage of decomposition - the breakdown of lignin - is much slower because lignin consists of very large and complex molecules.

1.3.10 Summary

The diversity of results from previous studies, considering these studies were related to sawlog only harvest and whole-tree harvest, along with the diversity of forests and soils makes it difficult to evaluate how study results may or may not apply to nutrient cycling observed for woody biomass harvests in the Missouri Ozarks. Considering the fact that woody biomass guidelines were developed bases upon the best available information, and the current BMPs for Missouri remain untested, the results of this study will help us evaluate the effect of woody biomass harvesting on the sustainability of forest production and the development of advanced biofuel and bioenergy production facilities. Although silvicultural practices vary from state to state depending upon species distribution, harvesting practice and site characteristics, similarities lie between harvesting recommendations regardless of geographic region. The recommendations presented from other states should serves as a background for Missouri's BMP technical committee in developing and evaluating the current guidelines that are being tested in this study.

Soil weathering rates are not easily determined, and the variability in nutrient supplying capacity of soils by region may account for differences when comparing study results from different forested ecosystems. In addition, the highly weathered soils of the Ozarks are not likely to supply a sustained source of base cations with removal of woody biomass from a site. Thus, this study is important to help us understand nutrient flux in Missouri Ozark forest soils. Western Ag Innovation's PRS^{TM} probes were chosen as the primary sampler to monitor nutrient flux in this study. The PRS^{TM} probes are an example of the commercial application of the resin membrane technology that allows for

reinsertion in the same location after a set burial period, something that is not generally feasible with resin bags. The PRS^{TM} probes have been used in multiple studies to assess labile nutrients in agricultural soils, but have not been used in many forest soils due to the relatively low labile nutrient concentrations.

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Chapter 2: Soil Solution Chemistry and Nutrient Flux in Forests Harvested for Woody Biomass

2.1 Abstract

Altered soil solution chemistry and nutrient flux within forests harvested for woody biomass may result from disturbance, slash removals, slash decomposition, and mineralization processes. Because of the potential adverse effects of woody biomass harvest to soil nutrient pools and overall soil quality, the Missouri Department of Conservation (MDC) has developed Best Management Practices (BMPs) to retain coarse woody residues associated with biomass harvesting to retain nutrient capital and sustain forest productivity. However, these BMPs remain untested. To investigate the potential impacts of woody biomass harvest and use of BMPs to mitigate deleterious effects, this study examined soil nutrient concentrations and nutrient flux in Missouri Ozark forest soils immediately following harvest to 1.5 years post-harvest. The eight treatments investigated were Missouri's 1/3 harvest residue retention BMP for thinning and commercial biomass harvests and other alternative harvest scenarios. Chemical properties of soils within the harvest treatments were quantified immediately after harvest and one year post-harvest, and analysis of variance results are presented. Total organic carbon (TOC) was the only dependent variable that was affected by harvest treatment (p-value = 0.0467); where TOC content for clearcut A (Missouri's BMP) and clearcut B (removal of all biomass) were significantly greater than for clearcut C (alternative BMP). Changes in nutrient flux were monitored using Plant Root Simulator (PRS^{TM}) ion exchange membrane probes provided by Western Ag Innovations. Nutrient flux dynamics differed for the nutrients measured within harvest treatments and at two different depths. Results

indicate greater nutrient flux in the clearcut treatments compared to the intermediate thinning and control treatments for specific ionic species measured (NH_4^+, NO_3^-, P, K, S, Ca, Mg, Mn, Al, Fe, Cu, Zn, and B). This research will enhance our understanding of nutrient cycling in a forested ecosystem following a woody biomass harvest, which will aid in maintaining sustainable nutrient concentrations and long-term site productivity.

2.2 Introduction

Increasing demands for cleaner, renewable energy sources has expanded interest in utilizing woody biomass as bioenergy or advanced liquid biofuels. In some regions of the U.S., large quantities of woody biomass are potentially available from existing forests. However, soils underlying many forest ecosystems are generally of lower quality (e.g. low nutrient availability, acidic, and stony). Adverse effects of woody biomass harvesting to soil nutrient pools and overall soil quality may, subsequently, diminish forest productivity, particularly over multiple harvest rotations (Mann et al., 1988; Belleau et al., 2006; Eriksson et al., 2007). As a consequence, several states have developed formal biomass harvesting guidelines. Best Management Practices (BMPs) for sustaining forest productivity associated with biomass harvesting have been developed based on upon the best available information. Little is known, however, about the effectiveness of these management actions on the ecological impacts of biomass harvesting. Therefore, it is necessary to develop and evaluate the sustainability of such harvests.

It is important to understand the cumulative effects of biomass harvesting alternatives. Woody debris or residue management is crucial for sustaining woody

biomass harvest operations since residue retention onsite returns essential nutrients and organic matter to the soil. Most nutrients in trees are more concentrated in logging slash (i.e. branches and foliage) than other aboveground tree components (i.e. stemwood) (Wang et al., 1995; Klockow, 2012). Logging slash is typically unmerchantable in conventional harvest (stem-only harvest, SOH) systems. Tree tops are retained on site following harvest to provide inputs of nutrients and organic matter into the soil (Johnson and Todd, 1998; Belleau et al., 2006). Whole-tree harvesting (WTH) is a common practice in which the entire tree is harvested with no intentional woody retention onsite. This practice generally has the largest impact on the net nutrient removal (Kimmins, 1996; Belleau et al., 2006; Thiffault et al., 2006). The effects of SOH and WTH onsite nutrients and organic matter have been widely studied (Hendrickson et al., 1987; Mann et al., 1988; Thiffault et al., 2011). In contrast, little information exists for woody biomass harvests that fall between SOH and WTH in terms of biomass removed from or retained within the forest. This study fills this void in the literature by studying eight treatments including Missouri's 1/3 harvest residue retention BMP for thinning and commercial biomass harvests, SOH, WTH, other alternative harvest scenarios, and non-harvested sites.

While conventional timber harvesting generally removes only merchantable sawlogs, woody biomass harvesting can remove all forms (i.e. live and dead standing woody vegetation, downed woody debris, and stumps) resulting in a greater loss of nutrients. To investigate the potential impacts of biomass removal, several studies have evaluated how this practice affects nutrient stocks in forest ecosystems. In a study conducted by Klockow et al., (2013) they found that despite the common

recommendation of 20% slash retention for mitigating the impacts of WTH, there was no difference in biomass, C, N, Ca, and P stocks between the 20% slash retention treatment and the WTH treatment. However, there were significant differences in biomass, C, Ca, K, and P between WTH and SOH treatments, which were consistent with trends observed elsewhere (Mann et al., 1988; Rittenhouse et al., 2012). Potassium was the only element that differed significantly between all three slash retention levels and the only element to have significantly greater stocks in the 20% slash retention treatment than in WTH. Therefore, they concluded that their results suggested that biomass and nutrients within the 20% slash retention treatment are variable and that this level does not necessarily represent a distinct threshold of slash retention greater than WTH. Moreover, longer-term monitoring would be helpful in determining if the levels of woody debris in treatments represent a large enough pool of nutrients to maintain site quality following biomass harvesting, which has been suggested by other work for WTH (Alban and Perala, 1992; Johnson and Todd, 1988; Tamminen et al., 2012). In a study conducted by Olsson (1999) on the effects of biomass removal in thinnings on exchangeable base cation pools in forest soils in Sweden, it was concluded that there were no general treatment effects in the soil profile five years after harvesting across all sites. However, effects of harvesting intensity were detected on two sites, indicating reduced pools of exchangeable K, Mg, and Ca after WTH.

Since the soils found at the study site in the Missouri Ozarks are widespread, and inherently have low nutrient availability [i.e. low cation exchange capacity (CEC), low base saturation, and relatively low concentrations of exchangeable Ca^{2+} and Mg^{2+}], they are good indicators of any potential problems from nutrient removals associated with

biomass harvesting (Kabrick et al., 2011). Changes in soil solution chemistry and nutrient flux following forest harvesting may adversely affect nutrient-deficient soils more than nutrient-rich soils. Highly weathered soils with inherently low nutrient supply capacity may be more vulnerable to decreased soil fertility due to forest harvest than soils with greater nutrient supply capacity.

The use of ion-exchange resins has been used to determine plant-available nutrients since approximately 1951 (Pratt, 1951). The majority of ion exchange resin studies have focused on their use in exchanging initial counterions for other ions (i.e. nutrient ions) in the soil, thereby acting as a nutrient sink during the burial period in soil (Qian and Schoenau, 2001). Western Ag Innovation's (Saskatoon, Saskatchewan, Canada) Plant Root Simulator (PRS^{TM}) probes are an example of the commercial application of resin membrane technology. The membrane is encased in a plastic probe to ease insertion into the soil and minimize disturbance (Western Ag Innovations, 2001). It also allows the probes to be replaced in the same location after a set burial period.

This study tracked changes in plant available nutrients associated with different woody biomass harvest treatments through time and as a function of soil depth. The objectives were to: (1) investigate changes in soil nutrient flux and soil nutrient concentrations under conditions representative of various types of woody biomass harvest and, subsequently, different residue retention levels; and (2) evaluate the efficacy of current BMPs for woody biomass harvest to determine if they adequately protect soil nutrients and the sustainability of forest growth in the Ozark Highlands.

2.3 Materials and Methods

2.3.1 Site Selection and Description

The study site was located at the Missouri Department of Conservation's Indian Trail Conservation Area in the Ozark Highlands of Dent County, Missouri near Salem, MO ($37^{o}41'38N$; $91^{o}22'11W$; Fig. 2.1). The study site consists of a randomized complete block design with three blocks. The three blocks (i.e. full replications) contain each of the eight treatments being investigated. Subsequently, there are 24 total plots covering 36 ha with each treatment plot ~1.5 ha in size. Plots (*ca*. 60 m width x 245 m length) within each block are oriented parallel with the slope, resulting in nearly all plots extending from shoulder slope to footslope landscape positions. Slopes of the study site ranged from 7 to 32 percent with north- and northeast-facing aspects. Within each plot, 4 soil pits (located approximately in the middle of each plot on the backslope landscape position) were dug to a depth of 40 cm.

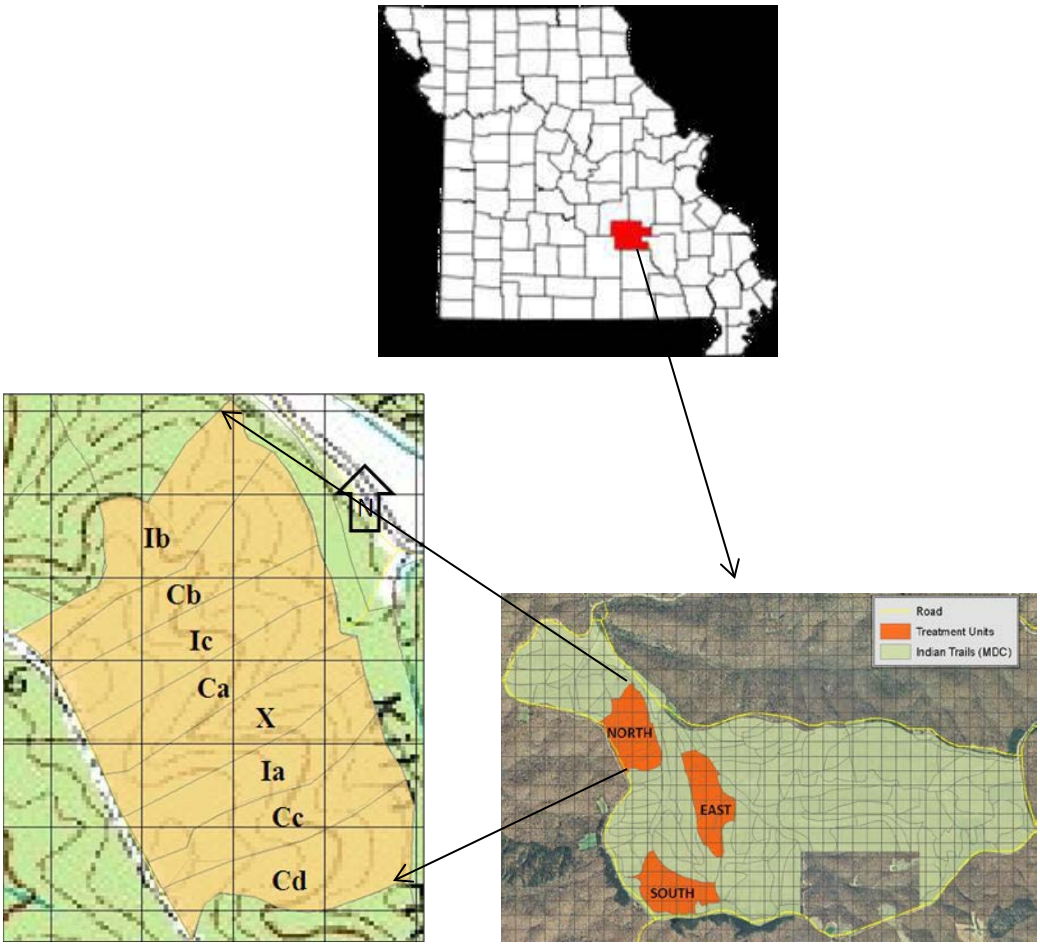


Figure 2.1. Map of Missouri showing location of Dent County where Indian Trail Conservation Area is located, and schematic of site layout in the North Block.

The species most commonly found on site were white oak (*Quercus alba*), black oak (*Quercus velutina*), post oak (*Quercus stellate*), northern red oak (*Quercus rubra*), and hickory (*Carya spp.*). Hickories occur in the mid and understory and include in order of abundance pignut hickory (*Carya glabra*), black hickory (*Carya texana*), and mockernut hickory (*Carya tomentosa*). Also present are shortleaf pines (*Pinus echinata*), blackgum (*Nyssa sylvatica*), and red maple (*Acer rubrum*).

The soil map unit identified within the boundaries of the timber harvest at Indian Trail Conservation Area is a Clarksville very gravelly silt loam, 15-35% slope, formed in gravelly hillslope sediments over clayey residuum weathered from dolomite (Gilbert, 1971). The Clarksville soil is classified as loamy-skeletal, siliceous, semi-active, mesic Typic Paleudults, and this soil is commonly mapped in the Ozark Highlands and very representative of the soils found in this region (hillslope sediments over residuum). These soils are considered to be extensions of Red-Yellow Podzolic soils into a region of Gray-Brown Podzolic soils (Kabrick et al., 2008). The Clarksville soil is an Ultisol, based upon the less than 35% base saturation in the profile and continued decrease in base saturation with increase in depth. In general, the Clarksville soil is a well-drained very cherty soil that often has a pale brown silt loam A horizon, the B horizon is typically thicker and has textures ranging from silt loam in the upper Bt to clay in the lower Bt (Miller, 1965). In the soils studied, at the depth 0-30cm, the soil textural class was identified as a silt loam, while at the depth 30-40cm, the soil textural class was identified as a silty clay loam. Soil particle size became increasingly finer with depth (i.e. clay content increased). In the control treatment sites, the percentage of clay content increased from 14% in the 0-10cm depth to 34% in the 30-40cm depth.

Two different silvicultural treatments were imposed on forest stands at Indian Trail Conservation Area: intermediate thinning and clearcut. For the purpose of this study, intermediate thinnings are defined as the selection of crop trees during mid-rotation by harvesting all undesirable trees and processing large tops and small tress into woody biomass after extracting other commercial products. The clearcut treatments were applied to remove the entire overstory and begin a new cohort or trees. This study incorporates a variety of eight scenarios that include intermediate thinning, clearcutting, and a control (no harvest). Harvest scenarios for the plots are **(a)** thinning with one of three residue retention scenarios **(i-iii)** or **(b)** clearcutting with one of four residue retention scenarios **(i-iv)**: **(i)** retain in place the tops of one in three harvested trees ≥ 25 cm diameter breast height (dbh) and one in three cut trees < 25 cm in their entirety (i.e., follow Missouri BMP guidelines); **(ii)** retain tops of all harvested trees ≥ 20 cm dbh while removing all biomass for trees between 7.5 and 20 cm dbh; **(iii)** remove all woody biomass for trees > 7.5 cm dbh, including tops; and **(iv)** harvest of trees ≥ 25 cm dbh with only sawlogs removed from the forest (current harvested practice for the region). The eighth treatment was no harvest (control). Each treatment was designed to address different BMPs and the impacts of biomass harvesting on soil nutrients. The intent of these different scenarios is to compare the current harvest practice (clearcutting with removal of sawlogs only) to Missouri's BMPs for residue management in forests harvested for woody biomass. Missouri currently recommends that in thinning and commercial harvest using a feller buncher, 1/3 of treetops from sawtimber harvest and 1/3 of the typical size small trees cut on site be left and evenly distributed throughout the harvest area (Missouri Woody Biomass Harvesting: Best Management Practices Manual,

2010). However, limited knowledge is available about nutrient recycling as it is related to woody biomass harvesting on Ultisol soils in Missouri.

Table 2.1. Harvest treatments investigated. Missouri's woody biomass BMP guidelines state that harvesters should retain at least 1/3 of the tops and small tress felled during operations. All merchantable sawlogs were removed for all treatments.

Treatment	Associated BMP
Clearcut A (CA)	1/3 of tops of sawlog-size trees and 1/3 of small diameter trees left on ground to provide wildlife habitat and nutrients for future cycling
Clearcut B (CB)	Remove all biomass from harvested trees
Clearcut C (CC)	Retain tops of all cut trees ≥ 20 cm dbh; remove boles, tops and limbs of all cut trees ≤ 20 cm dbh
Clearcut D (CD)	Traditional harvest of only sawtimber ≥ 25 cm dbh
Intermediate A (IA) †	1/3 of tops of sawlog-size trees and 1/3 of small diameter trees left on ground to provide wildlife habitat and nutrients for future cycling
Intermediate B (IB)	Remove all biomass from harvested trees
Intermediate C (IC)	Retain tops of all cut trees ≥ 20 cm dbh; remove boles, tops and limbs of all cut trees ≤ 20 cm dbh
Control (X)	No harvest or removal of woody residues

† Intermediate thinnings are defined as the selection of crop trees during mid-rotation by harvesting all undesirable trees and processing large tops and small trees into woody biomass after extracting other commercial products.

According to the timeline presented by the Missouri Forest Foundation, harvesting was to begin in September 2011 but it did not begin until January 2012. This process was further delayed due to equipment breakdown, weather, and other complications; thus, harvesting was not complete until June 2012.

2.3.2 Soil Sampling and Processing

In July 2012, immediately after harvest (July 2012) and one-year post-harvest (July 2013) soil samples were collected within each plot. Soil samples were collected in 10 cm increments from a 0 – 40 cm depth from each of the four soil pits hand-dug within each plot. A quart sized zip-lock bag was filled with soil from each depth, labeled, and stored in a cooler until the end of the sampling trip. Samples were then air-dried for 48 hours, and then kept in storage. Sub-samples (100 g) from each depth and soil pit within a plot were combined to create a composite soil sample for each plot, thus giving 96 total soil samples (4 depths x 24 sites). Soil samples were ground, passed through a 2mm sieve, and sent to the Missouri Soil Characterization Laboratory (Columbia, MO) and analyzed using methods detailed in the UDSA-NRCS *Soil Survey Laboratory Methods Manual* (Burt, 2004). Standard pipette analysis was used to determine particle size. Soil CEC and exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) were determined using 1 M ammonium acetate (CH_3COONH_4) extraction, ammonium chloride (NH_4Cl) extraction technique, steam distillation, HCl titration and atomic absorption spectrophotometry (CEC-7, method 4B1a1a1a1a1). These effective CEC values were used for statistical analysis and to calculate percent base saturation (BS). Cation exchange capacity was determined by the summation of extractable bases plus the $BaCl_2$-triethanolamine released extractable acidity (EA). Extractable Al was determined using 1 M KCl extraction and inductively coupled plasma – atomic emission spectrophotometry (ICP-AES). Soil pH was measured in 1:1 soil-to-water ratio and 1:2 soil-to-0.01 M $CaCl_2$ salt solution. Total organic carbon (TOC) and total nitrogen (TN) were determined using dry

combustion methods. These data were used to quantify changes in the soil solid phase that may not have been captured by the nutrient flux measurements.

2.3.3 PRS Probe Sampling and Processing

In this experiment PRS^{TM} cation and anion exchange probes were used to monitor nutrient flux in the soil at depths of 10 and 30 cm for 1.5 years. Each of the 24 sites contains 4 soil pits that were dug to a depth of 40 cm. At each depth, (10 and 30 cm) one cation and one anion probe were installed by creating a slot in the soil profile using a chisel and hammer. Before installation, the probe membrane was coated with a soil paste to maximize soil contact. The soil paste was made in the field at each pit by using a zip lock bag to mix soil from each depth with ultrapure, 18 megohm, water. To achieve good soil to probe contact, a chisel was used to create a back-cut and gently push the soil against the probe after installation (Figure 2.2; Western Ag Innovations Inc. 2010). PRS^{TM} probes were placed in the ground for 30 days, and nutrient flux was monitored on an every other month basis (six sampling periods per year). During the months the probes were not in the ground, a plastic ruler was placed in each slot as a place holder. Western Ag allows up to 4 pairs of probes per analysis, thus for each plot, the 4 pairs of probes at 10 cm were combined and the 4 pairs at 30 cm were combined prior analysis. Thus, giving 48 total samples to be analyzed (24 samples at the 10 cm depth and 24 samples at the 30 cm depth). At the end of each sampling period, probes were removed, washed with deionized water, and grouped into a sealable plastic bag.

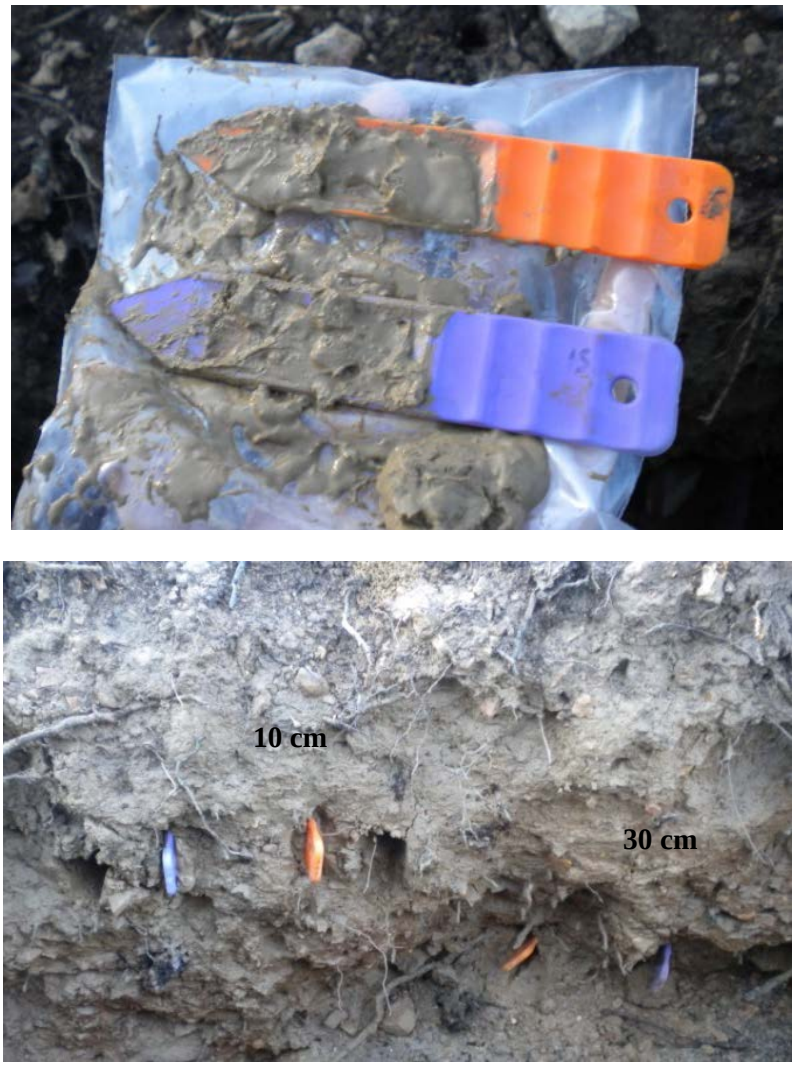


Figure 2.2. PRS^{TM} probes covered in soil paste before insertion and probes inserted at 10 cm and 30 cm in the soil profile.

The probes were stored at 4°C and sent to Western Ag Innovations (Mandan, North Dakota) for extraction and analysis. The analytes monitored were NH_4^+, NO_3^-, P, K, S, Ca, Mg, Mn, Al, Fe, Cu, Zn, and B. Ions were eluted from the probe membranes with 0.5 M HCl. NH_4^+, NO_3^-, and P analyzed colorimetrically using an automated flow injection analysis system. The remaining ions were analyzed using inductively coupled plasma – optical emission spectrometry (ICP-OES). Nutrient flux is reported as micrograms of nutrient per 10 cm^2 per length of burial. The ion exchange membrane is meant to act as an infinite sink for readily labile soil nutrients until membrane saturation for a particular nutrient or the soil buffer capacity is reached (Table 2.2) (Western Ag Innovations, 2001). The manufacturer claims that the probes mimic plant root nutrient sorption dynamics based on Donnan exchange principles. Thus, the amount of nutrients absorbed by the probe in a period of time could be interpreted as total potential nutrient availability for plant uptake for that time period or nutrient flux through the location of installation.

Table 2.2. Maximum sorption capacity of Plant Root Simulator (PRS^{TM}) probes for individual ions as determined by the manufacturer (Western Ag Innovations, 2001).

Ion Capacity									
Cl^-	Na^+	SO_4^--S	NO_3^--N	NH_4^+-N	PO_4^{3-}-P	K^+	Ca^+	Mg^{2+}	Al^{3+}
µg 10 cm^{-2}									
5288	5455	4782	2088	3320	4620	9273	4753	2883	4131

2.3.4 Statistical Analysis

Microsoft Excel 2010 was used to calculate sample mean values along with standard deviations, and 95% confidence intervals for soil characterization and nutrient flux data for each burial period. Differences in the average soil chemical properties at four different sampling depths immediately post-harvest and one year post-harvest across all treatment types were analyzed. Difference values for soil solid phase characteristics were then calculated by subtracting the immediate post-harvest analyte concentrations from the one year post-harvest analyte concentrations for each harvest treatment at each depth of study. The resulting value was negative if the soil at a particular depth demonstrated a loss in analyte concentration and positive if the soil demonstrated a gain in analyte concentration. All data analysis was carried out in SAS^{TM} Statistical Software Version 9.4 (SAS Institute Inc., 2008, Cary, NC, USA). Soil solid phase data and PRS probe data was analyzed with SAS using the PROC GLIMMIX procedure. Prior to analysis, the PROC UNIVARIATE program in SAS was used to test for *normal*, *lognormal*, *gamma*, and *exponential* sample distributions for all dependent variables. The Shapiro-Wilk test for normality determined whether there was sufficient evidence to reject the null hypothesis that the residuals were normally distributed for all response variables. The Tukey-Kramer least squared differences LSMEANS test was used for determining significant differences (α=0.05). The soil solid phase data used a *normal* distribution with the *identity* link, while the PRS probe data used a *lognormal* distribution with the *identity* link. A repeated measures randomized complete block generalized linear model was developed to compare harvest treatment and soil depth through time (Appendix B.1). For significant interactions (α=0.05), differences between individual

(least squares) means were determined using fisher's least significant differences (LSD). Pearson correlation coefficients (Appendix C and D) were evaluated in order to determine relationships among soil solid phase analytes and PRS^{TM} probe analytes.

2.4 Results

2.4.1 Soil Characteristics and Chemical Properties

In this study, soil samples were collected for each harvest treatment immediately following harvest and one year post-harvest. A comparison of the average soil chemical properties for each harvest treatment between these two time periods and all four depths studied is displayed in Table 2.3. It is important to note that forest soils have been shown to have little nutrient storage in the mineral horizons, as the quick decomposition of soil organic matter leads to the greater overall percentage of nutrient retention occurring within biomass (Fisher et al., 2000; Fölster and Khanna, 1997). The low values presented in Table 2.3 indicate potential susceptibility of such soils to nutrient depletion if insufficient residues are left on site following woody biomass harvest. Throughout the soil profile, and throughout time, the clearcut treatments revealed nominally greater concentration values for exchangeable Ca^{2+} and Mg^{2+}, sum of exchangeable base cations, ECEC, BS, TOC, and TN. More specifically, on average, the greatest concentration values for these soil properties occurred within the clearcut B treatment (removal of all biomass). Across all harvest treatments and all four depths, the pH ranged from 4.0 – 4.5 (Table 2.3).

Table 2.3. Average soil chemical properties for field sampling locations at (a) 0-10 cm depth, (b) 10-20 cm depth, (c) 20-30 cm depth, and (d) 30-40 cm depth for samples collected immediately post-harvest and one year post-harvest by harvest treatment. Refer back to Table 1 for treatment descriptions.

Soil properties include exchangeable concentrations of Ca^{2+}, Mg^{2+}, K^{+}, sum of exchangeable base cations, effective cation exchange capacity (ECEC), total percentage of base saturation by weight, extractable acidity (EA), total percentage aluminum saturation (Al sat), soil pH measured in 0.01 M $CaCl_2$ soil slurry (pH salt), total organic carbon (TOC), and total nitrogen (TN). Standard error is stated in parentheses.

(a)

		Soil Property										
Time	**Treatment**	**Ca^{2+}**	**Mg^{2+}**	**K^{+}**	**Sum of Cations**	**ECEC**	**Base sat**	**EA**	**Al sat**	**pH_{salt}**	**TOC**	**TN**
		$cmol_c\ kg^{-1}$				$cmol_c\ kg^{-1}$	%	$cmol_c\ kg^{-1}$	%		$g\ kg^{-1}$	$g\ kg^{-1}$
Immediately	Control	0.83 (0.59)	0.50 (0.17)	0.17 (0.03)	1.47 (0.75)	3.20 (0.06)	16.00 (7.37)	7.43 (0.29)	54.67 (22.66)	4.20 (0.15)	14.67 (0.88)	0.90 (0.08)
Post-Harvest	Intermediate A	0.47 (0.20)	0.33 (0.12)	0.13 (0.03)	0.93 (0.32)	2.27 (0.19)	11.00 (3.51)	7.30 (0.17)	60.67 (11.20)	4.20 (0.00)	15.00 (2.08)	0.95 (0.09)
	Intermediate B	0.80 (0.27)	0.43 (0.15)	0.13 (0.03)	1.37 (0.44)	2.70 (0.32)	15.00 (3.22)	7.30 (0.49)	52.00 (9.64)	4.13 (0.07)	16.33 (3.18)	1.04 (0.18)
	Intermediate C	0.37 (0.03)	0.33 (0.03)	0.20 (0.00)	0.87 (0.07)	2.53 (0.26)	13.00 (3.22)	8.17 (0.38)	64.67 (4.67)	4.13 (0.07)	16.67 (0.67)	0.98 (0.05)
	Clearcut A	1.27 (0.32)	0.47 (0.03)	0.23 (0.03)	2.00 (0.30)	3.20 (0.40)	19.67 (2.19)	7.90 (0.27)	36.00 (9.54)	4.30 (0.12)	18.00 (2.31)	1.05 (0.12)
	Clearcut B	1.77 (0.97)	0.73 (0.34)	0.23 (0.03)	2.80 (1.36)	3.60 (1.02)	23.67 (8.41)	7.90 (0.46)	31.00 (14.64)	4.33 (0.19)	21.33 (1.86)	1.29 (0.21)
	Clearcut C	0.73 (0.29)	0.63 (0.29)	0.17 (0.03)	1.50 (0.60)	2.77 (0.61)	17.33 (4.84)	6.73 (0.43)	47.67 (10.41)	4.20 (0.10)	13.33 (1.86)	0.89 (0.08)
	Clearcut D	0.77 (0.32)	0.40 (0.15)	0.13 (0.03)	1.30 (0.50)	2.33 (0.19)	16.67 (6.17)	6.43 (0.46)	45.67 (16.15)	4.30 (0.15)	14.33 (1.76)	0.92 (0.08)
One Year	Control	1.47 (0.71)	0.47 (0.18)	0.17 (0.03)	2.10 (0.91)	3.60 (0.30)	22.33 (9.60)	7.23 (0.87)	44.67 (19.92)	4.33 (0.24)	16.33 (1.20)	0.95 (0.01)
Post-Harvest	Intermediate A	0.93 (0.41)	0.47 (0.15)	0.20 (0.00)	1.60 (0.55)	3.30 (0.17)	16.33 (4.63)	7.87 (0.26)	52.33 (14.77)	4.17 (0.12)	16.33 (4.63)	1.13 (0.18)
	Intermediate B	1.03 (0.240)	0.47 (0.07)	0.20 (0.00)	1.70 (0.31)	3.40 (0.50)	18.33 (1.33)	7.53 (0.71)	50.33 (2.33)	4.17 (0.03)	16.00 (2.65)	1.04 (0.12)
	Intermediate C	0.63 (0.26)	0.33 (0.07)	0.20 (0.00)	1.17 (0.32)	3.17 (0.30)	13.33 (2.60)	7.50 (0.55)	64.67 (6.94)	4.13 (0.03)	13.67 (2.03)	0.91 (0.19)
	Clearcut A	1.93 (0.66)	0.43 (0.03)	0.17 (0.03)	2.53 (0.67)	4.10 (0.53)	30.00 (5.69)	8.43 (0.73)	40.33 (9.29)	4.47 (0.19)	18.00 (1.00)	1.28 (0.07)
	Clearcut B	2.37 (0.72)	0.67 (0.37)	0.13 (0.03)	3.17 (1.07)	4.30 (0.85)	26.33 (6.01)	8.43 (0.63)	30.00 (9.17)	4.40 (0.15)	19.33 (3.76)	1.21 (0.14)
	Clearcut C	0.97 (0.17)	0.53 (0.29)	0.17 (0.03)	1.67 (0.42)	3.37 (0.29)	19.00 (4.04)	7.17 (0.57)	52.00 (8.02)	4.30 (0.15)	12.00 (1.00)	0.80 (0.08)
	Clearcut D	1.60 (0.85)	0.43 (0.23)	0.13 (0.03)	2.17 (1.12)	3.50 (0.70)	21.67 (8.69)	6.90 (0.23)	45.00 (17.90)	4.27 (0.12)	14.00 (1.73)	0.98 (0.16)

(b)

		Soil Property										
Time	**Treatment**	**Ca^{2+}**	**Mg^{2+}**	**K^{+}**	**Sum of Cations**	**ECEC**	**Base sat**	**EA**	**Al sat**	**pH_{salt}**	**TOC**	**TN**
		$cmol_c\ kg^{-1}$				$cmol_c\ kg^{-1}$	%	$cmol_c\ kg^{-1}$	%		$g\ kg^{-1}$	$g\ kg^{-1}$
Immediately	Control	0.43 (0.20)	0.63 (0.30)	0.10 (0.00)	1.20 (0.53)	3.20 (0.60)	19.33 (9.21)	6.43 (0.50)	64.67 (10.91)	4.13 (0.07)	7.00 (0.58)	0.51 (0.03)
Post-Harvest	Intermediate A	0.17 (0.07)	0.30 (0.06)	0.13 (0.03)	0.60 (0.12)	1.97 (0.19)	9.00 (2.31)	6.27 (0.78)	69.33 (6.98)	4.13 (0.07)	8.33 (0.88)	0.57 (0.03)
	Intermediate B	0.33 (0.09)	0.40 (0.06)	0.10 (0.00)	0.83 (0.13)	2.50 (0.55)	11.67 (0.67)	6.37 (0.52)	65.67 (1.67)	4.13 (0.07)	8.00 (0.58)	0.57 (0.03)
	Intermediate C	0.13 (0.13)	0.30 (0.10)	0.13 (0.03)	0.57 (0.27)	2.10 (0.06)	9.33 (3.33)	5.90 (0.35)	71.00 (10.60)	4.17 (0.07)	7.67 (0.88)	0.60 (0.09)
	Clearcut A	0.73 (0.15)	0.43 (0.07)	0.23 (0.03)	1.40 (0.10)	2.77 (0.47)	17.33 (2.60)	6.67 (0.60)	46.33 (11.39)	4.27 (0.13)	11.00 (1.53)	0.70 (0.10)
	Clearcut B	1.13 (0.84)	0.73 (0.44)	0.17 (0.03)	2.03 (1.30)	2.93 (0.98)	21.33 (10.33)	6.00 (0.40)	44.67 (19.75)	4.30 (0.15)	10.33 (0.33)	0.64 (0.03)
	Clearcut C	0.43 (0.23)	0.67 (0.32)	0.10 (0.00)	1.20 (0.55)	2.60 (0.67)	15.67 (5.18)	5.90 (0.32)	57.00 (8.33)	4.17 (0.03)	8.67 (0.88)	0.58 (0.09)
	Clearcut D	0.37 (0.22)	0.33 (0.09)	0.10 (0.00)	0.80 (0.30)	2.03 (0.24)	12.67 (4.18)	5.43 (0.38)	58.00 (17.56)	4.20 (0.16)	7.67 (0.88)	0.56 (0.11)
One Year	Control	0.70 (0.47)	0.67 (0.47)	0.13 (0.03)	1.50 (0.97)	3.83 (1.24)	17.00 (9.07)	6.13 (0.32)	67.67 (13.69)	4.23 (0.07)	7.00 (1.00)	0.57 (0.04)
Post-Harvest	Intermediate A	0.30 (0.12)	0.27 (0.09)	0.17 (0.03)	0.73 (0.20)	2.70 (0.27)	11.33 (3.18)	5.73 (0.20)	72.00 (8.72)	4.23 (0.03)	7.33 (0.33)	0.63 (0.04)
	Intermediate B	0.50 (0.06)	0.40 (0.00)	0.17 (0.03)	1.07 (0.03)	3.20 (0.46)	14.33 (0.33)	6.37 (0.34)	65.67 (3.67)	4.13 (0.03)	8.00 (0.58)	0.59 (0.02)
	Intermediate C	0.23 (0.03)	0.23 (0.07)	0.13 (0.03)	0.60 (0.12)	2.70 (0.10)	8.67 (1.20)	6.17 (0.43)	77.67 (4.67)	4.23 (0.07)	9.00 (0.58)	0.57 (0.02)
	Clearcut A	0.53 (0.09)	0.30 (0.06)	0.17 (0.03)	1.00 (0.06)	2.93 (0.24)	14.00 (2.08)	6.23 (0.74)	65.67 (4.18)	4.23 (0.07)	8.33 (0.33)	0.56 (0.05)
	Clearcut B	1.50 (0.85)	0.60 (0.40)	0.13 (0.03)	2.23 (1.24)	3.57 (0.87)	23.67 (8.97)	6.23 (0.52)	49.00 (19.01)	4.33 (0.15)	11.33 (1.45)	0.67 (0.10)
	Clearcut C	0.67 (0.37)	0.60 (0.35)	0.13 (0.03)	1.40 (0.71)	5.93 (0.61)	17.00 (6.11)	5.93 (0.61)	61.67 (13.37)	4.27 (0.09)	6.67 (1.20)	0.57 (0.09)
	Clearcut D	0.73 (0.38)	0.40 (0.17)	0.13 (0.03)	1.27 (0.67)	3.03 (0.67)	17.67 (7.22)	5.67 (0.57)	58.33 (16.76)	4.17 (0.09)	7.67 (0.88)	0.47 (0.02)

(c)

		Soil Property										
Time	**Treatment**	**Ca^{2+}**	**Mg^{2+}**	**K^{+}**	**Sum of Cations**	**ECEC**	**Base sat**	**EA**	**Al sat**	**pH_{salt}**	**TOC**	**TN**
				$cmol_c\ kg^{-1}$		$cmol_c\ kg^{-1}$	%	$cmol_c\ kg^{-1}$	%		$g\ kg^{-1}$	$g\ kg^{-1}$
Immediately	Control	0.57 (0.37)	0.97 (0.52)	0.13 (0.03)	1.67 (0.92)	4.93 (1.36)	15.67 (6.49)	7.83 (0.97)	67.67 (10.65)	4.07 (0.09)	5.67 (0.33)	0.40 (0.04)
Post-Harvest	Intermediate A	0.40 (0.15)	0.40 (0.17)	0.10 (0.00)	0.90 (0.32)	2.57 (0.20)	13.67 (4.37)	5.97 (0.43)	65.33 (9.77)	4.17 (0.03)	6.67 (0.88)	0.47 (0.05)
	Intermediate B	0.27 (0.03)	0.40 (0.12)	0.10 (0.00)	0.77 (0.12)	2.63 (0.78)	11.33 (0.88)	6.10 (1.07)	68.33 (4.33)	4.13 (0.07)	6.00 (0.58)	0.46 (0.05)
	Intermediate C	0.23 (0.19)	0.50 (0.06)	0.13 (0.03)	0.87 (0.27)	3.37 (0.43)	11.33 (3.84)	6.90 (0.62)	71.67 (12.35)	4.10 (0.10)	6.33 (0.88)	0.49 (0.10)
	Clearcut A	0.40 (0.06)	0.60 (0.25)	0.20 (0.00)	1.20 (0.30)	3.20 (1.25)	15.67 (1.33)	6.67 (1.31)	58.33 (4.84)	4.17 (0.09)	7.00 (1.53)	0.53 (0.05)
	Clearcut B	1.20 (0.83)	1.07 (0.62)	0.13 (0.03)	2.43 (1.46)	4.37 (1.23)	24.33 (9.96)	6.43 (0.37)	51.33 (16.22)	4.17 (0.12)	5.67 (0.33)	0.43 (0.06)
	Clearcut C	0.63 (0.48)	1.17 (0.62)	0.10 (0.00)	1.90 (1.100	4.00 (1.36)	20.33 (7.88)	6.40 (0.95)	56.00 (11.55)	4.13 (0.12)	6.33 (0.33)	0.42 (0.05)
	Clearcut D	0.53 (0.29)	0.93 (0.37)	0.10 (0.00)	1.23 (0.64)	4.33 (1.45)	17.67 (6.77)	7.20 (2.11)	62.33 (14.67)	4.13 (0.09)	5.00 (0.58)	0.37 (0.05)
One Year	Control	0.77 (0.62)	0.97 (0.77)	0.17 (0.07)	1.90 (1.45)	4.93 (2.04)	16.33 (9.06)	7.07 (1.27)	69.67 (13.30)	4.20 (0.10)	6.33 (0.88)	0.43 (0.03)
Post-Harvest	Intermediate A	0.33 (0.12)	0.33 (0.12)	0.10 (0.00)	0.77 (0.23)	2.90 (0.21)	13.00 (4.04)	5.17 (0.41)	72.33 (9.35)	4.20 (0.06)	5.00 (0.00)	0.46 (0.03)
	Intermediate B	0.57 (0.09)	0.63 (0.13)	0.17 (0.03)	1.37 (0.22)	4.03 (1.18)	18.00 (1.16)	6.57 (1.57)	64.00 (4.04)	4.13 (0.07)	5.33 (0.33)	0.43 (0.05)
	Intermediate C	0.30 (0.06)	0.47 (0.15)	0.17 (0.03)	0.93 (0.22)	3.50 (0.51)	13.33 (3.18)	6.37 (1.08)	72.67 (6.64)	4.23 (0.13)	5.33 (0.88)	0.45 (0.03)
	Clearcut A	0.57 (0.03)	0.43 (0.15)	0.17 (0.03)	1.17 (0.17)	3.47 (0.79)	15.67 (0.33)	6.20 (0.91)	65.00 (3.61)	4.23 (0.12)	6.00 (0.00)	0.42 (0.04)
	Clearcut B	1.87 (1.19)	1.20 (0.77)	0.17 (0.03)	3.23 (1.99)	5.33 (1.77)	27.67 (12.73)	6.40 (0.59)	51.00 (18.25)	4.30 (0.15)	5.67 (0.33)	0.47 (0.03)
	Clearcut C	0.77 (0.37)	1.03 (0.48)	0.17 (0.03)	1.97 (0.82)	4.57 (0.98)	21.33 (6.57)	6.73 (0.76)	59.33 (9.53)	4.20 (0.10)	5.00 (0.58)	0.50 (0.03)
	Clearcut D	1.13 (0.64)	1.07 (0.49)	0.17 (0.03)	2.37 (1.14)	5.27 (1.73)	23.33 (10.87)	7.50 (2.26)	56.33 (16.23)	4.20 (0.15)	6.33 (0.88)	0.47 (0.04)

(d)

		Soil Property										
Time	**Treatment**	**Ca^{2+}**	**Mg^{2+}**	**K^{+}**	**Sum of Cations**	**ECEC**	**Base sat**	**EA**	**Al sat**	**pH_{salt}**	**TOC**	**TN**
				$cmol_c\ kg^{-1}$		$cmol_c\ kg^{-1}$	%	$cmol_c\ kg^{-1}$	%		$g\ kg^{-1}$	$g\ kg^{-1}$
Immediately	Control	1.03 (0.60)	1.93 (0.74)	0.17 (0.03)	3.17 (1.37)	8.17 (2.23)	24.00 (6.93)	9.80 (1.93)	60.00 (11.53)	4.03 (0.07)	5.67 (0.33)	0.43 (0.06)
Post-Harvest	Intermediate A	0.70 (0.31)	0.77 (0.30)	0.10 (0.00)	1.57 (0.60)	3.50 (0.42)	19.67 (6.89)	6.40 (0.30)	56.33 (13.54)	4.17 (0.03)	5.67 (0.67)	0.46 (0.06)
	Intermediate B	0.43 (0.09)	0.70 (0.06)	0.10 (0.00)	1.27 (0.13)	4.17 (0.86)	14.67 (1.76)	7.47 (1.27)	67.33 (7.69)	4.00 (0.06)	5.33 (0.88)	0.39 (0.07)
	Intermediate C	0.33 (0.15)	0.93 (0.15)	0.20 (0.06)	1.47 (0.29)	5.13 (1.11)	11.33 (3.84)	6.90 (0.62)	71.67 (12.35)	4.10 (0.10)	6.33 (0.88)	0.49 (0.10)
	Clearcut A	0.47 (0.15)	0.73 (0.33)	0.20 (0.00)	1.40 (0.46)	3.80 (1.65)	15.00 (2.52)	7.70 (1.69)	60.00 (7.00)	4.07 (0.09)	7.33 (0.88)	0.57 (0.15)
	Clearcut B	2.13 (1.44)	1.90 (0.90)	0.20 (0.06)	4.27 (2.38)	7.07 (1.79)	28.33 (12.60)	8.30 (0.58)	51.33 (18.42)	4.17 (0.17)	6.33 (0.33)	0.52 (0.14)
	Clearcut C	1.07 (0.57)	1.53 (0.74)	0.13 (0.03)	2.73 (1.33)	5.13 (1.39)	26.00 (7.77)	7.13 (1.01)	48.00 (12.29)	4.17 (0.13)	6.67 (0.88)	0.44 (0.07)
	Clearcut D	1.43 (0.84)	1.93 (0.67)	0.13 (0.03)	3.50 (1.46)	6.87 (1.350	26.67 (9.28)	8.80 (1.89)	52.00 (16.17)	4.13 (0.13)	6.00 (1.16)	0.41 (0.06)
One Year	Control	1.07 (0.82)	1.77 (1.09)	0.20 (0.06)	3.03 (1.95)	8.07 (3.22)	19.67 (7.69)	9.77 (2.59)	66.33 (10.14)	4.17 (0.09)	6.00 (0.58)	0.41 (0.04)
Post-Harvest	Intermediate A	0.63 (0.19)	0.60 (0.20)	0.17 (0.03)	1.40 (0.35)	3.80 (0.25)	20.33 (6.06)	5.83 (0.81)	61.67 (10.98)	4.27 (0.12)	4.67 (0.33)	0.48 (0.06)
	Intermediate B	0.73 (0.18)	1.00 (0.15)	0.20 (0.06)	1.93 (0.26)	5.80 (1.71)	21.67 (2.91)	7.63 (2.24)	64.00 (5.13)	4.10 (0.06)	5.00 (0.58)	0.44 (0.05)
	Intermediate C	0.50 (0.06)	0.83 (0.30)	0.20 (0.00)	1.53 (0.35)	5.17 (1.39)	17.00 (3.06)	8.17 (2.35)	69.00 (5.13)	4.10 (0.10)	5.33 (1.33)	0.45 (0.08)
	Clearcut A	0.63 (0.07)	0.60 (0.31)	0.17 (0.03)	1.40 (0.36)	3.93 (1.64)	18.67 (2.73)	6.63 (2.44)	59.33 (8.41)	4.30 (0.15)	5.00 (0.00)	0.38 (0.05)
	Clearcut B	2.17 (1.20)	1.53 (0.81)	0.20 (0.00)	3.90 (2.01)	6.33 (1.57)	31.33 (12.25)	7.10 (0.60)	46.33 (16.51)	4.30 (0.21)	5.67 (0.33)	0.44 (0.06)
	Clearcut C	1.47 (0.67)	1.60 (0.67)	0.20 (0.00)	3.27 (1.27)	6.27 (1.20)	30.00 (9.24)	7.63 (1.71)	48.33 (14.31)	4.27 (0.15)	5.33 (0.88)	0.55 (0.04)
	Clearcut D	2.27 (1.45)	2.43 (1.18)	0.20 (0.06)	4.90 (2.63)	9.13 (2.83)	29.00 (13.20)	10.13 (3.34)	53.00 (19.22)	4.20 (0.20)	6.67 (1.33)	0.48 (0.08)

Total organic carbon (TOC) was the only dependent variable that was affected by harvest treatment (p-value = 0.0467) (Table 2.4). The Tukey-Kramer analysis indicated that TOC content for clearcut A (Missouri BMP) and clearcut B (complete biomass removal) were significantly greater than clearcut C (alternative BMP) (Figure 2.3). Depth had a significant effect on TOC ($p < 0.0001$), where TOC at a depths of 20-30 and 30-40cm (the bottom two depths) were significantly different from the 0-10cm and 10-20cm depths. The interaction between treatment type and depth also had a significant effect on TOC ($p = 0.0222$) and can be seen in Figure 2.4. Mean concentration of TOC was significantly greater for all treatments in the 0-10cm depth compared to that at 20-30cm and 30-40cm depths, with the greatest TOC concentration in clearcut B (40.7 g kg^{-1} TOC). More specifically, TOC content in clearcut A and B were significantly greater than clearcut C and D at the 0-10cm depth. For clearcut B, TOC concentrations at 0-10 cm, 10-20 cm, and 20-30 cm depths are significantly different from each other. Furthermore, TOC concentration decreased in all treatment types as sample depth increased (Figure 2.4).

Mean TN content was only significantly affected by depth ($p < 0.0001$) (Table 2.4). The Tukey-Kramer analysis indicated that TN content at the 20-30 cm and 30-40 cm depths was significantly different from that at 0-10 cm depth and at 10-20 cm depth. Total N content was highly and positively correlated ($r = 0.93$, $p < 0.0001$) with TOC (Appendix C). The p-value for the interaction between treatment type and depth did not show a significant effect on TN, but the Tukey-Kramer analysis indicated that at the 0-10 cm depth, all of the treatments are significantly greater than that at the other three depths

(Figure 2.5). Furthermore, at the 0-10 cm depth, clearcut B contains the highest TN concentration (2.5 g kg^{-1}) and is significantly greater than that for clearcut C.

Table 2.4. Type 3 Tests of Fixed Effects, evaluating effects of harvest treatment (Trt), sample depth, time, and their interaction effects on soil chemical properties. Tukey-Kramer adjusted p-values of soil properties and nutrient concentrations from split-plot generalized linear mixed model.

Dependent variables include exchangeable concentrations of Ca^{2+}, Mg^{2+}, and K^{+}, sum of exchangeable base cations, effective cation exchange capacity (ECEC), base saturation (BS), extractable acidity (EA), aluminum saturation (Al), soil pH measured in 0.01 M CaCl2 soil slurry (pH salt), total organic carbon (TOC), and total nitrogen (TN).

	Analyte										
	Ca^{2+}	Mg^{2+}	K^{+}	Sum of Cations	ECEC	BS	EA	Al	pH	TOC	TN
Source	**p-values**										
Trt	0.5383	0.7226	0.1589	0.6666	0.7140	0.8043	0.9729	0.8067	0.9321	**0.0457**	0.1699
Time	**0.0007**	0.8376	0.1228	**0.0090**	**0.0010**	**0.0005**	0.8546	0.2255	**0.0008**	0.0941	0.8045
Depth	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**0.0007**	**< 0.0001**	**< 0.0001**
Trt*Time	0.6022	0.7315	0.2739	0.4398	0.6152	0.4163	0.9072	0.4162	0.7763	0.5005	0.8857
Trt*Depth	**0.0122**	**0.0009**	0.3437	**0.0028**	**0.0044**	**0.0040**	0.3174	0.0960	0.1705	**0.0222**	0.3048
Time*Depth	0.2461	0.9844	**0.0322**	0.6930	0.9703	0.1983	0.8941	0.1456	0.1638	0.9906	0.812
Trt*Time*Depth	0.9951	0.9994	0.8288	0.9978	0.9977	0.6976	1.0000	0.8708	0.9015	0.9589	0.8307

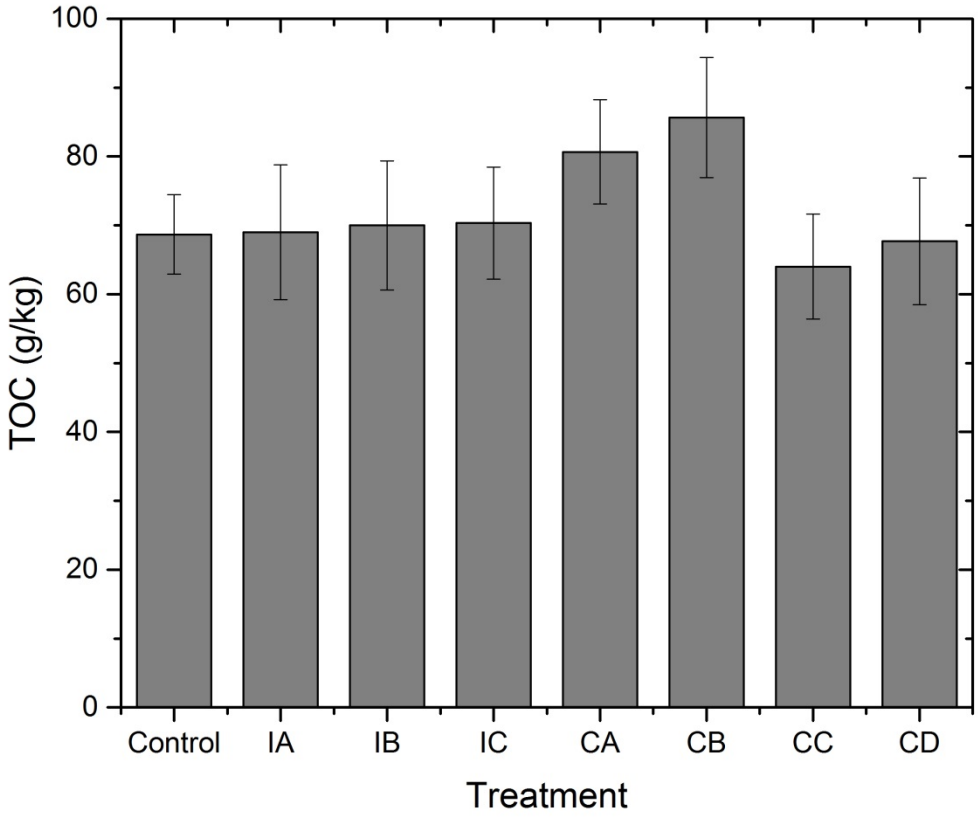


Figure 2.3. Mean total organic carbon (TOC) of whole soil for all harvest treatments. Error bars represent standard error. See Table 2.1 for description of treatment acronyms.

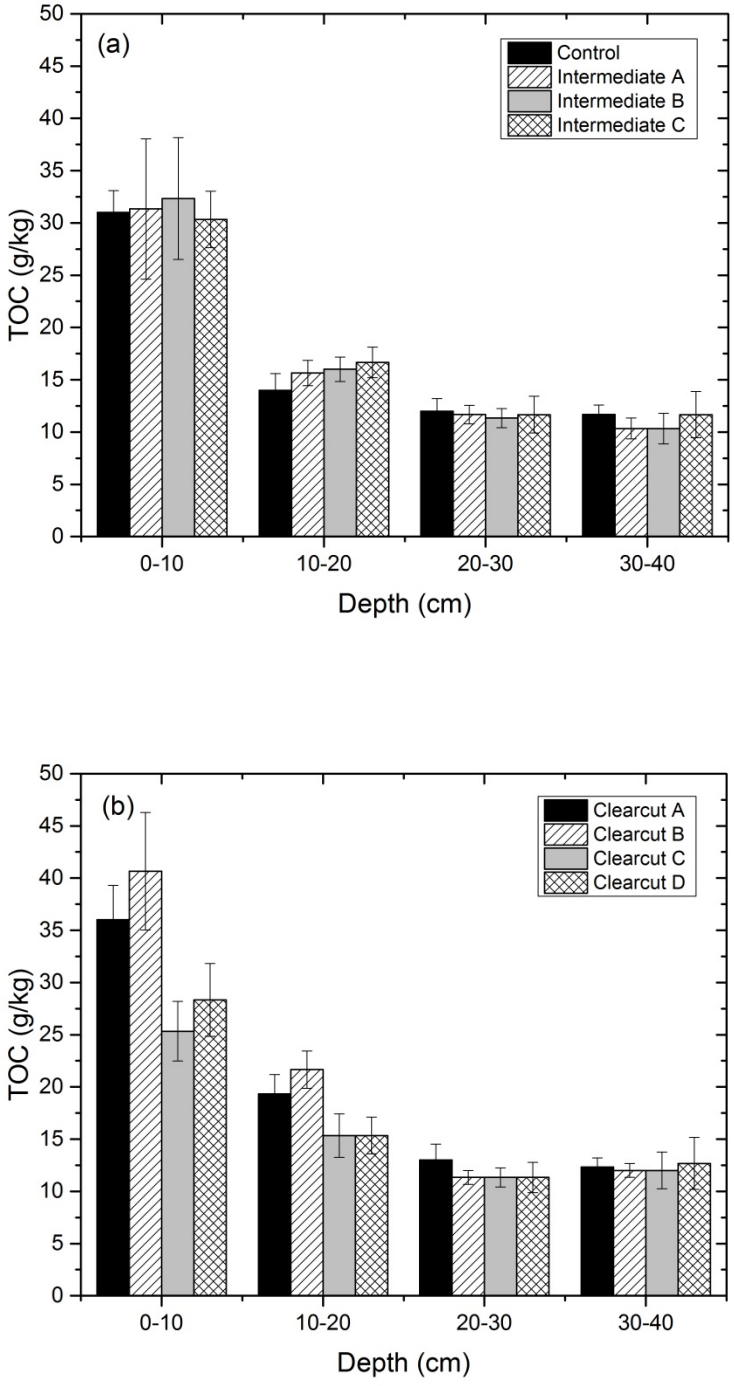
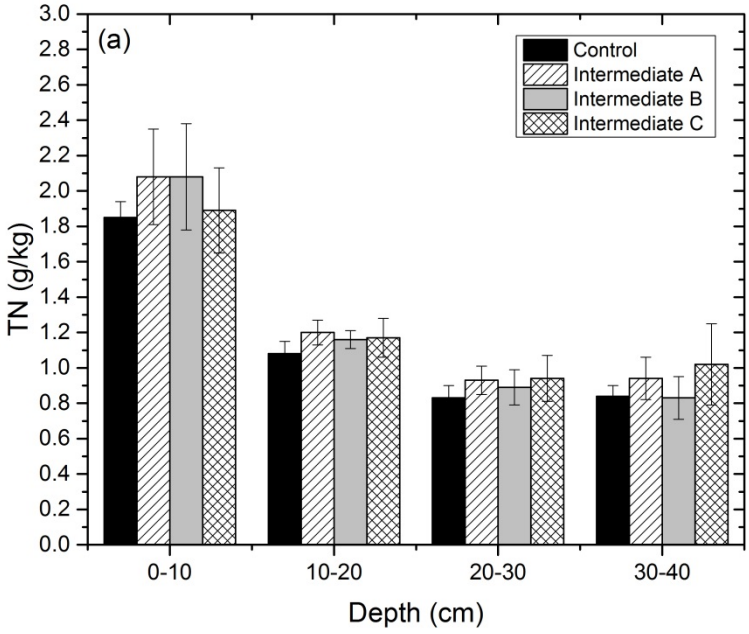


Figure 2.4. Comparison of mean total organic carbon (TOC) by depth and harvest treatments: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Error bars represent standard error.



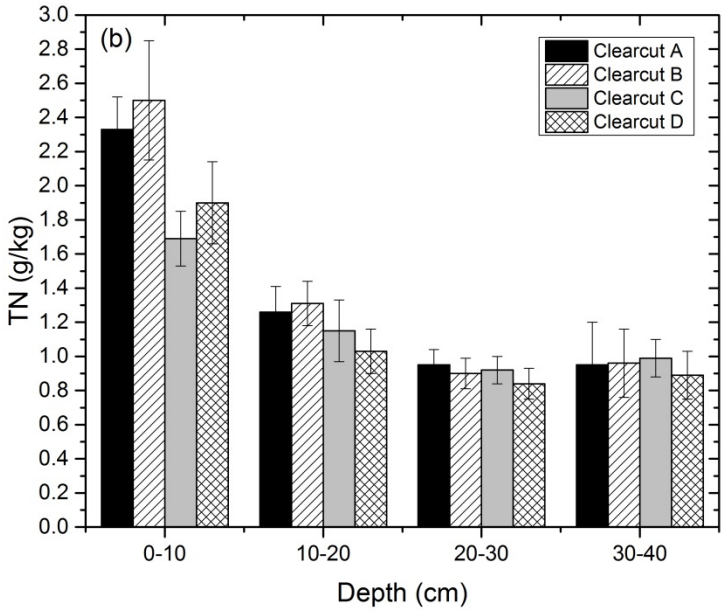


Figure 2.5. Comparison of mean total nitrogen (TN) by depth and harvest treatments: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Error bars represent standard error.

Time had a significant effect on Ca^{2+} and the sum of base cations, where the concentrations immediately post-harvest were significantly different from those one year post-harvest ($p = 0.0007$ for Ca^{2+} and $p = 0.0090$ for sum of base cations) (Table 2.4). Depth had a significant effect on Ca^{2+}, Mg^{2+}, K^{+}, and sum of base cations. For calcium ($p < 0.0001$), concentrations at the 0-10 cm depth and the 30-40 cm depth were significantly greater than samples from the 10-20 cm and 20-30 cm depths. For magnesium ($p < 0.0001$), concentrations in samples from the 0-10 cm and 10-20 cm depths are significantly less than that at the 20-30 cm and 30 – 40 cm depths. For potassium ($p < 0.0001$), concentrations at the 0-10 cm and 30-40 cm depths are significantly greater than that at the 10-20 cm and 20-30 cm depths. For the sum of base cations ($p < 0.0001$), concentration at the 0-10 cm depth is significantly greater than at the 10-20 cm depth, and significantly less than at the 30-40 cm depth.

The interaction between depth and harvest treatment had a significant effect on Ca^{2+} ($p = 0.0122$), Mg^{2+} ($p = 0.0009$), and sum of base cations ($p = 0.0028$) (Table 2.4). Figure 2.6 shows this interaction effect on calcium, which demonstrates that for all treatment types, concentration values decrease from the 0-10 cm depth to the 10-20 cm depth, but then nominally increases for the lower two depths. The fisher's least significant differences analysis indicated that concentration of calcium was significantly greater in clearcut B at the 0-10 cm and 30-40 cm depths, and in clearcut D at the 30-40 cm depth compared to the intermediate treatments at the 10-20 cm and 20-30 cm depths. The interaction between depth and treatment type for magnesium can be seen in Figure 2.7. Concentration values for clearcut B, clearcut C, and clearcut D at the 30-40 cm depth were significantly greater than the intermediate A treatment at 10-20 cm depth, and the

intermediate C treatment at the 0-10 cm and 20-30 cm depths. For clearcut D, concentration values at the 0-10 cm and 10-20 cm depths are significantly less than that at the 30-40 cm depth. The interaction between depth and treatment type also had a significant effect on the sum of exchangeable base cations (p-value = 0.0028) (Table 2.4). Clearcut B had the greatest mean concentration value for the sum of base cations at the 0-10 cm, 10-20 cm, and 20-30 cm depths (Figure 2.8). In the 30-40cm depth, clearcut D had the greatest value (8.4 $cmol_c\ kg^{-1}$) followed by clearcut B (8.17 $cmol_c\ kg^{-1}$). For clearcut D, the concentration at the 30-40 cm depth was significantly greater than that at the 10-20 cm depth. Mean concentration values at the 30-40cm depth are significantly greater for clearcut B and clearcut D compared to the intermediate treatments at all four depths and the control treatment at the 10-20 cm depth (Figure 2.8). Furthermore, concentration values for clearcut B and clearcut D at the 30-40 cm depth are significantly greater than concentration values for clearcut A, clearcut C, and clearcut D at the 10-20 cm depth. Thus, indicating that there are more bases in the subsoil compared to the surface within the clearcuts; and therefore demonstrating leaching of bases from the root zone.

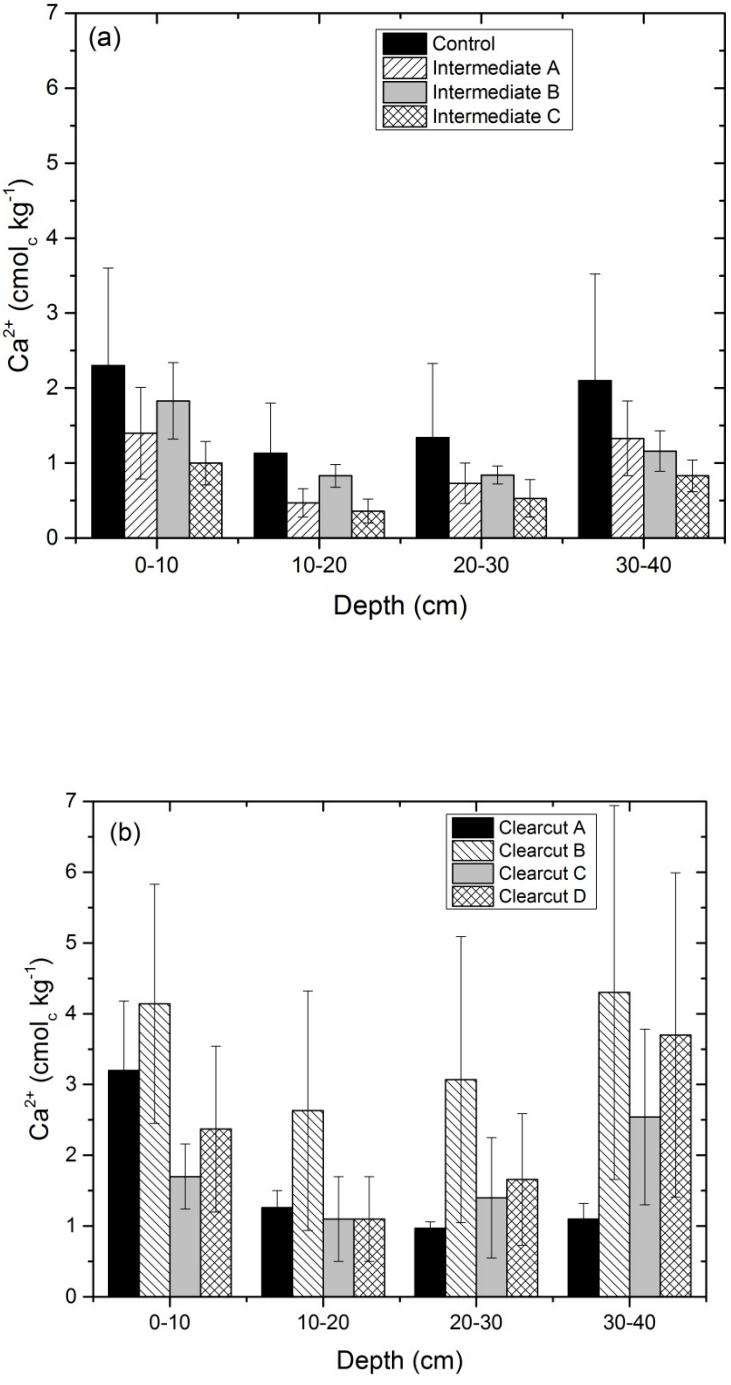
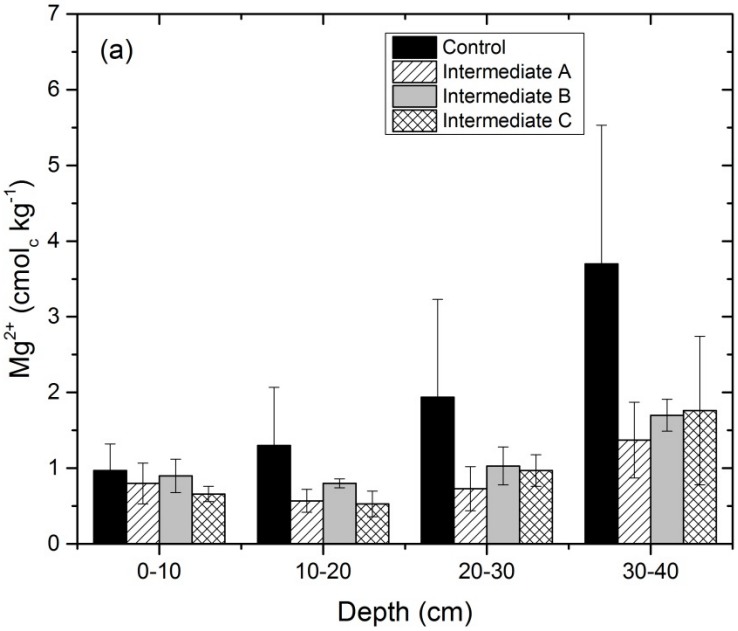


Figure 2.6. Comparison of mean calcium (Ca^{2+}) by depth and harvest treatments: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Error bars represent standard error.



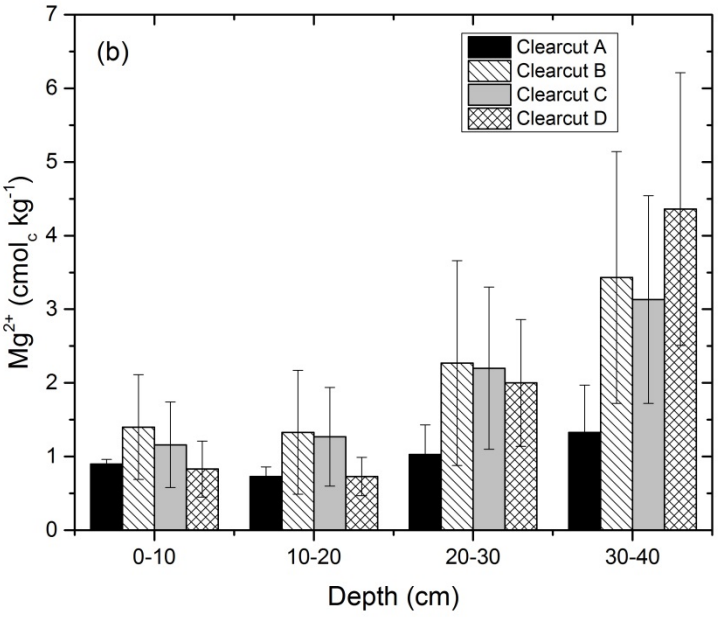


Figure 2.7. Comparison of mean magnesium (Mg^{2+}) by depth and harvest treatments: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Error bars represent standard error.

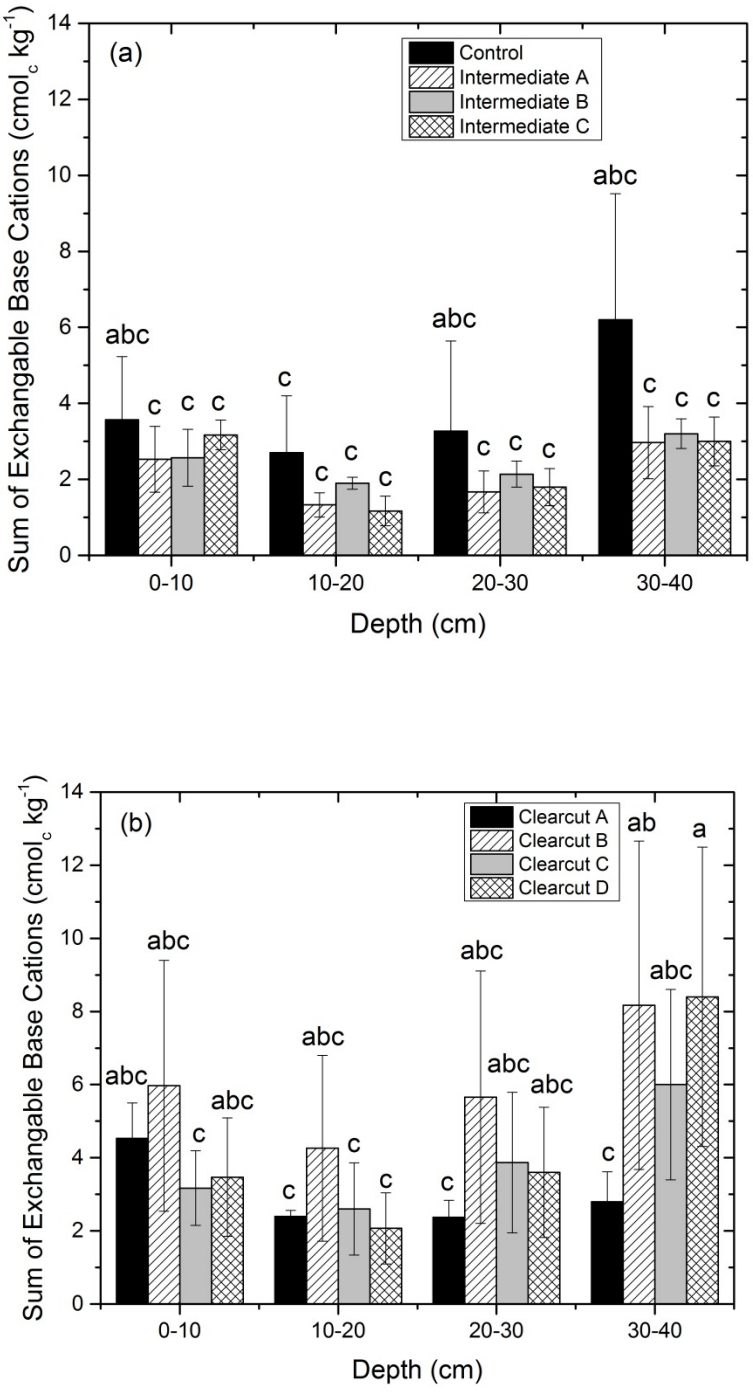


Figure 2.8. Comparison of mean sum of exchangeable (ex.) base cations (Ca^{2+}, Mg^{2+}, and K^{+}) by depth and harvest treatments: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Error bars represent standard error. Values followed by different letters were significantly different (using Fisher's LSD) at $\alpha = 0.05$.

Time and depth had a significant effect on ECEC ($p = 0.0010$ and $p < 0.0001$ respectively) (Table 2.4); where the concentrations immediately post-harvest were significantly smaller from those one year post-harvest, and concentrations at the 0-10 cm and 10-20 cm depths were significantly smaller than that at the 20-30 cm depth and significantly smaller than that at the 30-40 cm depth. The interaction between depth and harvest treatment had a significant effect on ECEC as well ($p = 0.0044$) (Table 2.4). The Tukey-Kramer analysis indicated that the ECEC was significantly greater for clearcut B and clearcut D at the 30-40cm depth compared to that at the 0-10 cm and 10-20 cm depths (Figure 2.9). Furthermore, Fisher's LSD analysis indicated that the ECEC was significantly greater for clearcut B, clearcut C, and clearcut D at the 30-40 cm depth compared to the control and intermediate treatments at the 0-10 cm and 10-20 cm depths. Across all four depths, the control treatment contained a nominally greater ECEC concentration compared to the intermediate treatments (Figure 2.9a). Furthermore, ECEC was highly and positively correlated with sum of exchangeable cations ($r = 0.76$, $p < 0.0001$) and extractable acidity ($r = 0.72$, $p < 0.0001$) (Appendix C).

Time and depth had a significant effect on base saturation (BS sat) ($p = 0.0005$ and $p < 0.0001$ respectively) (Table 2.4); where the concentrations immediately post-harvest were significantly smaller from those one year post-harvest, and concentrations at the 0-10 cm and 20-30 cm depths were significantly greater than that at the 10-20 cm depth and significantly smaller than that at the 30-40 cm depth. Furthermore, BS sat was significantly affected by the interaction between depth and harvest treatment (p-value = 0.0040) (Table 2.4). The Tukey-Kramer analysis indicated that at the 30-40cm depth, clearcut B, clearcut C, and clearcut D had significantly greater BS values compared to the

intermediate A and intermediate C treatments at the 10-20 cm depth, with the greatest value in clearcut B (59.7 % BS) (Figure 2.10). Moreover, BS sat for clearcut B was nominally greater than all other treatments at each depth. BS was strongly and positively correlated with the sum of exchangeable cations ($r = 0.91$, $p < 0.0001$) and was strongly and negatively correlated with aluminum saturation ($r = -0.86$, $p < 0.001$) (Appendix C).

Extractable acidity (EA) and aluminum saturation (Al) were only significantly affected by depth ($p < 0.0001$ for both) (Table 2.4). The Tukey-Kramer analysis indicated that for EA, values at the 0-10 cm and 30-40 cm depths were significantly greater than that at the 10-20 cm and 20-30 cm depths. The Tukey-Kramer analysis indicated that for Al, values at the 20-30 cm depth were significantly greater than the 0-10 cm depth and significantly greater than the 30-40 cm depth. Time and depth had a significant effect on the pH ($p = 0.0008$ and $p = 0.0007$ respectively) (Table 2.4); where the pH immediately post-harvest was significantly more acidic from that one year post-harvest, and the pH at the 0-10 cm depth was significantly greater than that at the 20-30 cm and 30-40 cm depths.

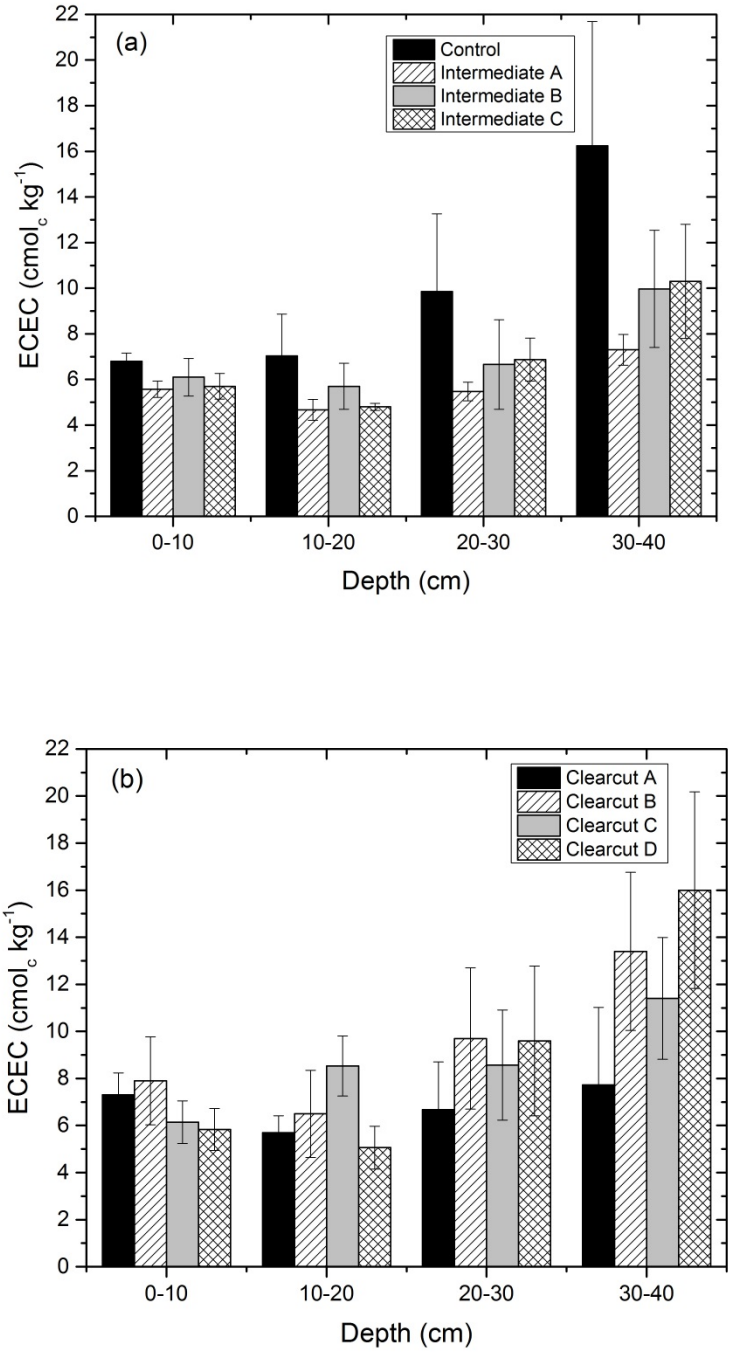
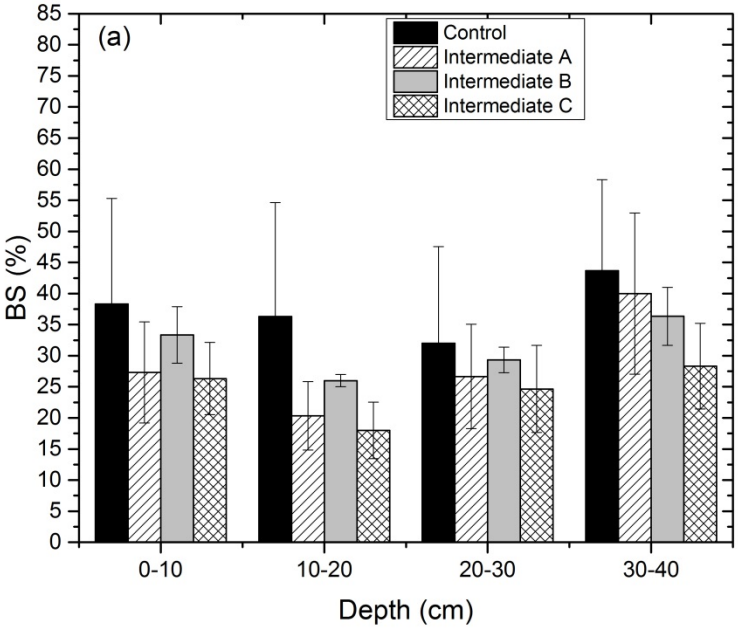


Figure 2.9. Comparison of mean effective cation exchange capacity (ECEC) by depth and harvest treatments: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Error bars represent standard error.



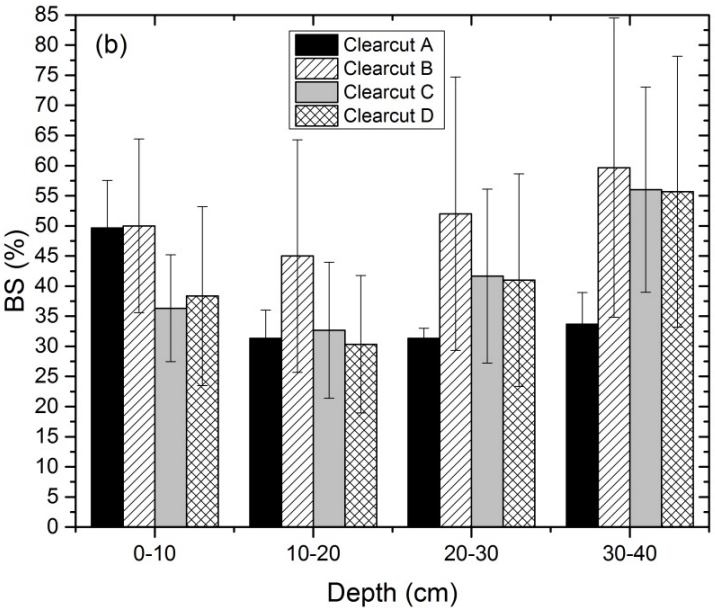


Figure 2.10. Comparison of mean percent base saturation (BS) by depth and harvest treatments: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Error bars represent standard error.

The analysis of difference values calculated by subtracting the immediately post-harvest analyte values from the one year-post harvest values determined that there was no significance of harvest treatment only on soil chemical properties (Table 2.5). However, depth had a significant effect on Ca^{2+}, K^{+}, BS, and Al saturation; and the interaction of harvest treatment and depth had an effect on base saturation. The Tukey-Kramer analysis indicated that difference in Ca^{2+} at the 0-10 cm depth was significantly greater than that at the 10-20 cm and 30-40 cm depths. The difference in K^{+} was negative for the 0-10 cm depth, and thus significantly different from the positive difference at the 20-30 cm and 30-40 cm depths. The difference in BS was significantly greater in the 0-10 cm depth compared to the 10-20 cm depth. The difference in Al saturation was negative for the 0-10 cm depth, and thus significantly different from the positive difference at the 10-20 cm depth.

Table 2.6 demonstrates the Tukey-Kramer analysis on the interaction effect between treatment type and depth on the difference values for soil solid phase characteristics. The p-values indicate that the interaction only had an effect on BS; however, the Tukey-Kramer analysis shows that the interaction had an effect on Mg^{2+}, ECEC, and Al sat as well. Exchangeable concentrations of Mg^{2+} mostly decreased with soil depth. Difference values for Mg^{2+} in clearcut B were negative and significantly different from that in clearcut D at the 30-40cm depth due to the -0.37 $cmol_c\ kg^{-1}$ decrease for clearcut B and a 0.50 $cmol_c\ kg^{-1}$ increase for clearcut D. This same pattern occurred in the difference values for ECEC, where clearcut B had a negative difference (-0.73 $cmol_c\ kg^{-1}$) at the 30-40 cm depth, and was significantly different from clearcut D

which had a positive difference (2.27 $cmol_c$ kg^-1) at the 30-40 cm depth. The negative difference values of BS for the control treatment at the 30-40 cm depth and for clearcut A at the 10-20 cm depth were significantly different from the positive difference value for clearcut A at the 0-10 cm depth. Clearcut A had the greatest difference between the 0-10cm depth and the 10-20cm depth, for base saturation, with a 10.33 % increase and then a -3.33 % decrease respectively. Aluminum saturation had the greatest negative difference values in the 0-10cm depth for the control and intermediate A harvest treatments (-10.00 % and -8.33 %), which were significantly different from the positive difference (19.33 %) in clearcut A at the 10-20 cm depth. Furthermore, clearcut A had the greatest difference between soil depths, with a 19.33 % increase at the 10-20cm depth, and then a -0.67% decrease at the 30-40cm depth.

Table 2.5. Type 3 Tests of Fixed Effects, evaluating effects of harvest treatment (Trt), sample depth, and their interaction effect on soil chemical properties difference values (one year post- and immediately post- harvest). Tukey-Kramer adjusted p-values of soil properties and nutrient concentrations from split-plot generalized linear mixed model.

Dependent variables include exchangeable concentrations of Ca^{2+}, Mg^{2+}, and K^{+}, sum of exchangeable base cations, effective cation exchange capacity (ECEC), base saturation (BS), extractable acidity (EA), aluminum saturation (Al), soil pH measured in 0.01 M $CaCl_2$ soil slurry (pH salt), total organic carbon (TOC), and total nitrogen (TN).

	Analyte										
	Ca^{2+}	Mg^{2+}	K^{+}	Sum of Cations	ECEC	BS	EA	Al	pH	TOC	TN
Source	**p-values**										
Trt	0.5298	0.3533	0.2739	0.3253	0.4357	0.5424	0.4714	0.3439	0.7612	0.3257	0.8753
Depth	**0.0107**	0.8473	**0.0090**	0.1260	0.7879	**0.0088**	0.6203	**0.0288**	0.1203	0.9855	0.6615
Trt*Depth	0.4770	0.1922	0.5620	0.2568	0.1569	**0.0167**	0.9555	0.4167	0.8270	0.8446	0.3438

Table 2.6. Difference values for soil solid phase characteristics by subtracting the immediately post-harvest values from the one year post-harvest values for each harvest treatment at each depth. The resulting value was negative if a loss in analyte concentration occurred and positive if a gain in analyte concentration occurred. Refer back to Table 1.1 for treatment descriptions.

Soil properties include exchangeable concentrations of Ca^{2+}, Mg^{2+}, K^{+}, sum of exchangeable base cations, effective cation exchange capacity (ECEC), total percentage of base saturation by weight, extractable acidity (EA), total percentage aluminum saturation (Al sat), soil pH measured in 0.01 M CaCl2 soil slurry (pH salt), total organic carbon (TOC), and total nitrogen (TN). Standard error is stated in parentheses.

		Soil Property									
Treatment	**Depth**	**Ca^{2+}**	**Mg^{2+}**	**K^{+}**	**ECEC**	**Base sat**	**EA**	**Al sat**	**pH_{salt}**	**TOC**	**TN**
	cm		$cmol_c\ kg^{-1}$		$cmol_c\ kg^{-1}$	%	$cmol_c\ kg^{-1}$	%		$g\ kg^{-1}$	$g\ kg^{-1}$
Control	0-10	0.63 (0.17)	-0.03 (0.03)ab	0.00 (0.00)	0.40 (0.25)ab	6.33 (2.33)ab	-0.20 (0.59)	-10.00 (5.86)a	0.13 (0.09)	1.67 (1.76)	0.04 (0.08)
	10-20	0.27 (0.27)	0.03 (0.19)ab	0.03 (0.03)	0.63 (0.63)ab	-2.33 (0.67)ab	-0.30 (0.32)	3.00 (3.51)ab	0.10 (0.00)	0.00 (1.16)	0.06 (0.01)
	20-30	0.20 (0.25)	0.00 (0.25)ab	0.03 (0.03)	0.00 (0.89)ab	0.67 (2.67)ab	-0.77 (0.49)	2.00 (4.16)ab	0.13 (0.03)	0.67 (0.88)	0.03 (0.01)
	30-40	0.03 (0.26)	-0.17 (0.38)ab	0.03 (0.03)	-0.10 (1.17)ab	-4.33 (3.33)a	-0.03 (1.19)	6.33 (5.84)ab	0.13 (0.03)	0.33 (0.33)	-0.02 (0.02)
Intermediate A	0-10	0.47 (0.37)	0.13 (0.03)ab	0.07 (0.03)	1.03 (0.23)ab	5.33 (2.40)ab	0.57 (0.24)	-8.33 (7.54)a	-0.03 (0.12)	1.33 (1.45)	0.18 (0.17)
	10-20	0.13 (0.13)	-0.03 (0.03)ab	0.03 (0.07)	0.73 (0.27)ab	2.33 (2.96)ab	-0.53 (0.62)	2.67 (5.04)ab	0.10 (0.06)	-1.00 (1.00)	0.06 (0.02)
	20-30	-0.07 (0.03)	-0.07 (0.12)ab	0.00 (0.00)	0.33 (0.41)ab	-0.67 (0.33)ab	-0.80 (0.40)	7.00 (2.31)ab	0.03 (0.09)	-1.67 (0.88)	-0.02 (0.05)
	30-40	-0.07 (0.20)	-0.17 (0.12)ab	0.07 (0.03)	0.30 (0.66)ab	0.67 (2.85)ab	-0.57 (0.56)	5.33 (3.28)ab	0.10 (0.10)	-1.00 (0.58)	0.02 (0.12)
Intermediate B	0-10	0.23 (0.03)	0.03 (0.09)ab	0.07 (0.03)	0.70 (0.23)ab	3.33 (2.03)ab	0.23 (0.30)	-1.67 (7.97)ab	0.03 (0.09)	-0.33 (0.67)	0.01 (0.07)
	10-20	0.17 (0.12)	0.00 (0.06)ab	0.07 (0.03)	0.70 (0.12)ab	2.67 (0.88)ab	0.00 (0.35)	0.00 (2.00)ab	0.00 (0.06)	0.00 (0.00)	0.03 (0.04)
	20-30	0.30 (0.10)	0.23 (0.07)ab	0.07 (0.03)	1.40 (0.40)ab	6.67 (1.20)ab	0.45 (0.58)	-4.33 (0.67)ab	0.00 (0.00)	-0.67 (0.33)	0.03 (0.04)
	30-40	0.30 (0.10)	0.30 (0.12)ab	0.10 (0.06)	1.63 (0.98)ab	7.00 (1.16)ab	0.17 (0.98)	-3.33 (5.24)ab	0.10 (0.00)	0.33 (0.33)	0.05 (0.02)
Intermediate C	0-10	0.27 (0.23)	0.00 (0.06)ab	0.00 (0.00)	0.63 (0.56)ab	0.33 (0.67)ab	-0.67 (0.84)	0.00 (3.51)ab	0.00 (0.10)	-3.00 (2.65)	-0.06 (0.23)
	10-20	0.10 (0.10)	-0.07 (0.09)ab	0.00 (0.00)	0.60 (0.12)ab	-0.67 (2.19)ab	0.27 (0.78)	6.67 (6.94)ab	0.07 (0.07)	1.33 (1.45)	-0.04 (0.06)
	20-30	0.07 (0.13)	-0.03 (0.12)ab	0.03 (0.03)	0.13 (0.18)ab	2.00 (1.53)ab	-0.53 (0.57)	1.00 (7.00)ab	0.13 (0.03)	-1.00 (1.16)	-0.03 (0.07)
	30-40	0.17 (0.13)	-0.10 (0.15)ab	0.00 (0.06)	0.03 (0.38)ab	1.67 (0.33)ab	-0.40 (1.10)	0.67 (4.18)ab	0.07 (0.03)	-0.67 (0.88)	0.02 (0.08)
Clearcut A	0-10	0.67 (0.38)	-0.03 (0.03)ab	-0.07 (0.07)	0.90 (0.25)ab	10.33 (5.81)b	0.53 (0.99)	4.33 (9.94)ab	0.17 (0.12)	0.00 (1.53)	0.23 (0.07)
	10-20	-0.20 (0.06)	-0.13 (0.03)ab	-0.07 (0.07)	0.17 (0.23)ab	-3.33 (0.88)a	-0.43 (0.45)	19.33 (7.31)b	-0.03 (0.07)	-2.67 (1.45)	-0.14 (0.09)
	20-30	0.17 (0.03)	-0.17 (0.12)ab	-0.03 (0.03)	0.27 (0.50)ab	0.00 (1.00)ab	-0.37 (0.49)	6.67 (3.28)ab	0.07 (0.03)	-1.00 (1.53)	-0.11 (0.05)
	30-40	0.17 (0.09)	-0.13 (0.07)ab	-0.03 (0.03)	0.13 (0.09)ab	3.67 (2.85)ab	-1.07 (0.81)	-0.67 (2.33)ab	0.23 (0.07)	-2.33 (0.88)	-0.18 (0.10)
Clearcut B	0-10	0.60 (0.29)	-0.07 (0.07)ab	-0.10 (0.06)	0.70 (0.30)ab	2.67 (2.40)ab	0.53 (0.18)	-1.00 (5.51)ab	0.07 (0.17)	-2.00 (4.00)	-0.08 (0.17)
	10-20	0.37 (0.09)	-0.13 (0.03)ab	-0.03 (0.03)	0.63 (0.24)ab	2.33 (1.45)ab	0.23 (0.15)	4.33 (3.48)ab	0.03 (0.09)	1.00 (1.53)	0.03 (0.07)
	20-30	0.67 (0.37)	0.13 (0.22)ab	0.03 (0.03)	0.97 (0.62)ab	3.33 (2.85)ab	-0.03 (0.03)	-0.33 (2.03)ab	0.13 (0.03)	0.00 (0.00)	0.04 (0.07)
	30-40	0.03 (0.29)	-0.37 (0.19)a	0.00 (0.06)	-0.73 (0.48)a	3.00 (1.16)ab	-1.20 (1.14)	-5.00 (2.00)ab	0.13 (0.07)	-0.67 (0.33)	-0.08 (0.15)
Clearcut C	0-10	0.23 (0.12)	-0.10 (0.00)ab	0.00 (0.06)	0.60 (0.46)ab	1.67 (1.20)ab	0.43 (0.95)	4.33 (5.36)ab	0.10 (0.15)	-1.33 (2.85)	-0.09 (0.08)
	10-20	0.23 (0.15)	-0.07 (0.03)ab	0.03 (0.03)	0.67 (0.22)ab	1.33 (1.20)ab	0.03 (0.52)	4.67 (5.04)ab	0.10 (0.06)	-2.00 (1.00)	-0.01 (0.15)
	20-30	0.13 (0.15)	-0.13 (0.13)ab	0.07 (0.03)	0.57 (0.38)ab	1.00 (1.73)ab	0.33 (0.29)	3.33 (2.03)ab	0.07 (0.03)	-1.33 (0.88)	0.09 (0.05)
	30-40	0.40 (0.21)	0.07 (0.12)ab	0.07 (0.03)	1.13 (0.46)ab	4.00 (2.65)ab	0.50 (0.92)	0.33 (2.03)ab	0.10 (0.06)	-1.33 (1.33)	0.10 (0.06)
Clearcut D	0-10	0.83 (0.54)	0.03 (0.09)ab	0.00 (0.06)	1.17 (0.52)ab	5.00 (2.52)ab	0.47 (0.42)	-0.67 (1.76)ab	-0.03 (0.03)	-0.33 (1.45)	0.06 (0.21)
	10-20	0.37 (0.18)	0.07 (0.09)ab	0.03 (0.03)	1.00 (0.46)ab	5.00 (3.22)ab	0.23 (0.33)	0.33 (0.88)ab	-0.03 (0.03)	0.00 (0.58)	-0.09 (0.12)
	20-30	0.60 (0.36)	0.13 (0.24)ab	0.07 (0.03)	0.93 (0.70)ab	5.67 (4.18)ab	0.30 (0.15)	-6.00 (2.08)ab	0.07 (0.07)	1.33 (0.88)	0.10 (0.03)
	30-40	0.83 (0.62)	0.50 (0.53)b	0.07 (0.03)	2.27 (1.48)b	2.33 (3.93)ab	1.33 (1.45)	1.00 (3.06)ab	0.07 (0.07)	0.67 (0.67)	0.07 (0.02)

Values followed by different letters within columns for a given soil property were significantly different (using Tukey's HSD) at $\alpha = 0.05$.

2.4.2 Soil Nutrient Flux

Analysis of the PRS^{TM} probe flux data determined that the harvest treatment only had a significant effect on total nitrogen, nitrate, iron, manganese, and sulfur; time had a significant effect on all analytes; and depth had a significant effect on all analytes except total nitrogen, nitrate, and manganese (Table 2.7). Moreover, the treatment x time interaction had a significant effect on total nitrogen, nitrate, and manganese. The treatment x depth interaction had a significant effect on magnesium, potassium, iron, and aluminum. The time x depth interaction had a significant effect on all analytes with exception for calcium, magnesium, and aluminum. However, the three way interaction between treatment, time, and depth did not have a significant effect on any of the analytes. As the primary objective of this research was to compare nutrient flux values from different sample depths and between different harvest treatments, data were averaged at each burial period and displayed in the following figures throughout the results section.

Soil temperature and moisture for the start and end dates for each burial period of the PRS^{TM} probes are presented in Table 2.8. Soil temperature was lowest during the fourth burial period (1/9/13-2/8/13), which was expected during the winter months; and was highest during the first burial period (7/2/12-7/31/12). Soil moisture was the lowest at the end of the seventh burial period (8/12/13-9/11/13), which corresponds to the least amount of precipitation that accumulated (1.37cm) over this burial period (Figure 2.11). The greatest amount of soil moisture occurred during the fourth through the six burial periods (January, 2013- June, 2013), which corresponds to the greatest amount of precipitation that fell during these burial periods.

Table 2.7. Type 3 Tests of Fixed Effects, evaluating effects of harvest treatment (Trt), sample depth, time, and their interaction effects on soil nutrient flux as measured using PRS^{TM} probes. Tukey-Kramer adjusted p-values of nutrient flux from split-plot generalized linear mixed model are presented. Total N (sum of NO_3^--N and NH_4^+-N).

	Analyte										
	Total N	NO_3^--N	NH_4^+-N	Ca	Mg	K	P	S	Al	Fe	Mn
Source	**p-values**										
Trt	**< 0.0001**	**< 0.0001**	0.9627	0.1915	0.5116	0.5782	0.0795	**0.0062**	0.5258	**0.0170**	**0.0092**
Time	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**
Depth	0.1681	0.5932	**0.0130**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	**< 0.0001**	0.6081
Trt*Time	**< 0.0001**	**< 0.0001**	0.0776	0.1105	0.9580	0.1560	0.2132	0.4938	0.1012	0.2132	**0.0094**
Trt*Depth	0.8732	0.2712	0.1534	0.1201	**0.0304**	**< 0.0001**	0.4931	0.2904	**0.0002**	**0.0039**	0.0618
Time*Depth	**0.0002**	**0.0101**	**0.0012**	0.3023	0.5513	**0.0035**	**0.0002**	**0.0003**	0.2173	**0.0325**	**0.0095**
Trt*Time*Depth	0.2658	0.3667	0.1163	0.7554	0.9924	0.9553	0.1446	0.7032	0.5106	0.1763	0.1642

Table 2.8. Soil temperature and moisture for the start and end date for each burial period by depth.

	Soil Temperature (°C)		Soil Moisture (%)	
	Depth (cm)		Depth (cm)	
Burial Period	10	30	10	30
7/2/12-7/31/12	30.6, 31.4	30.8, 31.1	8.4, 10.0	11.8, 13.3
9/9/12-10/7/12	22.8, 13.4	24.9, 16.0	26.0, 25.5	30.8, 30.5
11/8/12-12/11/12	9.5, 5.0	11.6, 8.3	24.8, 25.6	30.1, 30.1
1/9/13-2/8/13	4.0, 6.6	4.1, 6.9	26.4, 40.9	29.9, 51.4
3/20/13-4/21/13	6.5, 13.0	7.6, 12.6	37.0, 33.8	52.8, 47.2
5/27/13-6/29/13	20.9, 24.7	20.1, 23.9	30.9, 41.5	34.4, 51.3
8/12/13-9/11/13	23.3, 22.1	23.0, 22.4	18.5, 4.0	22.1, 6.3
10/22/13-11/25/13	11.5, 4.7	12.4, 5.7	9.3, 17.8	10.8, 22.3

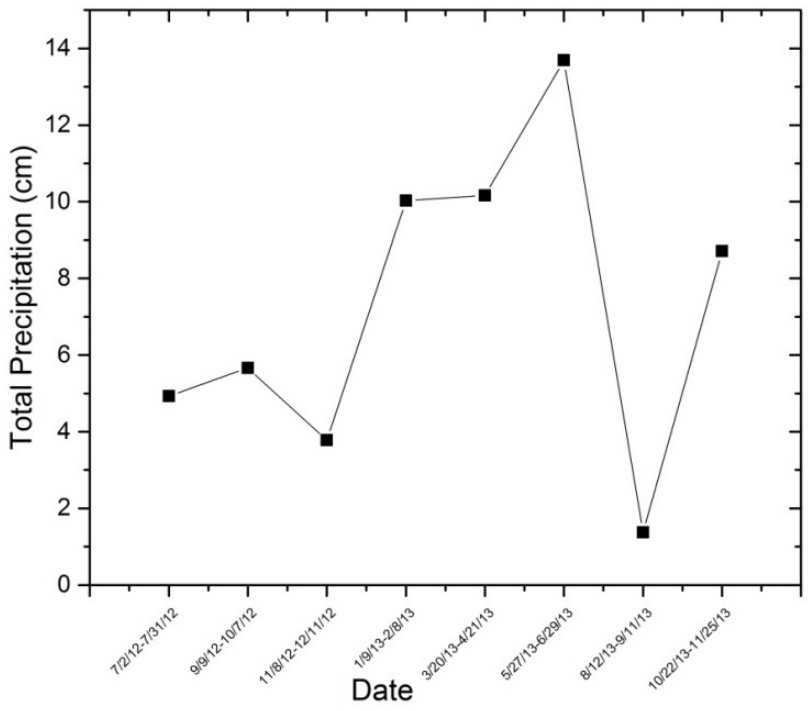


Figure 2.11. Total precipitation (cm) data for the burial periods of PRS™ probes. Collected at cook station at Wurdack Farms. (http://agebb.missouri.edu/weather/history/index.asp?station_prefix=wur)

Total Nitrogen (Nitrate + Ammonium)

Significant differences between harvest treatments and time were found for total nitrogen and nitrate flux measured using the PRS^{TM} probes (Table 2.7). The type of harvest treatment had a significant effect on total nitrogen ($p < 0.0001$). The total nitrogen flux values were significantly greater in the clearcut treatments than the control and intermediate treatments (Figure 2.12), and this same effect was observed for nitrate (Figure 2.13). The interaction between treatment and time and the interaction between time and depth had a significant effect on total nitrogen and nitrate flux ($p < 0.0001$ and $p = 0.0002$, respectively, for total nitrogen); $p < 0.0001$ and $p = 0.0101$, respectively, for nitrate). Total nitrogen and nitrate flux increased between the first and second burial period and then, on average, decreased with time (Figure 2.14 and 2.15). The Tukey-Kramer analysis indicated that for the treatment and time interaction effect, the clearcut treatments are no longer significantly different than the control after one year of monitoring, while the intermediate treatments are no longer significantly different than the control between 4-6 months of monitoring. Nitrogen flux to the PRS^{TM} probes during each burial period and at both burial depths was significantly greater in the clearcut treatments compared to the control and intermediate treatments from September, 2012 to June, 2013. During the burial period (8/12/13-9/11/13), flux greatly decreased at both burial depths and then increased in the last burial period (10/22/13-11/25/13). Moreover, during the last burial period, the flux in the clearcut treatments was nominally greater than the intermediate and control treatments at the 10 cm burial depth. This could be due to the fact that total precipitation was very low (1.37cm) between 8/12/13-9/11/13 and increased to 8.71cm during the time period between 10/22/13 and 11/25/13 (Figure 2.11).

There was a significant time, depth, and time x depth interaction effect on ammonium flux (Table 2.7). The Tukey-Kramer analysis for time indicated that the ammonium flux is significantly different between the first and fourth burial periods; thus, ammonium was not a susceptible to leaching after harvest as was nitrate (Figure 2.16). After 6-7 months, ammonium flux was not significantly different from the first burial period. According to the Tukey-Kramer analysis, ammonium flux at the 10 cm depth was significantly greater than the 30 cm depth. The interaction between time and depth indicated that ammonium flux at the 10 cm depth, during the seventh burial period (8/12/13-9/11/13) is significantly less than the 10 cm depth during the fourth burial period (1/9/13-2/8/13) (Figure 2.16). This observation is similar to that for total nitrogen and nitrate flux. No significant difference was observed between treatments unlike those found for total nitrogen and nitrate flux. However, at the 10 cm burial depth, clearcuts B and D had nominally greater flux in the first three burial periods (July, 2012 – December, 2012).

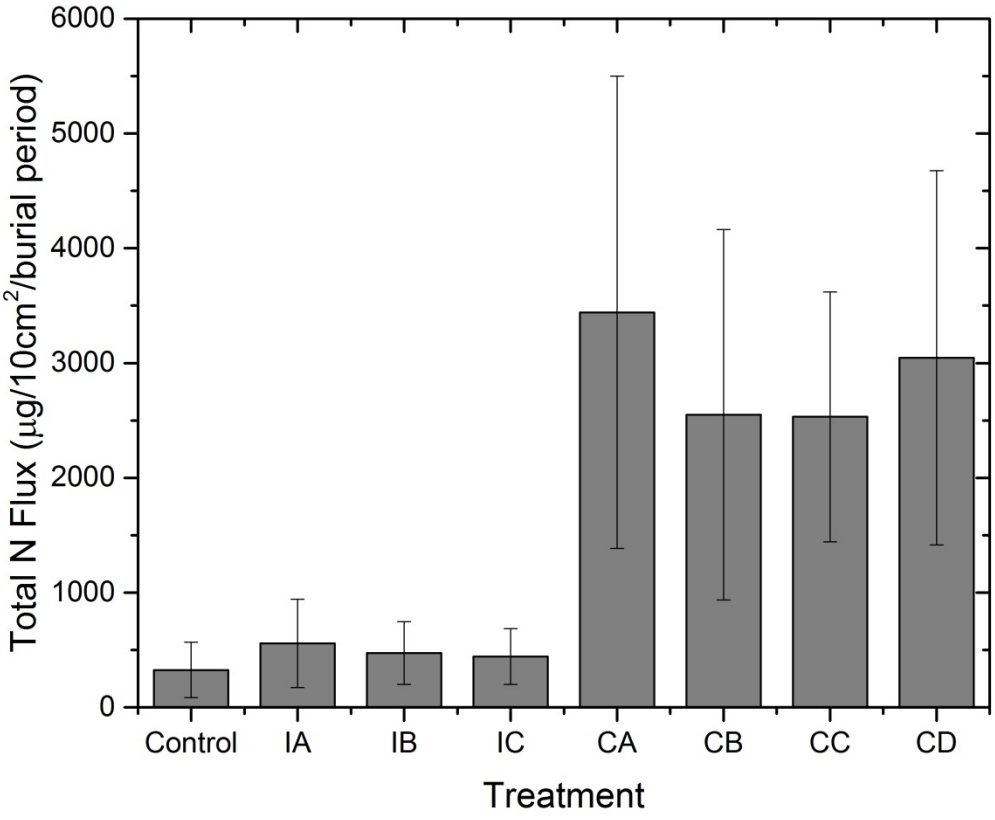


Figure 2.12. Total N flux (sum of NO_3^--N and NH_4^+-N) measured using PRS™ probes for all harvest treatments. Error bars represent 95% confidence intervals.

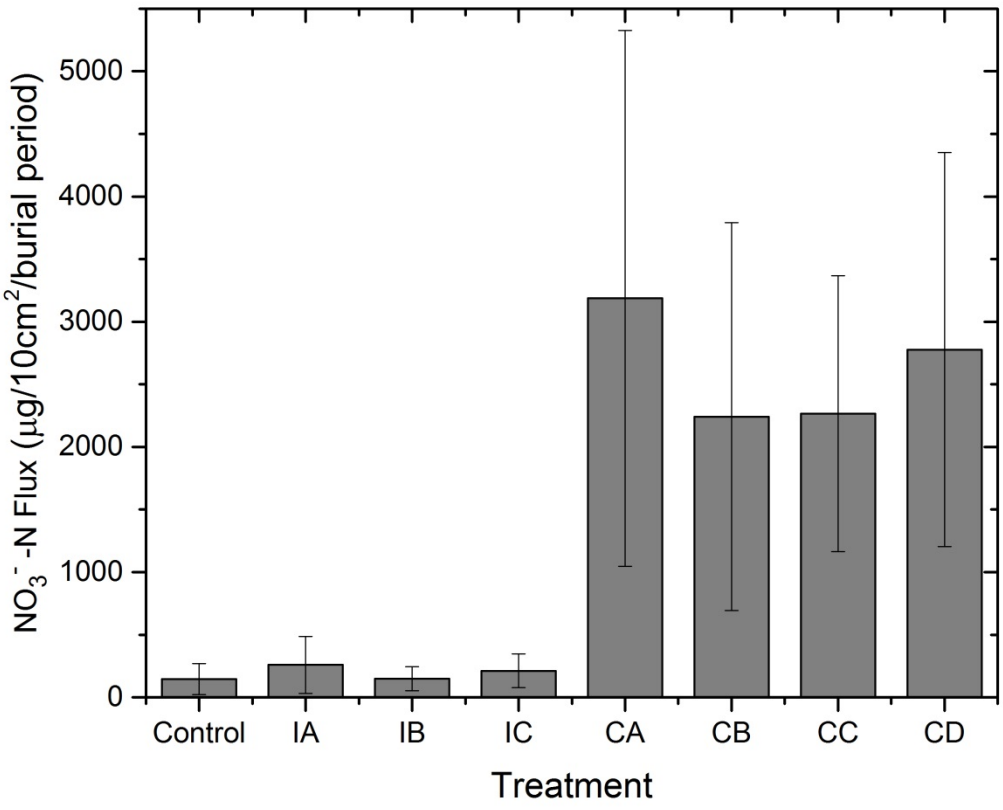


Figure 2.13. Nitrate (NO_3^--N) measured using PRS™ probes for all harvest treatments. Error bars represent 95% confidence intervals.

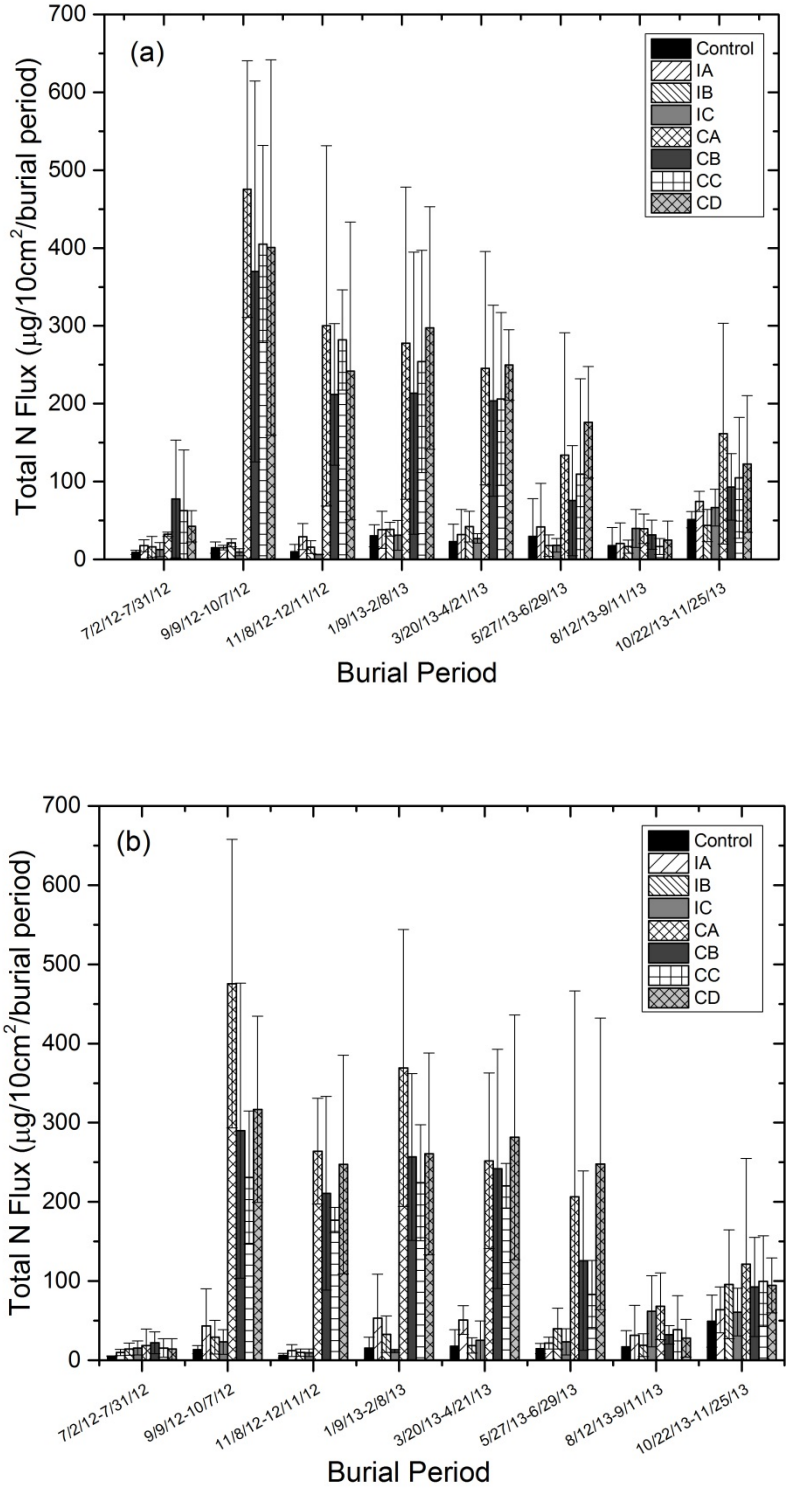


Figure 2.14. Mean total nitrogen (sum of NO_3^--N and NH_4^+-N) flux measured using PRS^{TM} probes for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

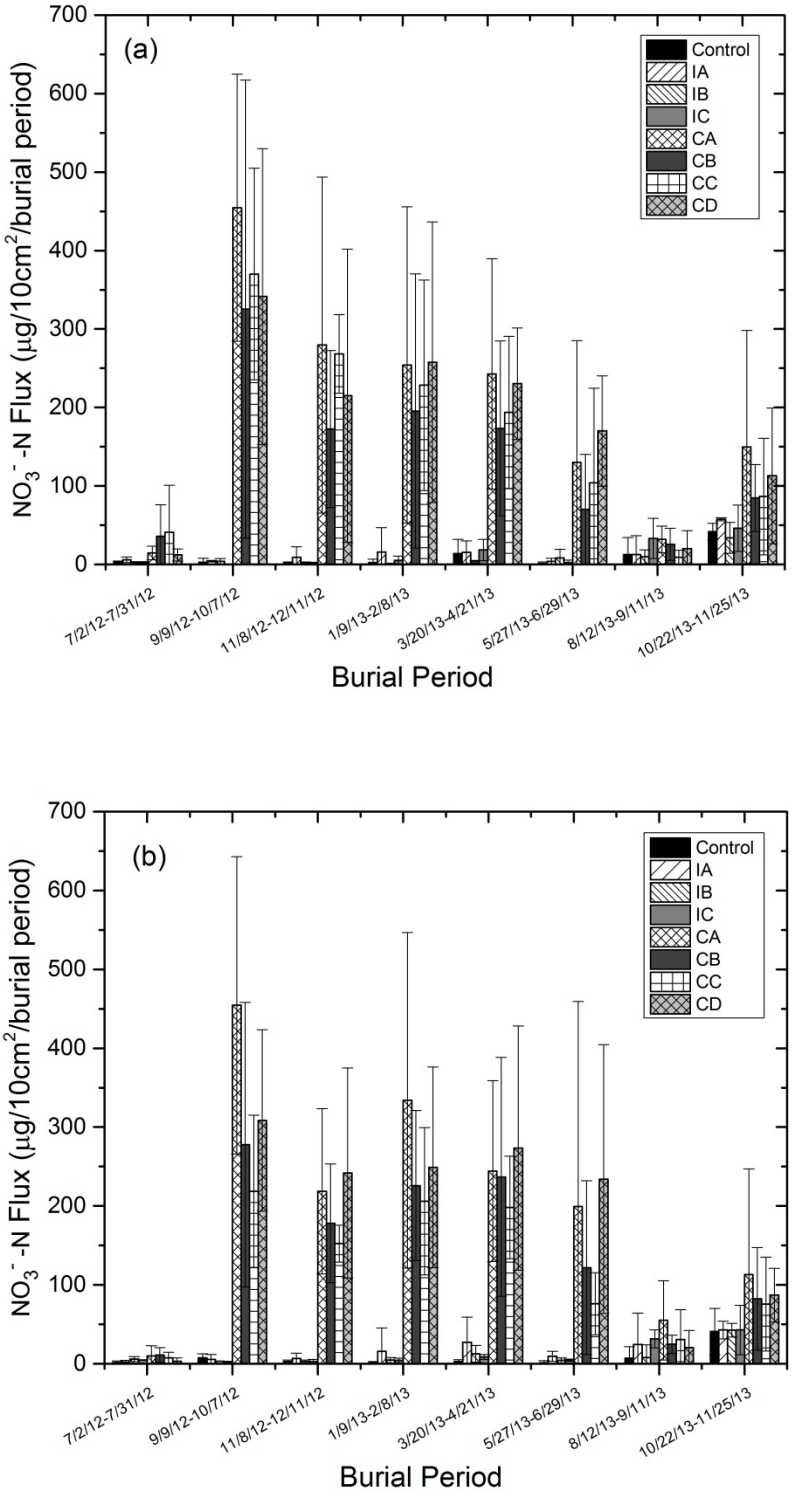


Figure 2.15. Mean nitrate (NO_3^- -N) flux measured using PRS^{TM} probes for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

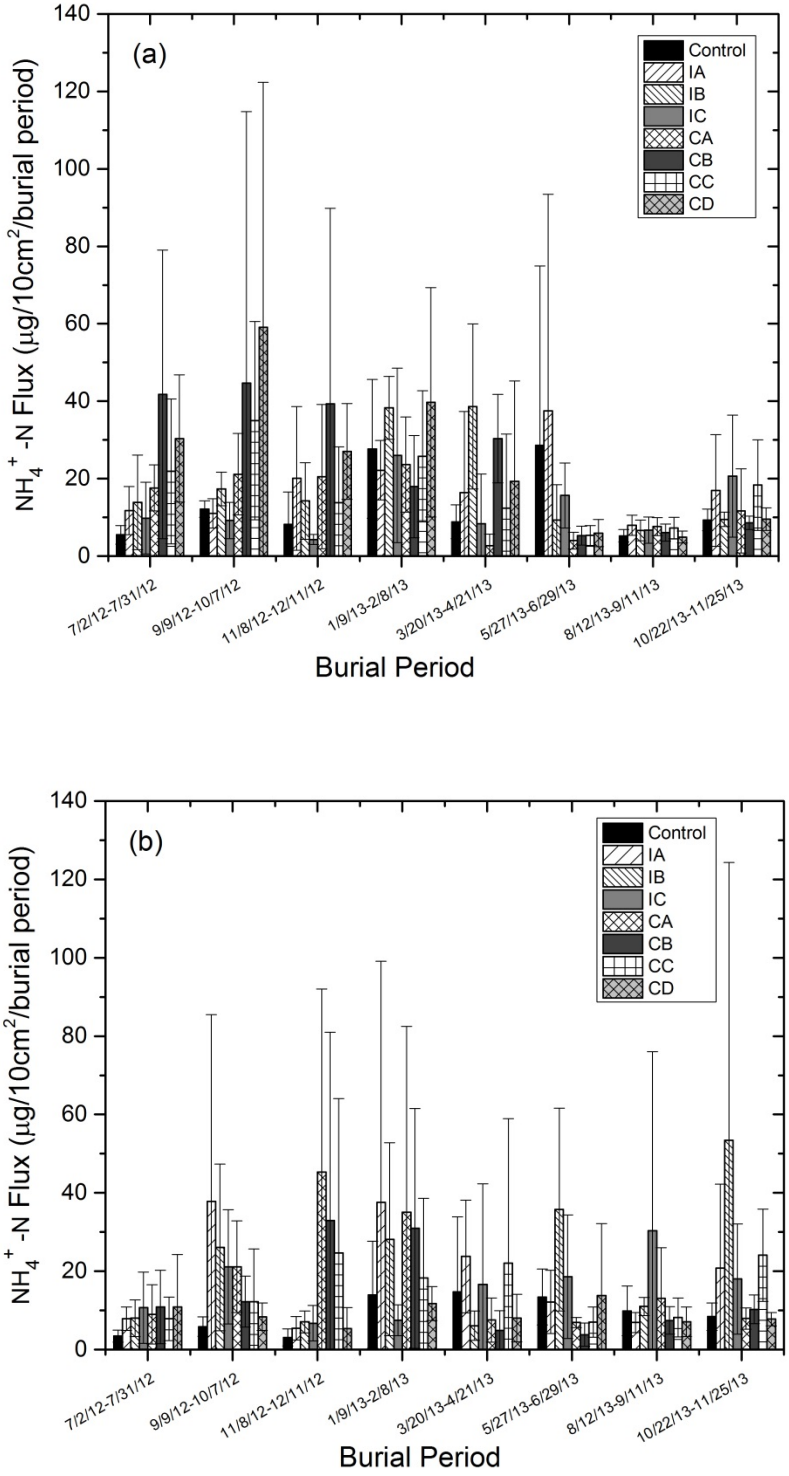


Figure 2.16. Mean ammonium (NH_4^+ -N) flux measured using PRS^{TM} probes for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

Calcium, Potassium, and Magnesium

Time and depth were the only two factors that had a significant effect on calcium flux ($p = <0.0001$ for both time and depth) (Table 2.7). According to the Tukey-Kramer analysis, calcium flux during the first burial period is significantly smaller compared to the remaining burial periods; and calcium flux during the second burial period is significantly greater than that during the last three burial periods (May, 2013 – November, 2013). The significant effect of depth on calcium flux indicated that the flux at the 30 cm depth was significantly greater than the flux at the 10 cm depth. Figure 2.17 exhibits that the Ca^{2+} flux nominally increases in the clearcut treatments during the fifth burial period (3/20/13-4/21/13), and then decreases, on average, with time. At the 10cm burial depth, the clearcut treatments had nominally greater flux values on average compared to the control and intermediate treatments (Figure 2.17a). Moreover, the greatest Ca^{2+} flux occurred in clearcut B during all burial periods at 10cm depth. Similar patterns were seen at the 30cm depth (Figure 2.17b). A slight decrease in flux can be seen during the winter months (November, 2012 - February, 2013).

There was a significant time, depth, and treatment x depth effect ($p < 0.0001$, $p < 0.0001$, and $p = 0.0304$ respectively) on magnesium flux (Table 2.7). According to the Tukey-Kramer analysis, magnesium flux during the first burial period is significantly less compared to the remaining burial periods; and magnesium flux during the second and fourth burial periods are significantly greater than that during the last two burial periods (August, 2013 – November, 2013). The significant effect of depth on magnesium flux indicated that the flux at the 30 cm depth was significantly greater than the flux at the 10 cm depth. The interaction between treatment type and depth indicate that at the 10cm

burial depth, clearcut treatments had nominally greater Mg^{2+} flux than the control and intermediate treatments, with clearcut C (alternative BMP) having the greatest flux during each burial period (Figure 2.18a). The greatest increase in flux occurs in the clearcut treatments between the first and second burial period. Similar, but not as extreme patterns occurred at the 30cm burial depth (Figure 2.18b); clearcuts C and D (alternative BMP and traditional harvest, respectively) had nominally greater Mg^{2+} flux values during each burial period at the 30 cm depth.

Time and depth had significant effects on potassium flux ($p < 0.0001$ for both time and depth) (Table 2.7). According to the Tukey-Kramer analysis, potassium flux during the first burial period is significantly smaller compared to the remaining burial periods; potassium flux during the third burial period is significantly greater than that during the first burial period, and is significantly smaller than the remaining burial periods; and potassium flux during the sixth burial period is significantly greater than that during the second burial period (September, 2012 – October, 2012) and last two burial periods (August, 2013 – November, 2013). The significant effect of depth on potassium flux indicated that the flux at the 10 cm depth was significantly greater than the flux at the 30 cm depth. The p-value for the interaction between treatment type and time indicates that it is not significant for potassium; however, the Tukey-Kramer analysis indicated that the flux for the intermediate A, intermediate B, and clearcut A treatments during the sixth burial period (5/27/13 – 6/29/13) were significantly greater than the flux for the control, intermediate A, and intermediate B treatments during the first burial period. During the first five burial periods (July, 2012-April, 2013), on average, the clearcut treatments had nominally greater K^{+} flux compared to the control and

intermediate treatments at both burial depths (Figure 2.19). During this time period, clearcuts A and D (Missouri's BMP and traditional sawlog harvest, respectively) demonstrated the greatest flux values at the 10cm burial depth (Figure 2.19a); while clearcut A (Missouri's BMP) demonstrated the greatest flux values at the 30 cm burial depth (Figure 2.19b). Potassium flux had similar patterns to calcium flux in the fact that a slight decrease in flux occurred during the winter months (November, 2012 - February, 2013), and then nominally increased during the fifth burial period. There was a significant treatment x depth interaction effect ($p < 0.0001$) on potassium flux; where the flux for the clearcut A (Missouri's BMP) treatment was greater at the 10 cm and 30 cm depths compared to the flux for the clearcut B, C, and D (removal of all biomass, alternative BMP, and traditional sawlog harvest respectively) treatments at the 30 cm depth. The Tukey-Kramer analysis indicated that the time x depth interaction ($p = 0.0035$) also had a significant effect on potassium flux. At the 30 cm depth, potassium flux at the first and third burial periods is significantly less than all of the other depth and time combinations. Moreover, at the 10 cm depth during the second, fifth, and sixth burial periods, potassium flux is significantly greater than during the first and third burial periods (Figure 2.19a).

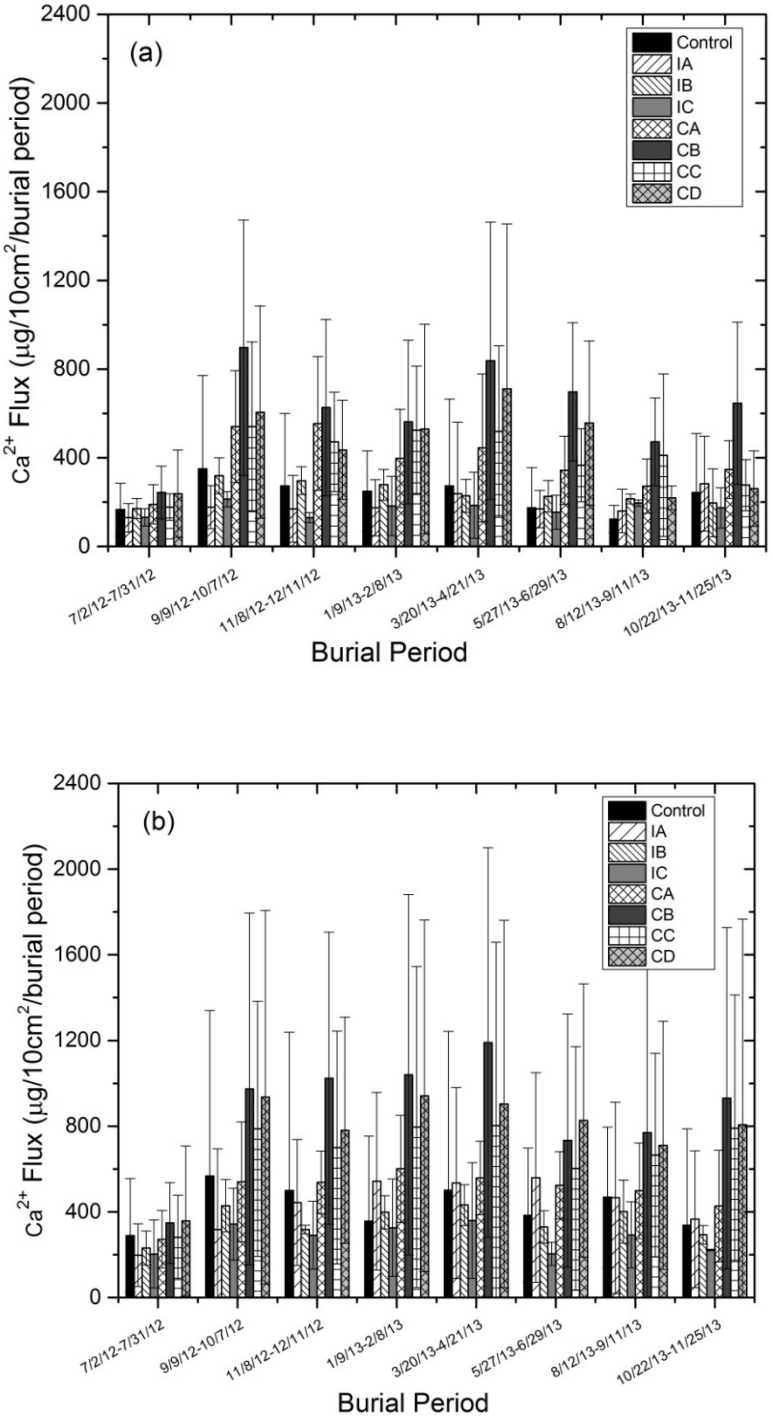


Figure 2.17. Mean calcium (Ca^{2+}) flux measured using PRS^{TM} probes for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

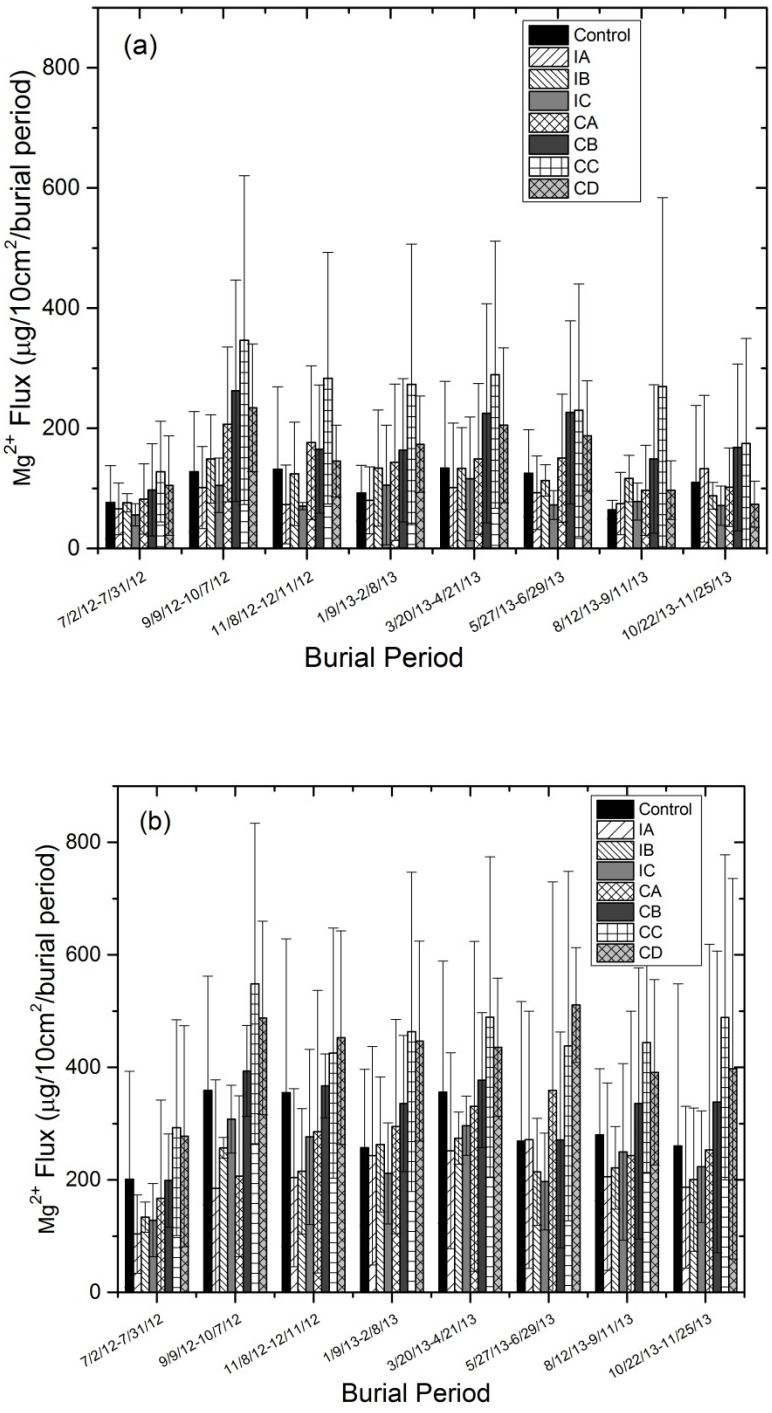


Figure 2.18. Mean magnesium (Mg^{2+}) flux measured using PRS^{TM} probes for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

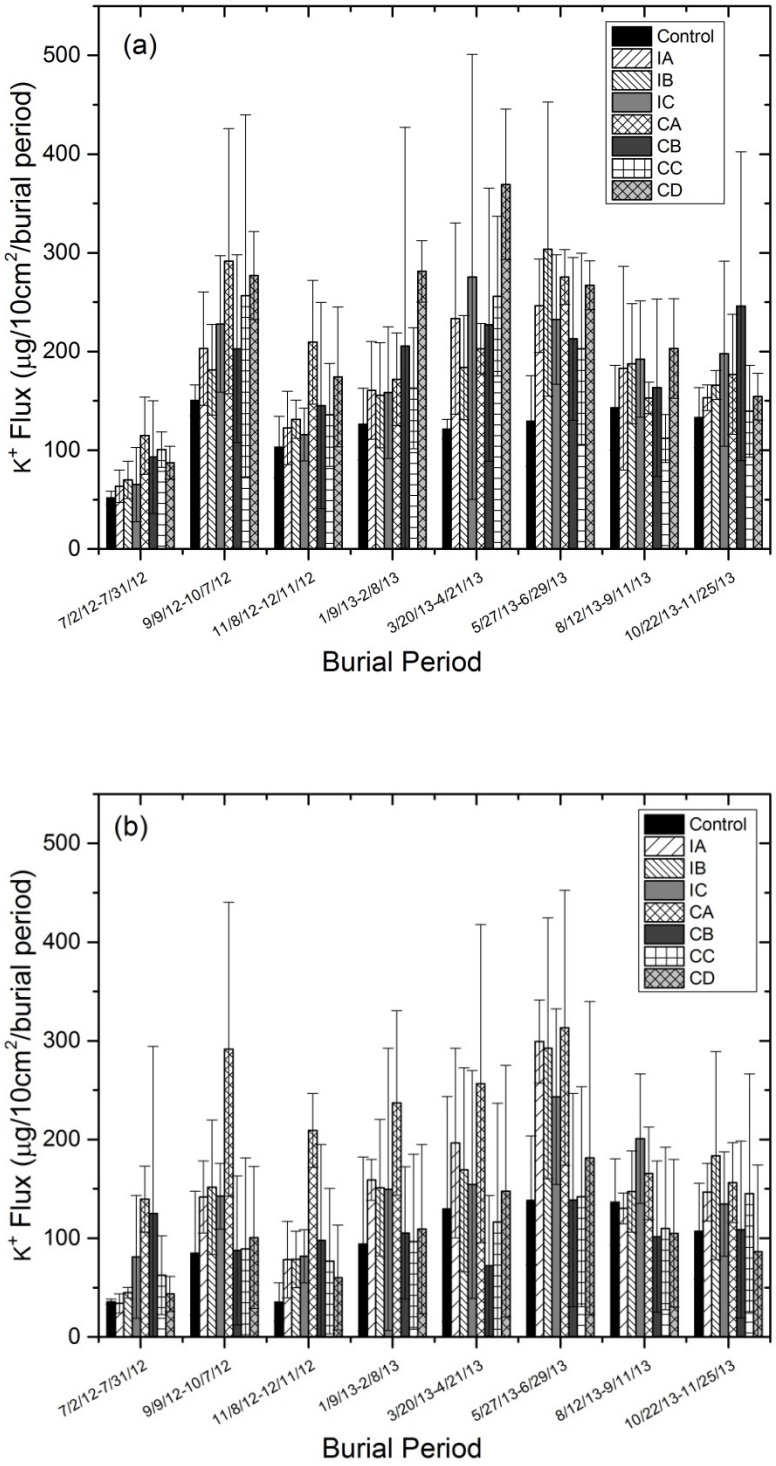


Figure 2.19. Mean potassium (K^+) flux measured using PRS^{TM} probes for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

Phosphorus

Time and depth had significant effects on phosphorus flux ($p < 0.0001$ for both) (Table 2.7). According to the Tukey-Kramer analysis, phosphorus flux during the last three burial periods (May, 2013 – November, 2013) is significantly greater than that during the second through the fifth burial periods (September, 2012 – April 2012); and flux during the second through the fifth burial periods is significantly greater than flux at the first burial period. The significant effect of depth on phosphorus flux indicated that P flux at the 10 cm depth was significantly greater than flux at the 30 cm depth. The p-value for the interaction between treatment type and time indicates that it is not significant for phosphorus; however, the Tukey-Kramer analysis indicated that P flux for the intermediate C treatment during the seventh burial period is significantly greater than the flux for the control and clearcut C (alternative BMP) treatments during the fourth burial period, and is significantly greater than the flux for the control, intermediate A, and clearcut C (alternative BMP) treatments during the first burial period (Figure 2.20). The Tukey-Kramer analysis also indicated that the flux for the clearcut A (Missouri's BMP) at the 10 cm depth is significantly greater than that for the control treatment at the 30 cm depth. The time and depth interaction effect indicates that during the first burial period at the 10 cm and 30 cm depths, phosphorus flux is the least, while during the seventh burial period at the 10 cm depth phosphorus flux is greatest.

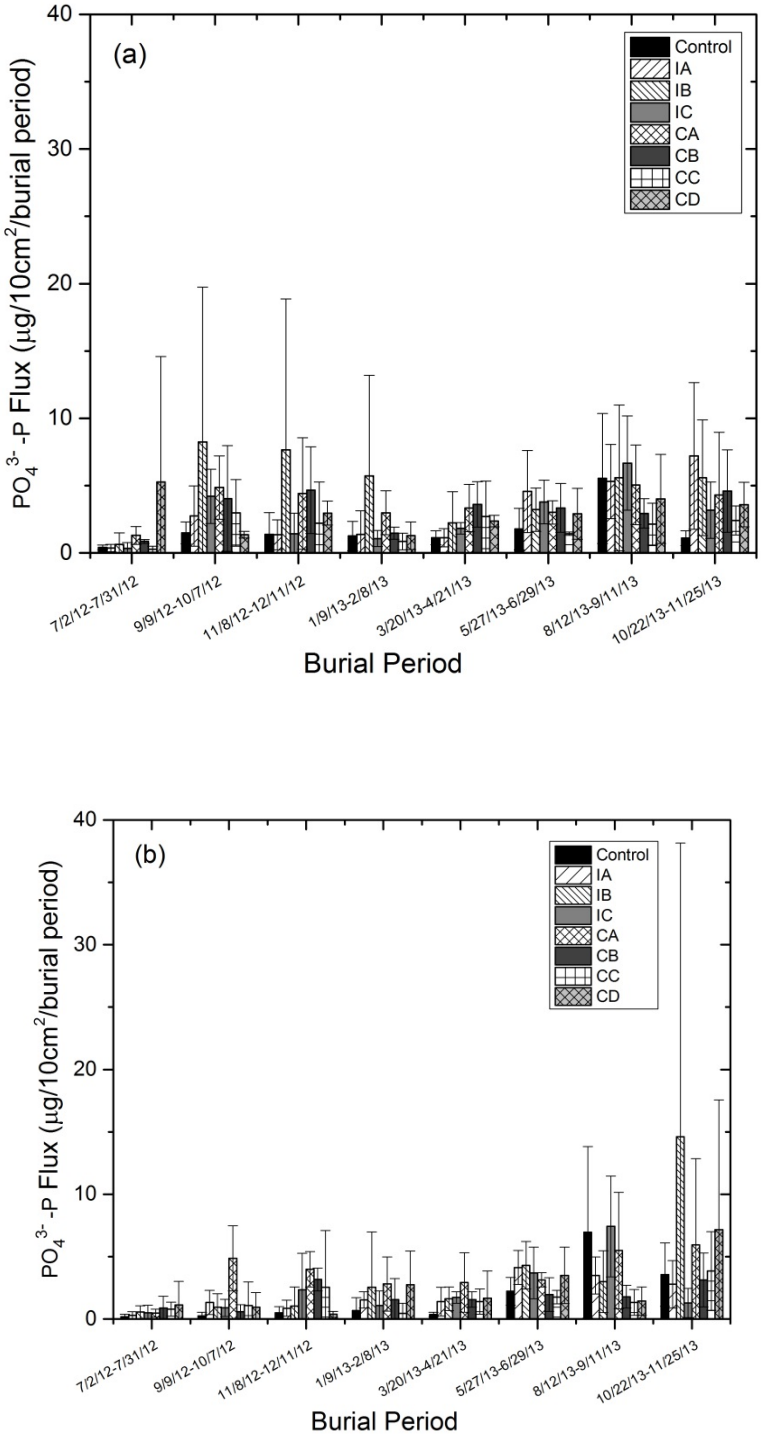


Figure 2.20. Mean phosphorus (PO_4^{3-} - P) flux measured using PRS^{TM} probes for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

Sulfur

Treatment, time, and depth ($p = 0.0062$, $p < 0.0001$, and $p < 0.0001$, respectively) had significant effects on sulfur flux. The effect of harvest treatment on mean sulfur concentration can be seen in Figure 2.21. Based on the Tukey-Kramer analysis, sulfate flux for clearcut C (alternative BMP) is significantly greater than the control and intermediate treatments. The Tukey-Kramer analysis indicated that at the first and seventh burial periods, sulfate flux was significantly less compared to the remaining burial periods, and the greatest flux occurred during the fifth burial period (3/20/13 – 4/21/13). The significant effect of depth on phosphorus flux indicated that flux at the 30 cm depth was significantly greater than the flux at the 10 cm depth. The p-value for the interaction between treatment type and time indicates that it is not significant for sulfur; however, the Tukey-Kramer analysis indicated that the intermediate and clearcut treatments are no longer significantly different than the control after eight months of monitoring (after the fifth burial period) (Figure 2.22). The Tukey-Kramer analysis for the treatment and depth interaction indicates that in clearcut C (alternative BMP) at depths of10 cm and 30 cm, sulfate flux is significantly greater than the control, intermediate B, and intermediate C treatments. The time x depth interaction ($p = 0.0003$) also had a significant effect (Table 2.7). Sulfur flux followed the common pattern of a large increase in the clearcut treatments between the first and second burial periods (Figure 2.22). During the first, third, and seventh burial periods, the sorption of sulfur was the lowest for all treatments. This pattern coincides with the months were the least amount of precipitation occurred (Figure 2.11). At the 10cm burial depth, clearcut C (alternative BMP) exhibited the greatest flux values for all burial periods with exception for the first burial period (Figure 22.2a).

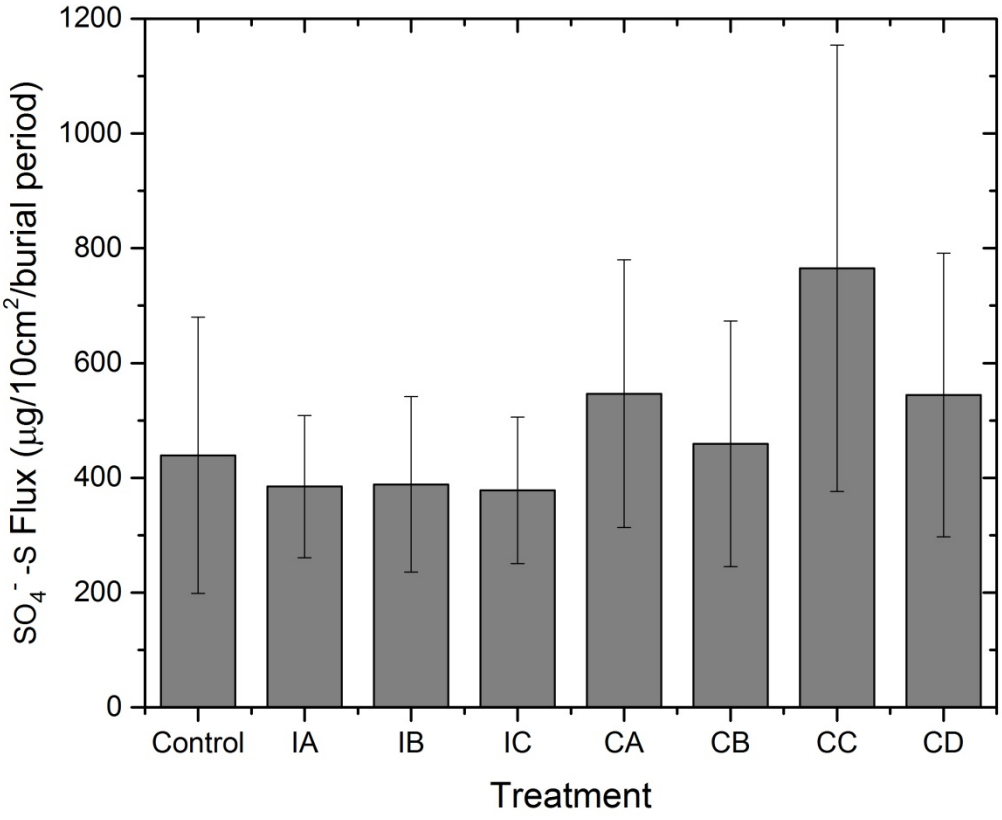


Figure 2.21. Mean sulfur flux measured using PRS™ probes for all harvest treatments. Error bars represent 95% confidence intervals.

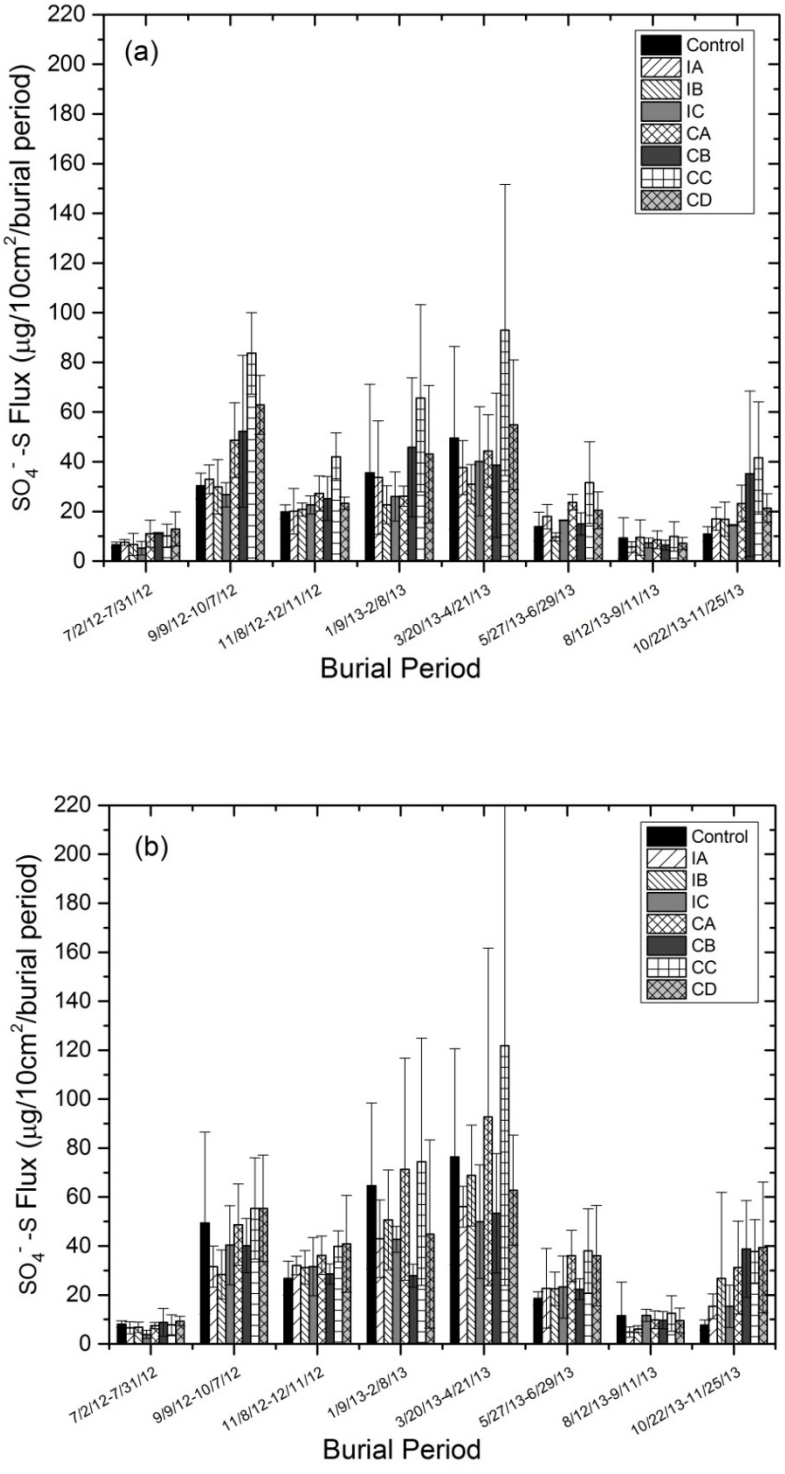


Figure 2.22. Mean sulfur (SO_4^- -S) sorption by PRS probe for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

Aluminum

Time, depth, and the treatment x depth interaction ($p < 0.0001$, $p < 0.0001$, and $p = 0.0002$ respectively) had significant effects on aluminum flux (Table 2.7). According to the Tukey-Kramer analysis, aluminum flux during the second burial period was significantly greater compared to the remaining burial periods; and aluminum flux during the third, fifth, and sixth burial periods were significantly greater than that during the last burial period. The significant effect of depth on aluminum flux indicated that flux was significantly greater at the 30 cm depth than at the 10 cm depth. The treatment by depth interaction indicated that clearcut B (removal of all biomass), clearcut C (alternative BMP), and clearcut D (traditional sawlog harvest) contained the greatest aluminum flux at the 30 cm depth. Aluminum flux increased between the first and second burial periods at both burial depths, and then continued to decrease over time (Figure 2.23). Between the second and sixth burial periods (September, 2012-June, 2013), at the 10cm burial depth, Al^{3+} flux was nominally greater in the clearcut treatments compared to the control and intermediate treatments (Figure 2.23a). Moreover, on average, clearcut A (Missouri's BMP) nominally contained the greatest flux values at the 10 cm depth. At the 30cm depth, similar patterns occurred with the clearcut treatments having greater flux values; however, the control treatment demonstrated nominally greater flux values than the intermediate treatments (Figure 2.23b). Between the second and sixth burial periods, Al^{3+} flux was nominally greater in the clearcut D (traditional sawlog harvest) treatment at the 30 cm depth.

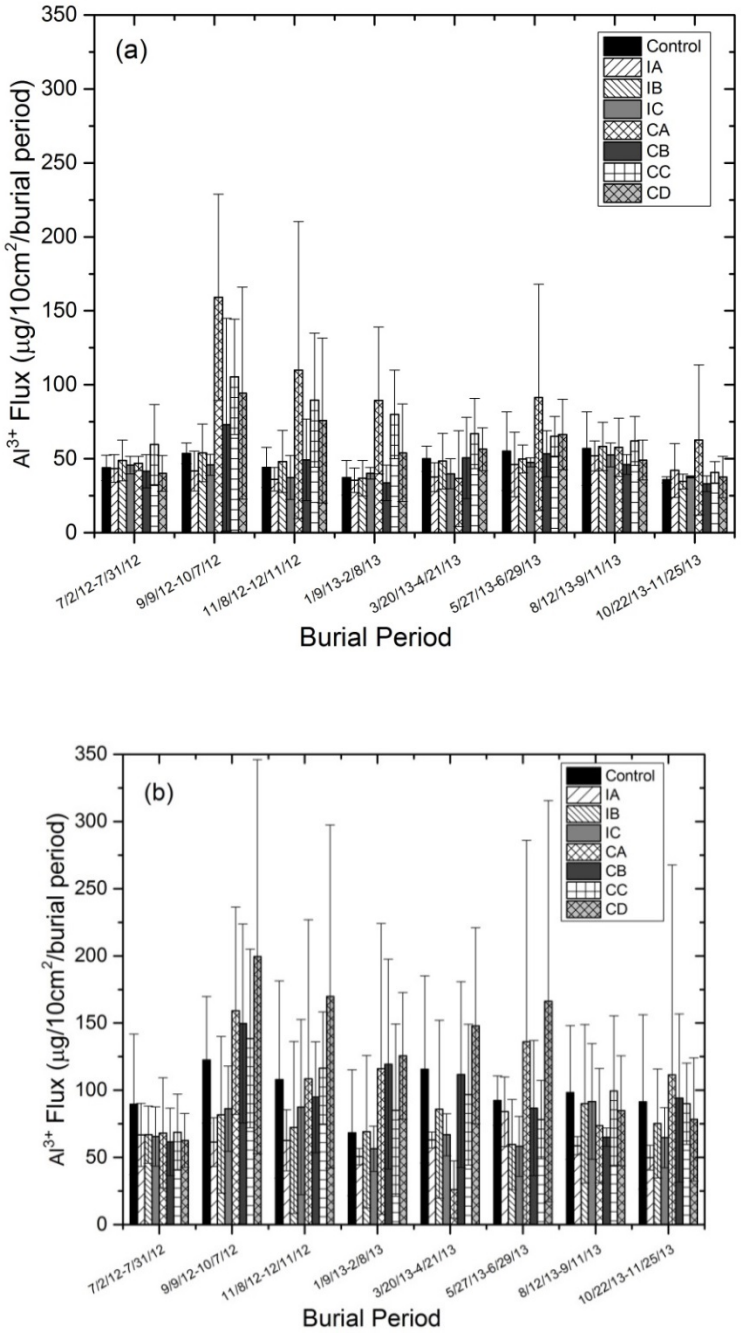


Figure 2.23. Mean aluminum (Al^{3+}) sorption by PRS probe for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

Iron

Harvest treatment, time, and depth ($p = 0.0170$, $p < 0.0001$, and $p < 0.0001$ respectively) had a significant effect on iron flux. The effect of treatment type on mean iron flux can be seen in Figure 2.24. The Tukey-Kramer analysis indicated that iron flux in clearcut C (alternative BMP) and clearcut D (traditional sawlog harvest) are significantly greater than the control and intermediate treatments. The Tukey-Kramer analysis indicated that at the fifth, sixth, and seventh burial periods, iron flux was significantly greater compared to the remaining burial periods; with the greatest flux occurring during the fifth burial period (3/20/13 – 4/21/13). The significant effect of depth on iron flux indicated that the flux at the 30 cm depth was significantly greater than the flux at the 10 cm depth. The treatment x depth interaction ($p = 0.0039$) and the time x depth interaction ($p = 0.0325$) also had significant effects on iron flux (Table 2.7). During the first five burial periods (July, 2012-April, 2013), at the 10cm burial depth, clearcut treatments demonstrated greater Fe^{3+} flux values than the control and intermediate treatments (Figure 2.25a). The greatest increase in iron flux occurred within the clearcut treatments between the first and second burial period, with clearcut C (alternative BMP) containing the nominally greatest flux value. On average, Fe^{3+} flux values decreased within the treatments over time at the 10 cm depth. Within the 30cm burial depth, Fe^{3+} flux values were nominally greater in the clearcuts at each burial period (Figure 2.25b). However, unlike the 10 cm depth where flux values decreased over time, Fe^{3+} increased significantly in the clearcut D (traditional sawlog harvest) treatment during the last four burial periods (March, 2013-November, 2013).

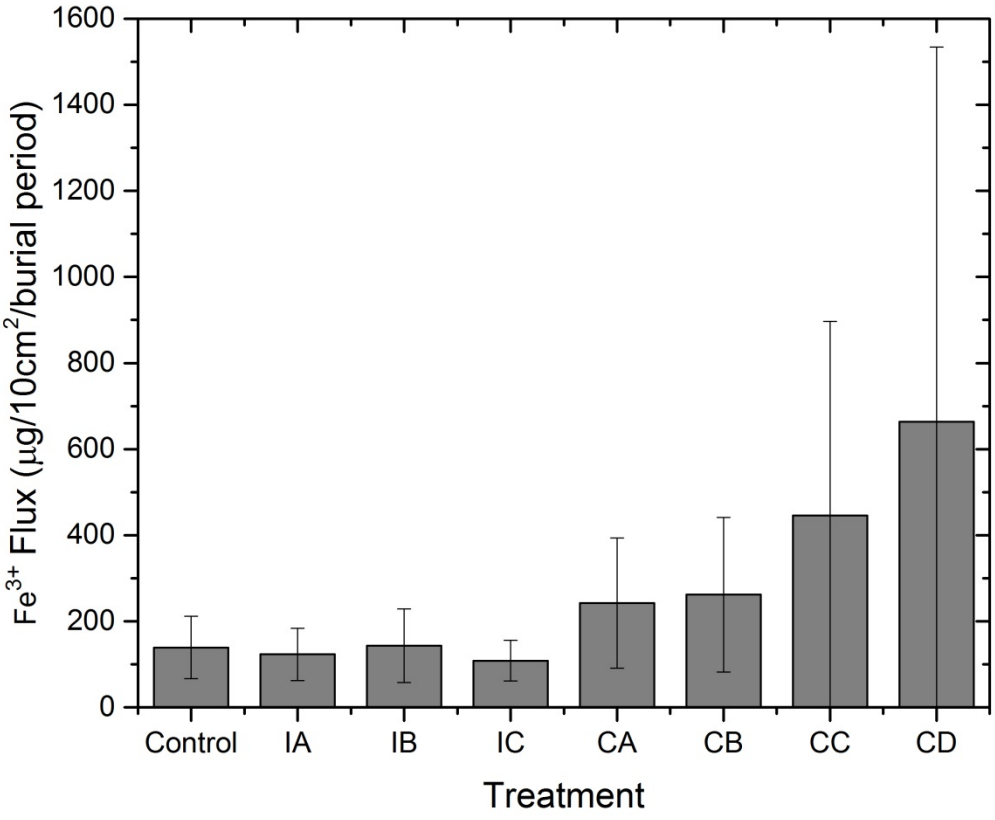


Figure 2.24. Mean iron (Fe^{3+}) flux measured using PRS™ probes for all harvest treatments. Error bars represent 95% confidence intervals.

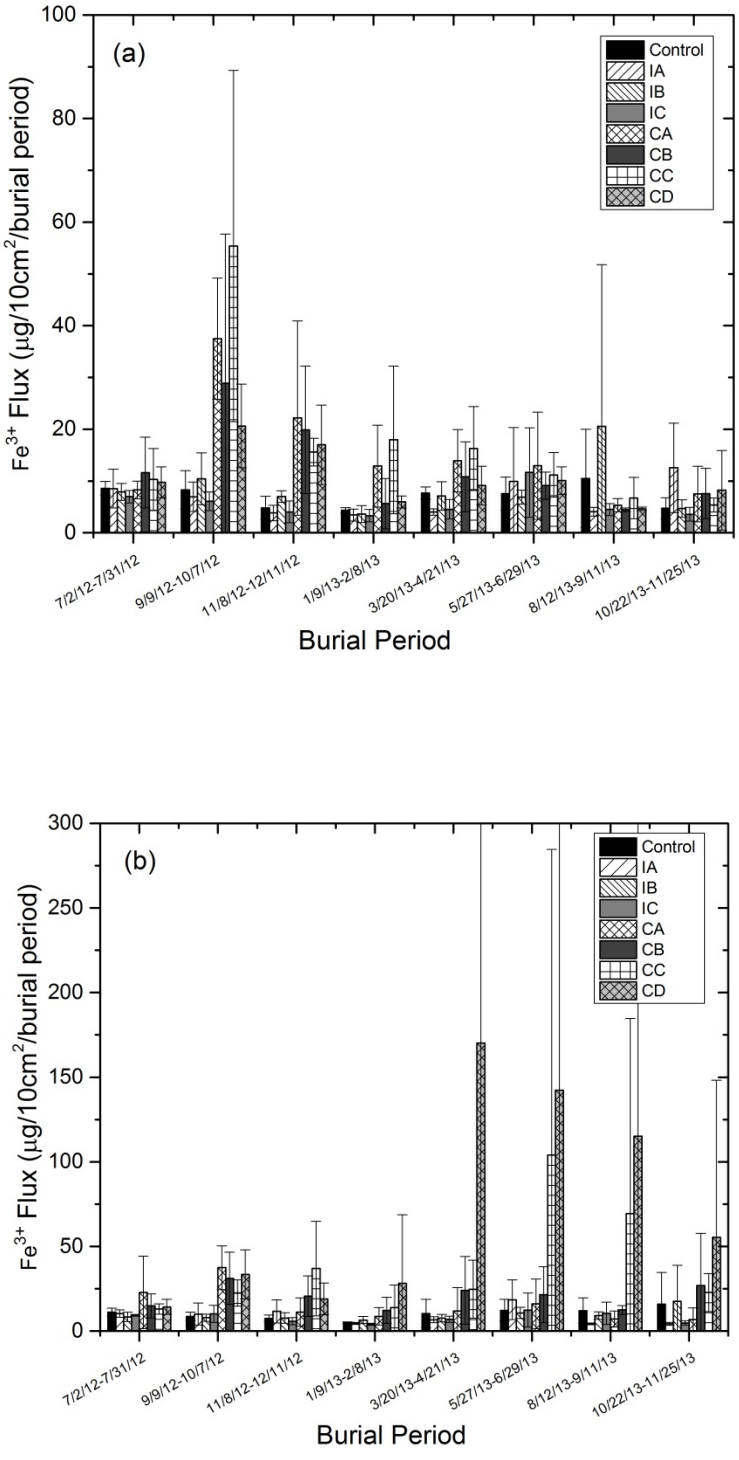


Figure 2.25. Mean iron (Fe^{3+}) sorption by PRS probe for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

Manganese

Treatment and time ($p = 0.0092$ and $p < 0.001$), along with the treatment x time interaction ($p = 0.0094$) and the time x depth interaction ($p = 0.0095$) had significant effects on manganese flux (Table 2.7). The effect of harvest treatment on mean manganese flux can be seen in Figure 2.26. According to the Tukey-Kramer analysis, manganese flux for clearcut C (alternative BMP) was significantly greater than the control, intermediate A, and intermediate B treatments. The Tukey- Kramer analysis indicated that manganese flux during the second burial period were significantly greater than all other burial periods. Moreover, manganese flux during the sixth burial period (5/27/13 – 6/29/13) was significantly greater than the flux during the last burial period (10/22/13 – 11/25/13). The Tukey-Kramer analysis indicated that during the second burial period, clearcut A (Missouri's BMP), clearcut B (removal of all biomass), and clearcut C (alternative BMP) exhibited manganese fluxes significantly greater than the intermediate A and intermediate B treatments during the third burial period; intermediate A and intermediate C treatments during the fourth burial period; control and intermediate A treatments during the fifth burial period; and the control treatment during the last burial period. The manganese flux nominally increased among the clearcut treatments between the first and second burial period at both burial depths (Figure 2.27). Flux values then continued to decrease over time. Clearcut C (alternative BMP) exhibited nominally greater Mn flux during the second burial period at 10cm burial depth. At the 30cm burial depth, during the first through the fifth burial periods (July, 2012-April, 2013), clearcut B (removal of all biomass) contained nominally greater flux values (Figure 2.27b).

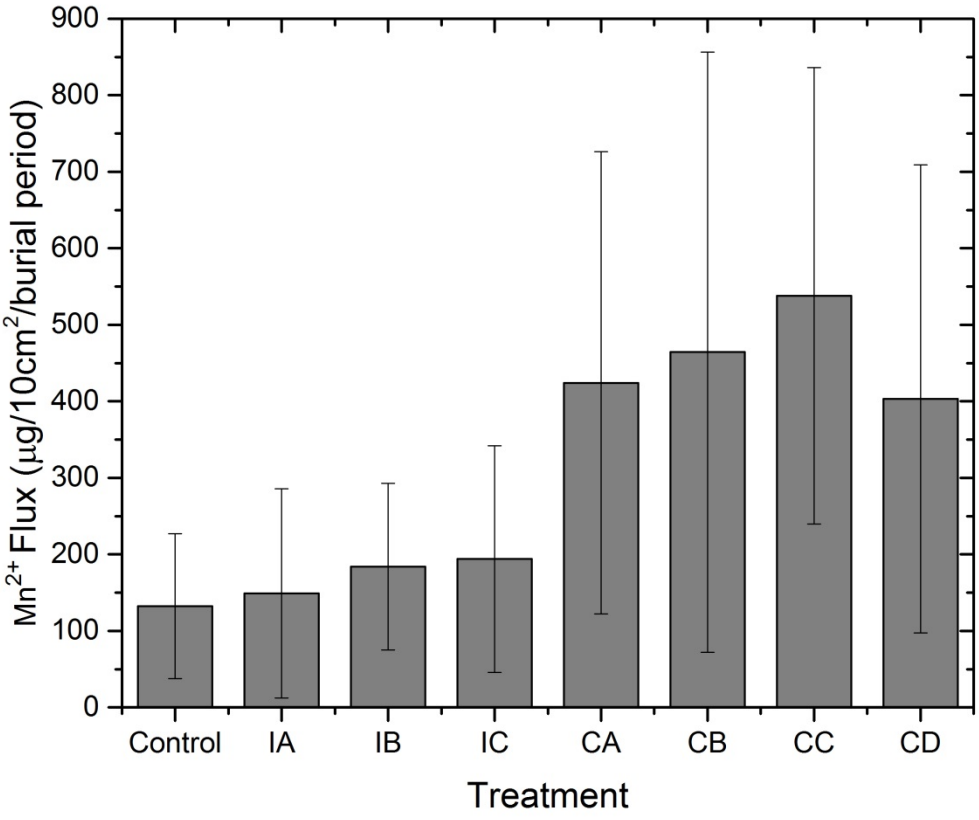


Figure 2.26. Mean manganese (Mn^{2+}) flux measured using PRS^{TM} probes for all harvest treatments. Error bars represent 95% confidence intervals.

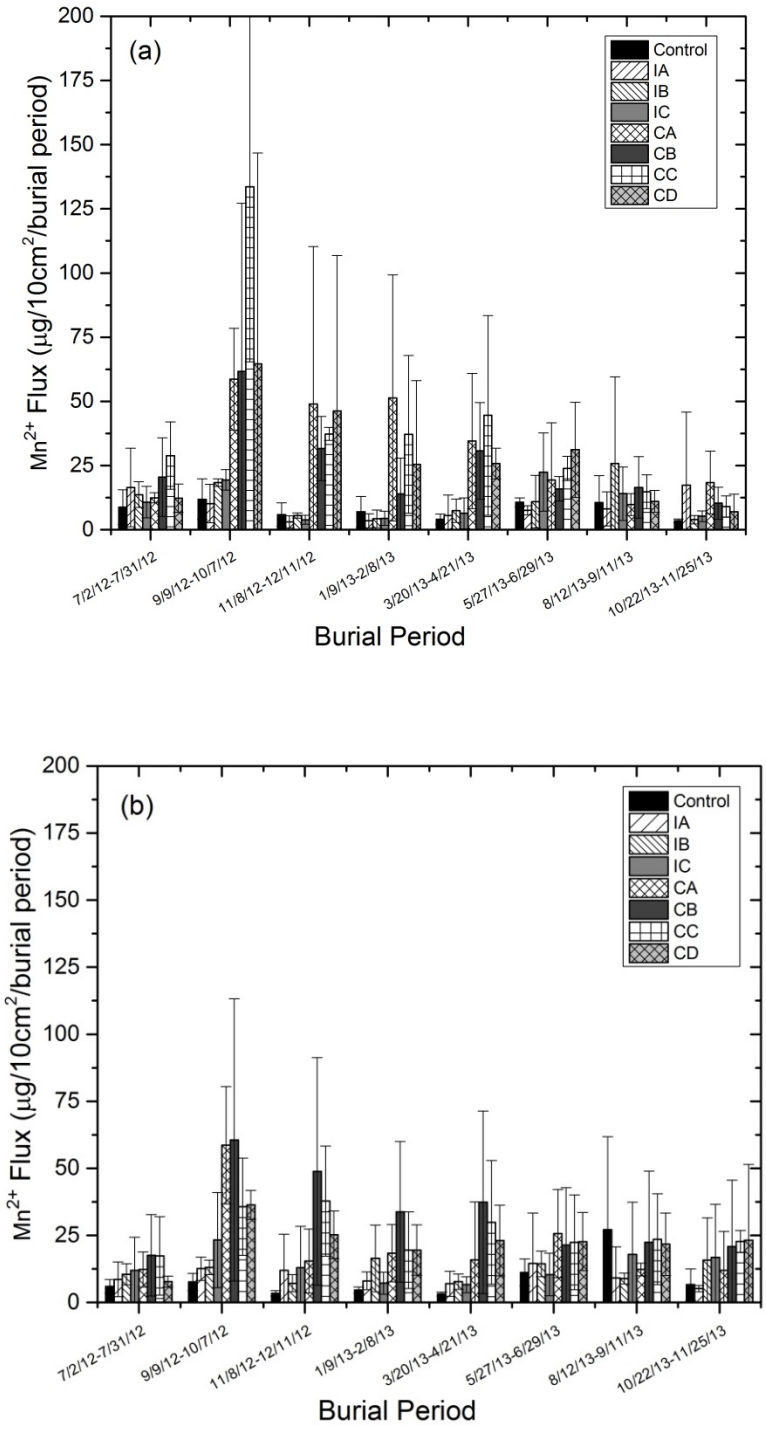


Figure 2.27. Mean manganese (Mn^{2+}) sorption by PRS probe for all harvest treatments over time at (a) 10cm depth and (b) 30cm depth. Error bars represent 95% confidence intervals.

2.5 Discussion

Short-term changes in forest floor nutrient dynamics after harvesting can be attributed to a number of factors, including increases in decomposition and mineralization rates, decreases in plant and microbial uptake, or nutrient leaching from woody debris (Abbott and Crossley, 1982; Burger and Pritchett, 1984; Keenan and Kimmins, 1993; Prescott, 1997). Given the growing interest in forest-derived biomass as a source of bioenergy and associated concerns regarding ecological impacts, it is crucial to study the impacts of operational biomass harvesting on post-harvest nutrient flux and soil quality. However, there are few studies that have assessed the effectiveness of woody biomass harvesting guidelines for sustaining forest productivity. Correspondingly, this study provides important insight on the consequences of potential biomass-utilization management strategies on soil chemistry and nutrient flux.

Bulk Soil Characteristics

Many studies have been conducted on nutrient removal from stand harvesting, and the possible impacts on soil productivity. Most of this previous research was conducted in eastern and southern forests and primarily focused on whole-tree harvesting compared to sawlog only harvesting (Belleau et al., 2006; Bormann and Likens 1979; Tritton et al., 1987). Knowing the total amount of nutrients removed in a thinning operation and the size of the soil pools would facilitate a management plan to replace or retain nutrients (Compton and Cole 1991; Page-Dumroese and Jurgensen 2006). No changes in bulk soil chemical properties were observed in association with the intermediate treatments compared to the control treatment. In a study conducted by Johnson and Curtis, (2001) they found that forest harvesting, on average, had little effect

on soil C and N. Within mixed and hardwood forests, sawlog harvesting and whole-tree harvesting caused slight decreases in soil C and N. Similar patterns can be seen in this study in relation to N, where soil N only slightly decreased in clearcut treatments compared to the intermediate treatments; however, TOC was dependent on harvest treatment (Table 2.6). Several studies indicated that time since harvest is an important variable. In particular, several studies found that soil C and N temporarily increased after sawlog harvesting, apparently as a result of residues becoming incorporated into the soil (Johnson, 1995; Knoepp and Swank, 1997; Pennock and van Kessel, 1997). However, in a study conducted by Belleau et al. (2006) slash treatments had little immediate effect on nutrient dynamics in the 0-10cm mineral soil. But they observed higher exchangeable acidity values under whole-tree harvesting compared to sawlog only. However, mineral soil changes in acidity after whole-tree harvesting may reflect complex interactions between slash loads and decomposition, vegetation uptake, and disruption of root networks induced by harvesting. The interaction between depth and harvest treatment had a significant effect on Ca^{2+}, Mg^{2+}, sum of exchangeable base cations, effective cation exchange capacity (ECEC), base saturation (BS), and total organic carbon (TOC) (Table 2.4). This interaction demonstrated that concentrations were significantly greater in the clearcut treatments at the 30-40 cm depth compared to the intermediate treatments at the surface depths; thus indicating that the intense harvests from the clearcuts could cause downward movement of base cations out of the root zone. Therefore, this might be problematic for future soil quality and forest productivity.

Nutrient Flux

Nitrogen availability limits growth in more forests in more regions than any other nutrient, and it can be important even when it is not limiting because substantial leaching of nitrate-nitrogen can occur when nitrogen availability exceeds plant uptake (Fisher and Binkley, 2000). The NH_4^+ -N and NO_3^- -N fluxes, measured with PRS^{TM} probes in this study, were consistent with values reported elsewhere (Hangs et al., 2004; Huang and Schoenau 1997; Johnson et al., 2001). Total nitrogen and nitrate flux was found to be significantly greater in the clearcut treatments relative to the control and intermediate treatments. Moreover, total nitrogen and nitrate-N were elevated in the 30 cm sampling depth, indicating potential loss of N from the rooting zone. However, the elevated flux approached background levels (i.e. fluxes observed in the control sites at comparable burial periods) after 12 to 14 months of harvest; therefore suggesting the *assart* effect occurring after harvest is relatively short-lived. Nutrient flux through the soil profile at depths of 10 and 30 cm were minimally altered by intermediate treatments. In instances where nutrient flux was elevated due to disturbance and slash deposition associated with the intermediate harvesting treatments, fluxes returned to background levels within four to six months after harvest. Additionally, there was no significant effect of treatment or treatment x depth on total N content in the bulk soils. The significantly greater increase of ECEC in clearcut B, clearcut C, and clearcut D could enhance nitrate leaching through the soil profile. The increase in soil N availability following clearcut harvesting treatments may be primarily attributed to the lack of N uptake by vegetation (due to harvesting), thereby leading to increased leaching throughout the soil profile. Within the nitrogen cycle, much of the ammonium produced in soils is oxidized to nitrite and then to nitrate through nitrification. This process could account for the low amounts of

ammonium flux, and for a higher amount of nitrate flux. Furthermore, ammonium has the potential to be absorbed onto cation exchange sites (which are negatively charged sites that arise from irregularities in the structure of clay minerals, such as broken edges and isomorphic substitution) and from dissociated organic acids (Essington, 2004; McFee and Kelly, 1995).

Soil nutrients such as calcium, potassium, and magnesium are essential for plant growth and development. Greater removals of woody biomass for bioenergy thus raise concerns about whether adequate levels of nutrients can be maintained to protect forest productivity. It is suggested that calcium is the dominant cation in most forest soil solutions, and thus, is most likely to become depleted in the long term (Boyle et al., 1973; Mann et al., 1988; Federer et al., 1989). However, the major exceptions are found in soils with pH values below 4.5, where dissolved aluminum ions become important (Fisher and Binkley, 2000). The increase in nitrate concentrations results in increases in cation concentrations. In this study, soil pH ranged from 4.0 to 4.5 and, while not significantly influenced by treatment, calcium flux was nominally greater in clearcut treatments and spikes of aluminum flux were also noted in the clearcut treatments. In terms of long-term depletion, Federer et al., (1989) concluded that the combination of leaching loss and whole-tree harvest at short (40 year) rotations could remove roughly 50% of biomass and soil calcium in only 120 years. The nutrients potassium and magnesium are also subject to depletion by leaching and harvest removal, although not as severely as calcium. In this study, potassium and magnesium showed elevated flux values at the 10 cm depth of the clearcut treatments relative to the control and intermediate treatments throughout time. However, the elevated leaching of potassium and magnesium was relative short (1 to 1.5

years). This increase of base cations along with the increase in base saturation at the 0-10 cm depth in clearcut A could indicate that base cations are replacing aluminum from the surface; resulting in the increase in aluminum at the 10-20 cm depth. Since the interaction between treatment and depth had an effect on extractable quantities of individual base cations, the sum of exchangeable base cations, and percent base saturation in the bulk soil, there is significant evidence of base cation leaching at deeper soil depths. This continued downward movement of base cations, particularly leaching below the root zone, warrants further and long-term monitoring.

Harvest treatment type also had a significant effect on sulfur, iron, and manganese. Since sulfate is a major anion in solutions specifically adsorbed on oxides, free sulfate in the soil can either be up taken by plants or microbes, absorbed in the soil, or leached from the rooting zone of the forest (Fisher and Binkley, 2000). Sulfate flux in the clearcut C (alternative BMP) was significantly greater than the sulfate flux in the control and intermediate treatments. Moreover, sulfate flux was greater in the 30 cm depth; therefore, more sulfur is leaching from the rooting zone in the clearcut treatments as compared to the intermediate treatments. Since plant roots and microbes excrete organic acids into soils, and organic acids leach from forest litter, the solubility of micronutrients such as iron increase due to the acids chelating metals (Hue et al., 1986). Iron is needed in plants for redox systems, and even though oxidized iron (Fe^{3+}) has a low solubility naturally, organic chelates can increase iron solubility by several orders of magnitude (Lindsay, 1979). Since iron flux was significantly greater in clearcut C (alternative BMP) and clearcut D (traditional sawlog harvest) than the control and intermediate treatments, the solubility of iron is greater in the clearcut treatments and is

not be taken up by plants as much as the intermediate treatments. Moreover, the increase of iron in the subsoil compared to the surface indicates that the increase of base cations released from residue at the surface is displacing iron from the surface and causing downward movement. Manganese flux was similarly affected by harvest treatment type; however flux in the clearcut C (alternative BMP) was only significantly greater than intermediate A and intermediate B. Manganese is also needed for redox systems; however manganese solubility increases as pH decreases (Fisher and Binkley, 2000). Since manganese flux values returned to background levels about 8 months after harvest, leaching below the root zone is not a concern, and thus does not warrant further and long-term monitoring.

Factors impacting nutrient flux

Competition for Ion Adsorption

Ion adsorption by the PRS probes can be affected by competition, both biologically and chemically when the probe is placed in the soil. For example, competition from nutrient conversion by microorganisms will affect the supply of available nutrients to the membrane for adsorption (Giblin et al., 1994; Subler et al., 1995). Furthermore, competition with the plant roots in the control and intermediate treatments is more severe (due to more trees standing) compared to the clearcut treatments; thus indicating why nutrient flux was lower for these treatments compared to the clearcuts. In a study conducted by Hangs et al. (2004), PRS^{TM} probes were used to quantify differences in soil N supply rate between different vegetation management treatments and the relationship of this N availability to early growth of conifer seedlings in boreal forests. Nitrate and total dissolved inorganic nitrogen supply rates were larger in

vegetation management treatments (harvested) than in the control plots (non-harvested) due to the removal of trees and thus the lack of N uptake by unharvest vegetation. A study by Johnson et al., (2007) showed that the presence of plants can have a positive or negative influence on the level of nutrient availability that is measured by the PRS^{TM} probes; however, the degree of influence appeared to be dictated by the type of soil and differed by nutrient. The physical and chemical properties of the membrane and soil are also important factors influencing flux of ions from the soil to the PRS^{TM} probes. Interference from other ions can lead to differences in adsorption (Drohan et al., 2005). For example, Qian and Schoenau (2002) reported that in soils in which more Ca is adsorbed by the membrane, there may be less adsorption of K and NH_4^+. In a study conducted by Drohan et al., (2005) they concluded that the sheer quantity of several ions such as Ca, Mg, and S in the soil could out-compete lesser ion quantities on the probe due to microbial interactions at the probe-soil interface.

Residue retention

Slash retention is a primary factor that affects post-harvest nutrient stocks. In a study conducted by Klockow et al. (2013), which looked at the impacts of post-harvest slash on nutrient stocks, the stocks of biomass carbon, and nutrients, including N, Ca, K, and P in woody debris were greater in all harvest treatments compared to the unharvested control. However, Klockow stated that given the high levels of slash retained within all slash retention treatments, it appeared difficult to retain a precise amount of slash following a harvest or to identify an ideal level for retention in harvested sites. Residue retention levels were analyzed by Dr. John Kabrick at the study site. Greater retention occurred in treatments where the Missouri BMP and the alternative BMP (leaving tops only) were applied than

when no BMPs were applied. In intermediate treatments, there were no significant differences in residues retained among BMP alternatives, and woody debris levels were the same as the control treatment. Calcium was retained in the greatest quantity followed by nitrogen and potassium. Only small amounts of phosphorus and magnesium were retained. Where the Missouri BMP and the alternative BMP were applied, woody debris and nutrient removals were approximately equal to retention in the woody debris. However, in the absence of a BMP, removals were 1.5 to 2.0 times greater than retention. While nutrients are leached back into the soil through slash left on the ground, future work will need to include an examination of the time required to replace the removed nutrients though atmospheric deposition, woody debris decomposition, and mineral weathering in the soil.

Soil moisture and temperature

Soil moisture and temperature are important factors affecting ion supply to and adsorption on the membrane. Qian and Schoenau (2002) stated that as the moisture content of the soil becomes lower, the diffusion path for adsorption becomes longer and more complex as the large pores are no longer filled with soil solution. Qian and Schoenau (1996) found that NO_3^-, P, K^+, and S adsorption significantly decreased with decreasing moisture content. Similar results were seen in this study, where sorption was lower during the months where little precipitation occurred and thus soil moisture was low (Figures 10, 13, and 18). Furthermore, increases in temperature leads to an increases rate of nutrient accumulation, subsequently increasing the quantity of the nutrient flux during the burial period, which results from microbial conversions as well as more dynamics of nutrient movement toward the membrane (Yang et al., 1991). Temperature

effects were specific to nutrients, which resulted in some nutrients (N, K, P, and S) to decrease in sorption during the winter months.

2.6 Conclusions

Ion exchange resins are a sensitive, biologically meaningful tool to study the behavior or inorganic and organic ions in the forest soil environment. While not always statistically significant, the PRS^{TM} probes were able to detect differences between harvest treatments, at two burial depths, and across time. Given that most of the nutrient fluxes were significantly greater in the clearcut treatments compared to the control and intermediate treatments, these elevations were short-lived (1 to 1.5 years) and approached fluxes observed in the control sites at comparable time periods. However, further research is needed in Ozark soils, and under different harvesting methods in order to compare more results and narrow down possible limiting factors. Based on the results from this experiment, a one-month burial period is likely suitable for detecting relative differences in ion chemistry at similar sites. However, a two-month burial period could be investigated in order to understand the sorption kinetics of resin membranes in nutrient-poor, low-pH, forest soils. Furthermore, some nutrient fluxes continued to move downward in the soil profile, particularly leaching below the root zone. Thus, further research is needed to study long-term monitoring and its effect on soil quality.

The effect of soil moisture and temperature on the probe's effectiveness at adsorbing ions in forest soils was not a dominant factor in interpreting relative differences by depth. Furthermore, since the probes were suitable for detecting relative

differences between depths (for most ions) that contain significantly different physical and chemical characteristics, it is concluded that PRS^{TM} probes would be useful in detecting differences among highly variable forest soils.

The results found in this study indicate that while the data for the intermediate treatments could be interpreted as indicating no need for the use of BMPs during thinning operations, use of the MDC's current BMP for thinning operations or the alternative BMP is still recommended to ensure long-term sustainability in forest ecosystems. Although nutrient flux was greater under the alternative BMP (clearcut C) compared to MDC's current BMP (clearcut A) for most nutrients, an overall view of all data collected indicates that practicing MDC's current BMP or the alternative BMP for woody biomass harvesting has no greater effect on short-term soil nutrient flux and concentrations than a traditional sawlog only harvest.

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Chapter 3: Leaf Litter Decomposition in Forests Harvested for Woody Biomass as Revealed by Solid-State ^{13}Carbon Nuclear Magnetic Resonance Spectroscopy

3.1 Abstract

Litter decomposition plays a major role in the cycling of energy and nutrients in woodland ecosystems. The influence of woody biomass harvest scenarios were investigated during a one year litterbag experiment in an oak-hickory forest of the Missouri Ozarks. Total nitrogen (TN), total organic carbon (TOC), C:N ratio, and percent mass loss of leaf litter material were analyzed and compared amongst eight harvest treatments. Percent mass loss was positively correlated to total nitrogen. Treatment type and decomposition time had a significant effect on TN ($p = 0.0474$ and $p < 0.0001$ respectively). To semi-quantitatively assess how decomposition processes vary in leaf litter material across different harvesting treatments, solid-state ^{13}C nuclear magnetic resonance spectroscopy with cross-polarization and magic-angle spinning (CPMAS-NMR) technique was applied to analyze the organic C dynamics of mixed leaf litter. The type of harvest treatment had a significant effect on the alkyl-C concentration ($p = 0.0411$), and on the aromatic-C concentration ($p = 0.0071$). Significant decreases were seen in the total aliphatic C functional groups amongst clearcut treatments compared to intermediate and control treatments. A significant interactive effect of treatment type and decomposition time was found for the concentrations of the alkyl-C, O-alkyl-C, and aromatic-C functional groups, indicating that the change in concentration of these functional groups with decomposition time was significantly different among the different harvest treatments.

3.2 Introduction

Litter decomposition plays a major role in the cycling of energy and nutrients in woodland ecosystems (Guo and Sims 1999). The litter accumulating on the forest floor provides energy, nutrients, and a living environment to the soil fauna and micro-organisms. Leaf tissue can account for 70% or more of aboveground litterfall in forests with the remainder composed of stems and small twigs (Robertson and Paul, 1999). As leaves are degraded by insect and microbial decomposers, organically-bound nutrients are released as free ions to the soil solution which are then available for uptake by plants. In most forests, leaf litter decomposition is the major source of nutrients for trees. Decomposition refers to processes that convert dead organic matter into smaller and simpler compounds. Decomposition is mainly a biological process carried out by insects, worms, bacteria, and fungi on the soil surface and in the soil. Decomposition processes play an important role in soil fertility in terms of nutrient cycling and the formation of soil organic matter (Bargali et al., 1993).

Buried bag studies investigating the decomposition of leaf litter mixtures is an active research area because it mimics the nature of leaf litter in most forests (Blair et al., 1990) and provides insight to leaf litter interactions during decay (Gartner and Cardon, 2004). Litter decomposition rates have been related to climate, organic composition, and nutrient contents (Moore et al., 1999, McClaugherty et al., 1985). Therefore, litter decay studies have been used to assess the loss of mass and to assess the impact of management on the persistence of forest residues (Ellert and Gregorich 1995). The litter bag technique has been used frequently in many decomposition studies (Lorenz et al., 2004), and is the most appropriate technique available to study organic matter breakdown in

decomposition studies under field conditions (Knacker et al., 2003). This technique involves collecting fresh litter and placing it in mesh litter bags which are returned to the environment for various lengths of time. Subsequently, leaf litter can be removed from the bags and characterized for mass loss, changes in C and N content, and other compositional changes.

The biodegradation of plant litter is greatly influenced by its chemical characteristics (Almendros et al., 2000). In fact, rapid and complete degradation of plant residues is connected with the productivity of the ecosystem and the minimal output of organic leachates. The biodegradability of litter is considered to depend on the concentration of lignin, the chemical composition of plant extractives (phenols, tannins, waxes, resins, etc.) as well as on the quality and quantity of water-soluble sugars and nitrogen compounds. Identification of litter characteristics that are consistently closely related to decomposability has proven surprisingly difficult; however, across a broad range of litter types, the C/N ratio appears to be the best predictor of decay rate (Enriquez et al., 1993; Lorenz et al., 2004). Initial litter N and P contents are often positively correlated with early decay rates (Berg, 2000; Vesterdal, 1999).

High-resolution solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy is a method of characterizing the carbon functional group composition of organic materials using characteristic spin frequencies in oscillating magnetic fields. Research based on NMR has shown the importance of alkyl-C as a source of stable structures contributing to the formation of humic substances (Wilson, 1987; Kogel-Knabner and Hatcher, 1989; Prestion, 1996). Furthermore, NMR is often considered as a technique especially suitable to analyze the aliphatic domain of complex macromolecular materials,

leading to a more apparent differentiation between alkyl-C and O-alkyl-C structures (Aertis 1997; Moore et al., 1999; Prescott et al., 2004). These studies suggest the accumulation of relatively recalcitrant aliphatic polyesters, such as cutins, and other carbohydrate-polyalkyl macromolecules in plants (Nip et al., 1986). Solid state ^{13}CNMR along with cross-polarization and magic-angle-spinning (CPMAS) has been proven useful to provide a description of the total organic chemical composition of complex matrices, such as plant litter (Bonanomi et al., 2013), through capture of the resonance signals of all carbon atoms within the analyzed sample. By analyzing litter samples at different decomposition stages, the changes in the different organic carbon fractions corresponding to different levels of litter decay can be assessed. In particular, the increases in the alkyl-C content (waxes and cutin), as determined by NMR, during decomposition and may be a useful indicator of litter decomposability (Baldock and Preston 1995).

The purpose of the present study was to (1) evaluate the pattern of mass loss and C functional group composition of leaf litter during decay, (2) investigate the effects of timber harvest on subsequent leaf litter decay, and (3) compare ^{13}C-NMR data and C/N ratios as functional indicators of litter quality and predictors of litter decay. It is predicted that litter decomposition on harvested treatments will be significantly more rapid than control sites.

3.3 Materials and Methods

3.3.1 Site Selection and Description

The study site was located at the Missouri Department of Conservation's Indian Trails Conservation Area in the Ozark Highlands of Dent County, Missouri near Salem, MO (37°41'38N; 91 °22'11W). The study site consists of a randomized complete block design with three blocks. The three blocks (i.e. full replications) contain each of the eight treatments being investigated. Subsequently, there are 24 total plots each approximately 4 acres in areal extent. The total area of the study site is 36 ha with each treatment plot ~1.5 ha in size. Plots (*ca*. 60 m width x 245 m length) within each block oriented parallel with the slope, resulting in nearly all plots extending from shoulder slope to footstep landscape positions. Slopes of the study site ranged from 7 to 32 percent and dependent upon replication, had north- and northeast-facing aspects. Within each plot, 4 soil pits (located approximately in the middle of each plot on the backslope landscape position) were dug to a depth of 40 cm.

The species most commonly found on site were white oak (*Quercus alba*), black oak (*Quercus velutina*), post oak (*Quercus stellate*), northern red oak (*Quercus rubra*), and hickory (*Carya spp.*) Hickories occur in the mid and understory and include in order of abundance pignut hickory (*Carya glabra*), black hickory (*Carya texana*), and mockernut hickory (*Carya tomentosa*). Also present are shortleaf pines (*Pinus echinata*), blackgum (*Nyssa sylvatica*), and red maple (*Acer rubrum*).

The soil map unit identified within the boundaries of the timber harvest at Indian Trail Conservation Area is the Clarksville soil series. These soils are a very gravelly silt loam, 15-35% slope, formed in gravelly hillslope sediments over clayey residuum weathered from dolomite (Gilbert, 1971). The Clarksville soil is classified as loamy-

skeletal, siliceous, semi-active, mesic Typic Paleudults, and this soil is commonly mapped in the Ozark Highlands. This is very representative of the soils found in this region (hillslope sediments over residuum). These soils are considered to be extensions of Red-Yellow Podzolic soils into a region of Gray-Brown Podzolic soils (Kabrick et al., 2008). The Clarksville soil is an Ultisol, based upon the less than 35% base saturation in the profile and continued decrease in base saturation with increase in depth. In general, the Clarksville is a well-drained very cherty soil that often has a pale brown silt loam A horizon, the B horizon is typically thicker and has textures ranging from silt loam in the upper Bt to clay in the lower Bt (Miller, 1965).

Two different silvicultural treatments were implemented to the forest stands at Indian Trails Conservation Area: intermediate thinning and clearcut. For the purpose of this study, intermediate thinnings are defined as the selection of crop trees during mid-rotation by harvesting all undesirable trees and processing large tops and small tress into woody biomass after extracting other commercial products. The clearcut treatments were applied to remove the entire over story and begin a new cohort or trees. This study incorporates a variety of eight scenarios that include intermediate thinning, clear-cut, and a control (no harvest). Harvest scenarios for the plots are **(a)** thinning with one of three residue retention scenarios **(i-iii)** or **(b)** clearcutting with one of four residue retention scenarios **(i-iv)**: **(i)** retain in place the tops of one in three harvested trees ≥ 25 cm diameter breast height (dbh) and one in three cut trees < 25 cm in their entirety (i.e., follow Missouri BMP guidelines); **(ii)** retain tops of all harvested trees ≥ 20 cm dbh while removing all biomass for trees between 7.5 and 20 cm dbh; **(iii)** remove all woody biomass for trees > 7.5 cm dbh, including tops; and **(iv)** harvest of trees ≥ 25 cm dbh with

only sawlogs removed from the forest (current harvested practice for the region). The eighth treatment will be a no harvest (control) plot. Each treatment was designed to address different best management practices (BMPs) and the impacts of biomass harvesting on soil nutrients. The intent of these different scenarios is to compare the current harvest practice (clearcutting with removal of sawlogs only) to Missouri's BMPs for residue management in forests harvested for woody biomass. Missouri's BMPs currently recommends that in thinning and commercial harvest using a feller buncher, 1/3 of treetops from sawtimber harvest and 1/3 of the typical size small trees cut on site be left and evenly distributed throughout the harvest area. However, limited knowledge is available about nutrient recycling as it is related to woody biomass harvesting on Ultisol soils in Missouri.

Table 3.1. Harvest treatments investigated. Missouri's woody biomass BMP guidelines state that harvesters should retain at least 1/3 of the tops and small tress felled during operations. All merchantable sawlogs are removed for all treatments.

Treatment	Associated BMP
Clearcut A (CA)	1/3 of tops of sawlog-size trees and 1/3 of small diameter trees left on ground to provide wildlife habitat and nutrients for future cycling
Clearcut B (CB)	Remove all biomass from harvested trees
Clearcut C (CC)	Retain tops of all cut trees ≥ 20 cm dbh; remove boles, tops and limbs of all cut trees ≤ 20 cm dbh
Clearcut D (CD)	Traditional harvest of only sawtimber ≥ 25 cm dbh
Intermediate A (IA) †	1/3 of tops of sawlog-size trees and 1/3 of small diameter trees left on ground to provide wildlife habitat and nutrients for future cycling
Intermediate B (IB)	Remove all biomass from harvested trees
Intermediate C (IC)	Retain tops of all cut trees ≥ 20 cm dbh; remove boles, tops and limbs of all cut trees ≤ 20cm dbh
Control (X)	No harvest or removal of woody residues

† Intermediate thinnings are defined as the selection of crop trees during mid-rotation by harvesting all undesirable trees and processing large tops and small trees into woody biomass after extracting other commercial products.

3.3.2 Soil Sampling and Processing

In July 2012, immediately after harvest (July 2012) and one-year post-harvest (July 2013) soil samples were collected within each plot. Soil samples were collected in 10 cm increments from a 0 – 40 cm depth from each of the four soil pits hand-dug within each plot. A quart sized zip-lock bag was filled with soil from each depth, labeled, and stored in a cooler until the end of the sampling trip. Samples were then air-dried for 48 hours, and then kept in storage. Sub-samples (100 g) from each depth and soil pit within a plot were combined to create a composite soil sample for each plot, thus giving 96 total soil samples (4 depths x 24 sites). Soil samples were ground, passed through a 2mm sieve, and sent to the Missouri Soil Characterization Laboratory (Columbia, MO) and analyzed using methods detailed in the UDSA-NRCS *Soil Survey Laboratory Methods Manual* (Burt, 2004). Standard pipette analysis was used to determine particle size. Soil CEC and exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) were determined using 1 M ammonium acetate (CH_3COONH_4) extraction, ammonium chloride (NH_4Cl) extraction technique, steam distillation, HCl titration and atomic absorption spectrophotometry (CEC-7, method 4B1a1a1a1a1). These effective CEC values were used for statistical analysis and to calculate percent base saturation (BS). Cation exchange capacity was determined by the summation of extractable bases plus the $BaCl_2$-triethanolamine released extractable acidity (EA). Extractable Al was determined using 1 M KCl extraction and inductively coupled plasma – atomic emission spectrophotometry (ICP-AES). Soil pH was measured in 1:1 soil-to-water ratio and 1:2 soil-to-0.01 M $CaCl_2$ salt solutions. Total organic carbon (TOC) and total nitrogen (TN) were determined using dry combustion methods.

3.3.3 Leaf Litter Decomposition Sampling and Processing

The litter bag technique was used to measure leaf litter decomposition over the course of one year (December 1, 2012 to November 30, 2013). Litter bags (12 x 20 cm width by length) were made of Nitex mesh with a mesh size of 1-mm. Mesh size is generally chosen to optimize access by all organisms to the litter while minimizing excessive particle loss. According to Robertson and Paul (1999), 20 x 20 cm bags with a 1-2mm mesh size are commonly employed. Fresh leaf litter was collected from each of the three control sites in Fall 2012 and air-dried for 24 to 48 hours. Leaf litter, 3-5 g (air-dried weight), was inserted into each bag and sewn shut (Figure 3.1). A total of 12 bags were placed into the litter layer of the forest floor, in the proximity of the nutrient flux sampling areas on each site, for a total of 288 bags. Every 90 days, three bags were collected from each site, dried and the leaf litter material was weighed to determine the amount of mass lost. Air-dried samples were ground using a Wiley mill to pass through a 0.85-mm sieve. Samples were analyzed for total organic carbon (TOC) and total nitrogen (TN) content using a LECO combustion C and N analyzer (Karberg et al., 2008; Robertson and Paul, 1999).

Figure 3.1. Leaf litterbag embedded into the forest floor on all treatments.

3.3.4 Solid State ^{13}C-Nuclear Magnetic Resonance Analysis

Due to the high cost of instrument time, ^{13}C NMR spectra of leaf litter material were collected from a composite of the three leaf litter bags collected at the 6 month and 12 month burial periods (one composite leaf litter sample x 24 sites x 2 time periods; n = 48). A total of three time zero ^{13}C NMR spectra were also collected as a reference point. Approximately 200-mg of oven-dried and ground leaf sample was packed in a 7-mm zirconia rotor with a Kel-F cap. The rotor was spun at 4.7 kHz at room temperature. Solid ^{13}C-NMR was performed on a Bruker Avance DRX300 widebore NMR spectrometer (Bruker, Billerica, MA) equipped with a 7-mm CPMAS probe. The operating frequency was 300.13 MHz for proton and 75.48 MHz for carbon, respectively. Cross-polarization with magic angle spinning and total sideband suppression (CPMAS-TOSS1) was acquired with 1 ms contact time and 2.03 s repetition delay (Dixon et al., 1982). Spectra were collected at a spin rate of 4.7 kHz, a recycle delay (relaxation time) of 1s and a contact time of 1-ms. The ^{13}C chemical shift was externally referenced to the carbonyl carbon signal of glycine at 176.03ppm. The location of an NMR signal in a spectrum is reported relative to the reference signal from standard. To provide an unambiguous location unit in the spectrum, the frequency differences (Hz) are divided by the spectrometer frequency (MHz). The resulting number is very small; thus, it is multiplied by 10^6, giving a locator number called Chemical Shift, having units of parts-per-million (ppm). A minimum of 5000 scans were collected for each sample. Line broadening of 50 Hz was applied to the data before Fourier transformation and baseline correction. Bruker XWIN-NMR version 3.6 software was used for data collection and initial processing.

Spectral areas were calculated by integration (Xing et al., 1999) using the regions defined by Baldock and Preston (1995) and Lorenz et al. (2000) as a guide (Table 3.2) and calculated as percentages of the total spectral area (0-185 ppm). Total aliphatic-C (0-110 ppm) was subdivided into alkyl-C (0-45 ppm), O-alkyl-C (45-90 ppm), and di-O-alkyl-C (90-110 ppm). Total aromatic-C (110-165 ppm) was subdivided into aryl-C (110-140 ppm) and phenolic-C (140-165 ppm). Total carbonyl-C was defined as the carboxyl-C (165-185 ppm). The proportion of each functional group, as determined by integration of the NMR spectra, was converted to leaf litter concentrations (g kg^{-1} leaf litter) by multiplying the functional group proportion by the TOC concentration of leaf material (Veum et al., 2013).

Table 3.2. ^{13}C nuclear magnetic resonance (^{13}C NMR) chemical shift (ppm) assignments used in this study from Baldock and Preston (1995) and Lorenz et al. (2000).

Assignment	**ppm**	**Representative Organic Functional Groups**
Total aliphatic-C	**0-110**	
Alkyl-C	0-45	Unsubstituted, non-polar aliphatic-C
O-alkyl-C	45-90	C-O, C-N bonds in carbohydrates, alcohols, esters and amino acids
di-O-alkyl-C	90-110	O-C-O anomeric-C
Total aromatic-C	**110-165**	
Aryl-C	110-140	Aromatic-C not substituted by O or N
Phenolic-C	140-165	O- and N-substituted aromatic groups: phenolic OH, aromatic NH_2
Total carbonyl-C	**165-185**	
Carboxyl-C	165-185	Carboxyl-C (COO), may overlap with phenolic-, amide-, and ester-C

3.3.5 Statistical Analysis

All data analysis was carried out in SAS^{TM} Statistical Software Version 9.4 (SAS Institute Inc., 2008, Cary, NC, USA). Dynamics of TOC, TN, C/N ratio, mass percent loss, ^{13}C NMR functional groups were statistically evaluated by PROC GLIMMIX, considering decomposition time (continuous variable) and harvest treatment (eight treatments), as well as their interaction, as independent factors (Appendix B.2). Results were based on arithmetic means (± standard error). 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). In order to account for repeated measures over time, several covariance correlation structures were tested; auto regressive order 1 covariance structure [*ar(1)*] and the heterogeneous autoregressive order 1 covariance structure [*arh(1)*]. The *ar(1)* structure was used with the proportion values for the C functional groups. The *arh(1)* structure was alternatively used in cases where the homogeneity of variance assumption was not met (dependent variables: concentration values for the C functional groups, TOC, TN, and MPL). The *geometric* distribution with the *log* link function was selected for TOC. The *lognormal* distribution with the *identity* link function was selected for C/N ratio. The *tcentral* distribution with the *identity* link function was selected for mass percent loss. The carbon functional groups and TN used a *normal* distribution with the *identity* link. The Pearson linear correlation coefficient was evaluated using PROC CORR for all variables.

3.4 Results

3.4.1 Relationships among leaf litter parameters

Immediate post-harvest soil properties at a depth of 0-10 cm are displayed in Table 3.3 for all of the eight harvest treatments. Soils found at the study location have an inherently low cation exchange capacity and extractable bases, and are considered acidic (pH = 4.2).

Within the leaf litter material, most of the parameters measured in this study along with the concentrations of organic carbon functional groups determined by ^{13}C-CPMAS NMR were significantly correlated with each other across time (Table 3.4). Total leaf organic C (TOC) was highly and positively correlated with the alkyl-C ($r = 0.87$, $p < 0.0001$), O-alkyl-C ($r = 0.94$, $p < 0.0001$), Di-O-alkyl-C ($r = 0.93$, $p < 0.0001$), and phenolic-C functional groups ($r = 0.88$, $p < 0.0001$). Less positive significant correlations occur with TOC and aromatic-C ($r = 0.66$, $p < 0.0001$) and carbonyl-C functional groups ($r = 0.43$, $p < 0.001$). Similar positive relationships were found with C/N ratio and the NMR concentrations. While the C/N ratio was positively and significantly correlated with TOC ($r = 0.76$, $p < 0.0001$), it was negatively correlated with total nitrogen ($r = -0.91$, $p < 0.0001$) and mass percent loss ($r = -0.56$, $p < 0.0001$). Total nitrogen (TN) was negatively and significantly correlated with ^{13}C NMR organic C functional groups and with TOC, except the carbonyl-C functional group ($r = 0.35$, $p < 0.01$). Total nitrogen was significantly and positively correlated with the percent mass loss (PML) ($r = 0.72$, $p < 0.0001$). Only three of the ^{13}C-CPMAS NMR organic C functional groups (Di-O-alkyl-C, phenolic-C, and carbonyl-C) had a significant correlation with the percent mass loss of leaf litter material. A significant negative correlation was found in the di-O-alkyl-C

region ($r = -0.29$, $p < 0.01$) and the phenolic-C region ($r = -0.33$, $p < 0.01$), while a significant positive correlation was found in the carbonyl-C region ($r = 0.41$, $p < 0.001$).

Table 3.3. Mean values for select soil properties immediately post-harvest from 0 to 10 cm depth for the given harvest treatments. Standard errors are stated in parentheses. Refer back to Table 3.1 for treatment descriptions.

Treatment	Soil Texture	Clay	TOC	TN	pH	ECEC	NH_4Cl Extractable Bases			
		%	g /kg	g/kg	salt	$cmol_c/kg$	$cmol_c/kg$			Sum of
						Bases+Al	Ca	Mg	K	Bases
Control	Silt Loam	13.5 (1.0)	14.7 (0.88)	0.9 (0.08)	4.2	3.2 (0.06)	0.83 (0.59)	0.50 (0.17)	0.17 (0.03)	1.47 (0.07)
Intermediate A	Silt Loam	11.3 (1.3)	15.0 (2.08)	1.0 (0.09)	4.2	2.3 (0.19)	0.47 (0.20)	0.33 (0.12)	0.13 (0.03)	0.93 (0.32)
Intermediate B	Silt Loam	12.1 (0.4)	16.3 (3.18)	1.0 (0.18)	4.1	2.7 (0.32)	0.80 (0.27)	0.43 (0.15)	0.13 (0.03)	1.37 (0.44)
Intermediate C	Silt Loam	12.3 (0.8)	16.7 (0.67)	1.0 (0.05)	4.1	2.5 (0.26)	0.37 (0.03)	0.33 (0.03)	0.20 (0.00)	0.87 (0.07)
Clearcut A	Silt Loam	11.6 (1.0)	18.0 (2.31)	1.0 (0.12)	4.3	3.2 (0.40)	1.27 (0.32)	0.47 (0.03)	0.23 (0.03)	2.00 (0.3)
Clearcut B	Silt Loam	14.4 (2.5)	21.3 (1.86)	1.3 (0.21)	4.3	3.6 (1.0)	1.77 (0.97)	0.73 (0.34)	0.23 (0.03)	2.80 (1.4)
Clearcut C	Silt Loam	12.3 (1.7)	13.3 (21.9)	0.9 (0.08)	4.2	2.8 (0.61)	0.73 (0.29)	0.63 (0.29)	0.17 (0.03)	1.50 (0.6)
Clearcut D	Silt Loam	12.5 (0.9)	14.3 (1.76)	0.9 (0.08)	4.3	2.3 (0.19)	0.77 (0.32)	0.40 (0.15)	0.13 (0.03)	1.30 (0.5)

Table 3.4. Pearson linear correlation coefficients across time and across all treatments for the concentration of the six organic C functional groups determined by ^{13}C NMR (g kg^{-1}), total organic carbon (TOC), total nitrogen (TN), total organic carbon/total nitrogen ratio (C/N), and percent mass loss (PML) of the leaf litter material in mesh bags.

	TOC	**TN**	**C/N**	**PML**
Alkyl-C	0.87***	-0.36*	0.68***	NS
O-Alkyl-C	0.94***	-0.39**	0.64***	NS
DI-O-Alkyl-C	0.93***	-0.69***	0.88***	-0.29*
Aromatic-C	0.66***	NS	0.33*	NS
Phenolic-C	0.88***	-0.63***	0.86***	-0.33*
Carbonyl-C	0.43**	0.35*	NS	0.41**
TOC	-	-0.47***	0.76***	NS
TN	NS	-	-0.91***	0.72***
PML	NS	NS	-0.56***	-

NS; not significant

*** Significant at $p < 0.0001$; ** significant at $p < 0.001$; * significant at $p < 0.01$

Variations over treatment and time were not statistically significant for TOC concentrations (Table 3.5). However, the ANOVA analysis showed that the type of treatment and decomposition time had a significant effect on TN ($p = 0.0474$ and $p < 0.0001$ respectively). When comparing the effect of treatment on TN, clearcut B (removal of all biomass) was significantly lower than the control, intermediate A, clearcut A, and clearcut C treatments (Figure 3.2). When comparing the effect of time on TN, the 3 month and 6 month time periods were significantly different from time zero and the 12 month time period. Concentrations of TN in decaying leaf litter progressively increased during the 12 months of decomposition (Figure 3.3). At the 12 month time period, TN concentrations for clearcut A and clearcut C were significantly greater than that at time zero, 3 months, and 6 months (Figure 3.3). Decomposition time had a significant effect on the C/N ratio ($p < 0.0001$), where all collection periods were significantly different from each other (Table 3.5). The C/N ratio for all treatments significantly decreased from time zero to 12 months, with clearcut A (current 1/3 BMP) showing the greatest decrease followed by clearcut C (alternative BMP) (Figure 3.4). The PML was significantly affected by decomposition time only ($p < 0.0001$), where the 3 month and 12 month time periods were significantly different from time zero and the 6 month time period (Table 3.5). Percent mass remaining of the leaf litter material over the 12 month decomposition period is displayed in Figure 3.4. Intermediate C treatment had the smallest percent mass loss after 12 months of decomposition (11.2%), while the control treatment had the biggest percent mass loss (32.5%) (Figure 3.5).

The Tukey-Kramer grouping for least square means ($\alpha = 0.05$) for TOC, TN, C/N ratio, and PML for leaf litter material over a period of one year decomposition is

displayed in Table 3.6. Total organic carbon contents (g kg^{-1}) were similar for all treatments and showed similar decreases throughout one year of decomposition. Clearcut B treatment (removal of all biomass) showed the greatest decrease, while intermediate A and B treatments were very similar to the control treatment. Total N concentrations showed similar increases for all treatments throughout one year of decomposition. All TN values for the 12 month decomposition were significantly different from the time zero concentrations for all of the treatments except for the clearcut B treatment. Clearcut A (current 1/3 BMP) showed the greatest increase in TN (5.23 g kg^{-1} to 10.67 g kg^{-1}) followed by clearcut C (alternative BMP) (5.23 g kg^{-1} to 10.25 g kg^{-1}). Since clearcut A and clearcut C demonstrated the greatest increase in TN, they also demonstrated the greatest decrease in C/N ratio. Table 3.6 shows that the PML at the 6 month time period for clearcut A is significantly different from the 12 month period for the control, intermediate A, and clearcut C treatments. While the percent mass loss did increase over the one year decomposition period for all treatments, they were not significantly greater at the 12 month period compared to time zero.

Table 3.5. Type 3 Tests of Fixed Effects, evaluating treatment (Trt), time, and the interaction effect on leaf litter properties. Dependent variable includes total organic carbon (TOC), total nitrogen (TN), C-to-N ratio (C/N), and percent mass loss (PML) of leaf litter material. Significant values (p-values <0.05) are placed in bold. TOC was evaluated with a geometric distribution of the data, C/N was evaluated with a lognormal distribution, and mass percent loss was evaluated with a t-central distribution.

	p-values		
	Source		
Analyte	**Trt**	**Time**	**Trt*Time**
TOC	1.0000	0.9142	1.0000
TN	**0.0474**	**<0.0001**	0.1087
C/N	0.4273	**<0.0001**	0.4124
Percent Mass Loss	0.5436	**<0.0001**	0.4922

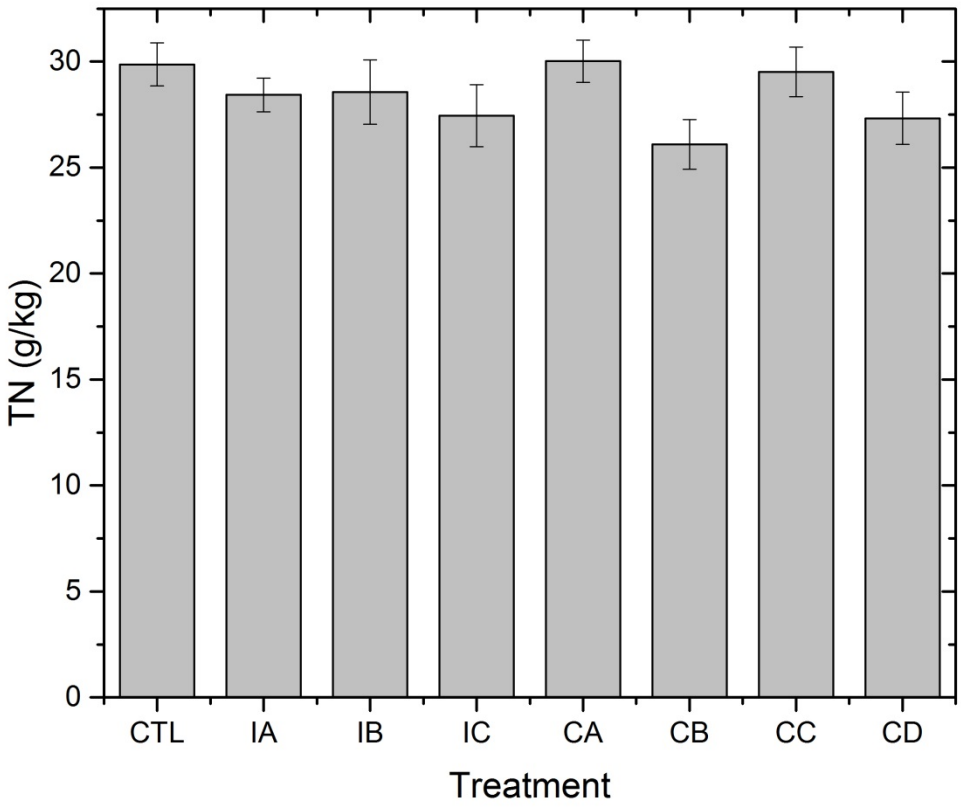


Figure 3.2. Total Nitrogen (TN) concentrations of leaf litter material for each treatment type during the one year decomposition period. Refer back to Table 3.1 for treatment descriptions. Error bars represent standard error.

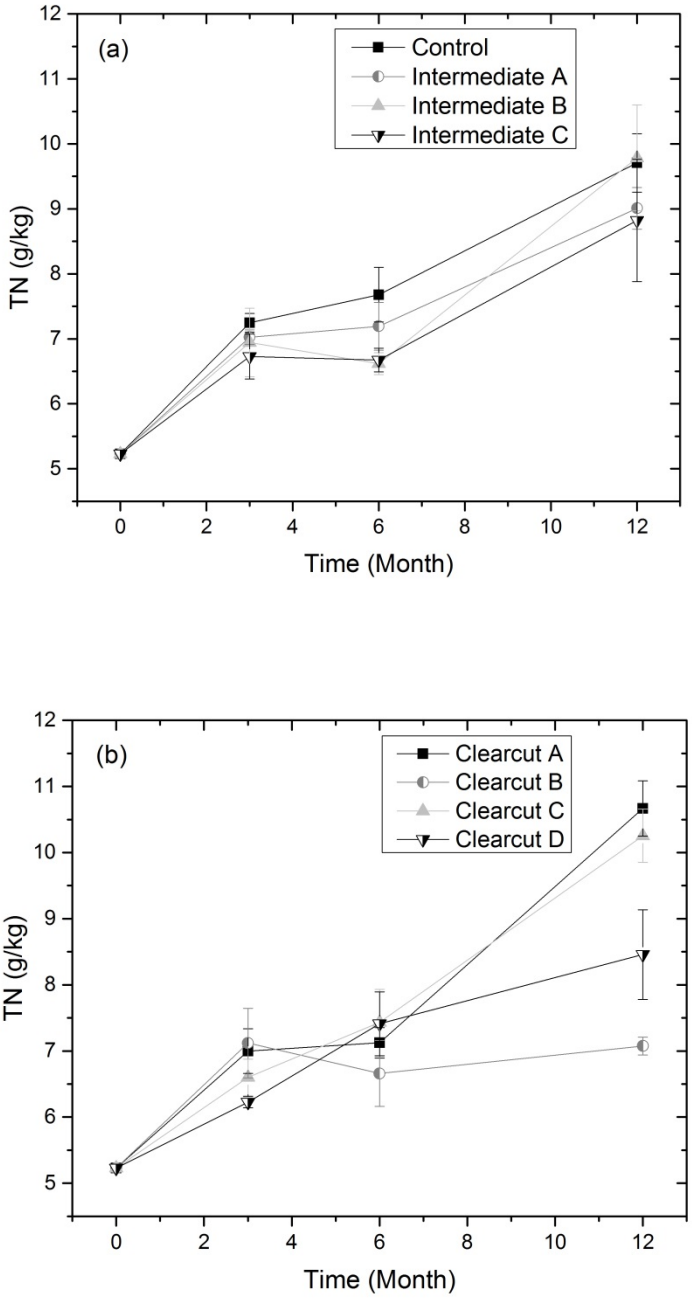


Figure 3.3. Total nitrogen (TN) concentrations of leaf litter material collected at 3, 6, and 12 months: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Time zero represents leaf litter material that was kept in the lab and is used as a reference of the starting leaf material. Refer back to Table 3.1 for treatment descriptions. Error bars represent standard error.

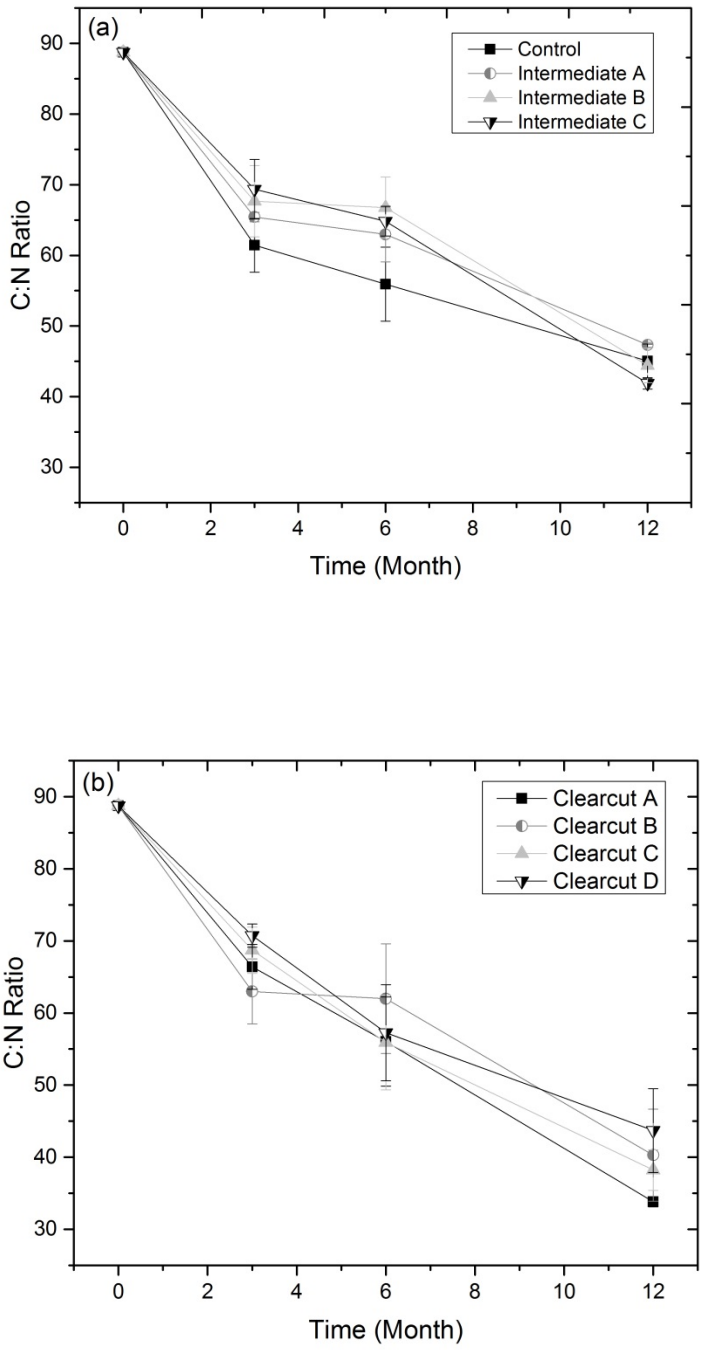


Figure 3.4. C/N ratio for leaf litter material collected at 3, 6, and 12 months: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Time zero represents leaf litter material that was kept in the lab and is used as a reference of the starting leaf material. Refer back to Table 3.1 for treatment description. Error bars represent standard error.

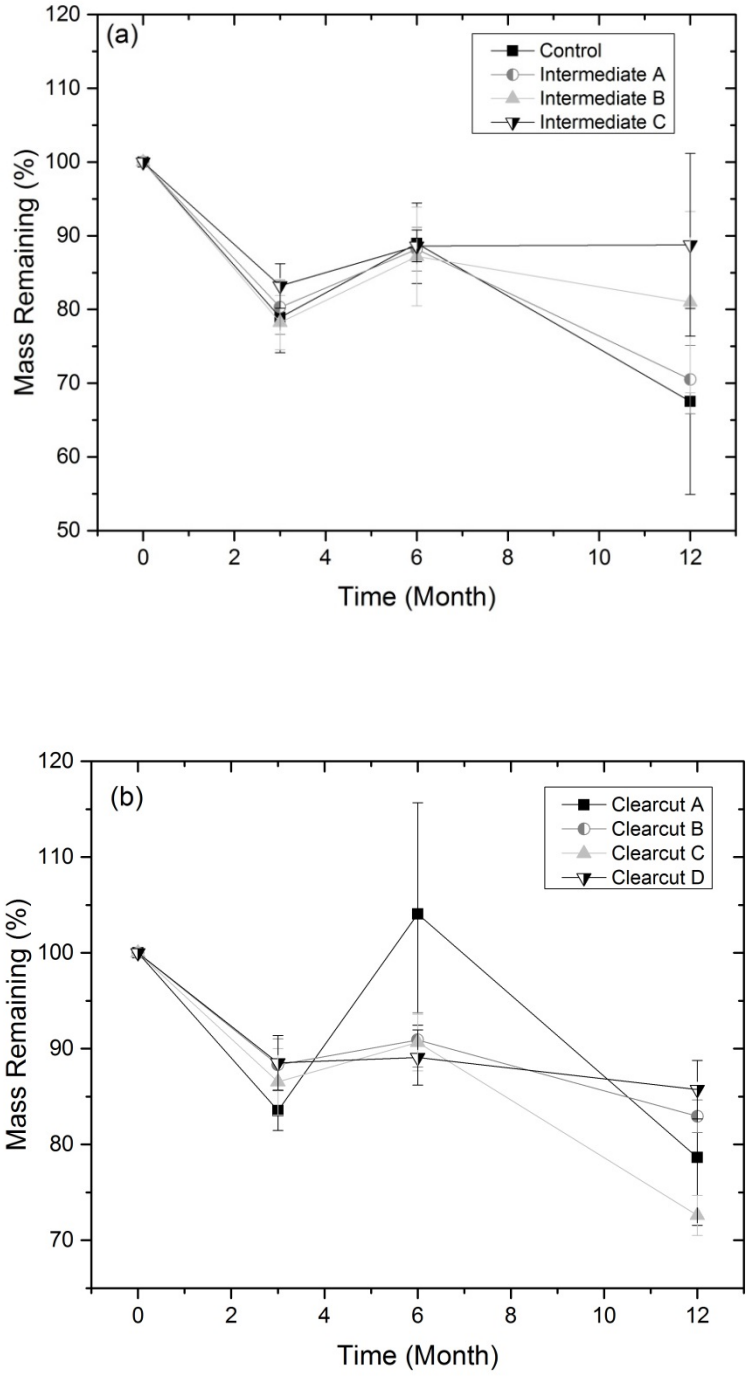


Figure 3.5. Leaf litter mass remaining (%) during decomposition for leaf litter material collected at 3, 6, and 12 months: (a) treatments: control, intermediate A, intermediate B, and intermediate C; (b) treatments: clearcut A, clearcut B, clearcut C, and clearcut D. Time zero represents leaf material that was kept in the lab and is used as a reference of the starting leaf material. Refer back to Table 3.1 for treatment description. Error bars represent standard error.

Table 3.6. Mean values for total organic carbon (TOC), total nitrogen (TN), C:N ratio (C/N), and mass percent loss (%) for each treatment. Time represents the burial period in months of the leaf litter bags. Time zero represents leaf litter material that was kept in the lab and is used as a reference of the starting leaf material. Values followed by a different lowercase letter for a given factor (TOC, TN, C/N, or Mass percent loss) were significantly different among treatments (using Tukey's HSD) at $\alpha = 0.05$. Standard error is stated in parentheses. For treatment descriptions, refer back to Table 3.1.

		Treatment							
		Control	Intermediate A	Intermediate B	Intermediate C	Clearcut A	Clearcut B	Clearcut C	Clearcut D
TOC (g/kg)	**Time**								
	T= 0	464 (0.0) a	464 (0.0) a	464 (0.0) a	464 (0.0) a	464 (0.0) a	464 (0.0) a	464 (0.0) a	464 (0.0) a
	T= 3	444 (20.8) a	459 (2.84) a	465 (1.35) a	464 (5.59) a	463 (1.02) a	444 (5.30) a	452 (4.62) a	441 (15.8) a
	T= 6	425 (15.7) a	450 (6.0) a	440 (18.2) a	432 (3.28) a	397 (31.9) a	407 (32.8) a	409 (23.1) a	418 (23.4) a
	T= 12	438 (43.7) a	426 (18.3) a	431 (18.0) a	368 (32.5) a	361 (19.9) a	286 (50.5) a	390 (12.8) a	369 (52.1) a
TN (g/kg)									
	T= 0	5.23 (0.0) e	5.23 (0.0) e	5.23 (0.0) e	5.23 (0.0) e	5.23 (0.0) e	5.23 (0.0) e	5.23 (0.0) e	5.23 (0.0) e
	T= 3	7.25 (0.14) abcd	7.03 (0.11) bcde	6.94 (0.53) cde	6.73 (0.35) cde	7.00 (0.34) cde	7.12 (0.53) abcd	6.60 (0.27) cde	6.23 (0.08) de
	T= 6	7.68 (0.42) abcd	7.19 (0.37) abcd	6.62 (0.17) cde	6.67 (0.18) cde	7.12 (0.23) bcde	6.66 (0.50) cde	7.43 (0.50) abcd	7.41 (0.48) abcd
	T= 12	9.71 (0.45) abc	9.01 (0.32) abcd	9.78 (0.82) ab	8.82 (0.94) abcd	10.67 (0.42) a	7.08 (0.14) abcde	10.25 (0.40) a	8.46 (0.68) abcd
C/N									
	T= 0	88.8 (0.0) a	88.8 (0.0) a	88.8 (0.0) a	88.8 (0.0) a	88.8 (0.0) a	88.8 (0.0) a	88.8 (0.0) a	88.8 (0.0) a
	T= 3	61.4 (3.8) abcd	65.4 (0.7) abcd	67.7 (5.0) abc	69.3 (4.2) ab	66.4 (3.1) abcd	63.0 (4.5) abcd	68.7 (3.2) abc	70.7 (1.6) ab
	T= 6	55.9 (5.2) bcde	63.0 (3.9) abcd	66.8 (4.3) abcd	64.8 (2.1) abcd	56.1 (6.2) bcde	62.0 (7.6) abcde	55.9 (6.6) bcdef	57.3 (6.7) bcde
	T= 12	45.04 (2.4) def	47.3 (0.3) cdef	44.4 (2.4) def	41.9 (0.8) def	33.8 (0.7) f	40.3 (6.4) def	38.2 (2.8) ef	43.7 (5.8) def
Percent Mass Loss (%)									
	T= 0	0.0 (0.0) ab	0.0 (0.0) ab	0.0 (0.0) ab	0.0 (0.0) ab	0.0 (0.0) ab	0.0 (0.0) ab	0.0 (0.0) ab	0.0 (0.0) ab
	T= 3	21.1 (4.8) ab	19.7 (3.7) ab	21.8 (3.7) ab	16.8 (3.0) ab	16.5 (2.1) ab	11.7 (2.7) ab	13.5 (3.5) ab	11.5 (2.8) ab
	T= 6	11.0 (5.4) ab	11.8 (3.0) ab	12.8 (6.7) ab	11.4 (2.1) ab	-4.05 (11.6) b	9.08 (2.8) ab	9.4 (3.0) ab	10.9 (2.9) ab
	T= 12	32.5 (12.6) a	29.5 (4.6) a	18.9 (12.3) ab	11.2 (12.4) ab	21.3 (7.1) ab	17.1 (1.7) ab	27.4 (2.1) a	14.3 (3.1) ab

3.4.2 ^{13}C- CPMAS NMR spectroscopy

Representative spectra can be found in Figures 3.6 and 3.7. The peak assignments and interpretation are based on previous NMR studies of foliage, litter, and humus (Almedros et al. 2000; Kogel-Knabner 2002; Lorenz et al. 2000; Manders 1987; Preston et al. 2000). Across treatments, the ^{13}C-NMR spectra of leaf litter material were dominated by total aliphatic-C, representing 70-80% of total organic C, and total aromatic-C, representing 13-15% of total organic C. The intensity in the alkyl region (0-45ppm) comes mainly from surface waxes and cutin. Long-chain CH_2 gives a split peak seen at 30 ppm and 33 ppm, which is associated with more mobile and rigid chains, respectively. Oak species have a distinct peak at 22 ppm, which has been noted to decrease over 2 years of decomposition (Lorenz et al. 2004). The sharp O- and di-O-alkyl peaks at 72 ppm and 105 ppm arise mainly from carbohydrates. Some differences can be seen in the shoulder peaks at 85 ppm within certain treatments over decomposition time (Figure 3.6 and 3.7). For oak species, the phenolic peaks at 145 ppm and 153 ppm may be largely due to lignins and tannins (Conte et al., 2010). Carboxyl, amide and ester carbons are represented in the peak at 175 ppm. These carbons are found in cutin, proteins, and tannins, thus only changing slightly in their concentrations over decomposition time.

Overall, the effect of treatment type did not have a significant effect on the proportions of the six carbon functional groups (Table 3.7). However, time had a significant effect on all of the proportions. A significant interactive effect of treatment type and decomposition time was found for the proportions of the O-alkyl-C ($p = 0.0278$), aromatic-C ($p = 0.0007$), and carbonyl-C ($p = 0.0482$) functional groups (Table

3.7) indicating that the change in proportions of these functional groups with decomposition time was significantly different among the different harvest treatments. The proportions of the ^{13}C NMR functional groups relative to the total organic C content were determined by dividing the integration of each functional group by the sum of the integrated functional groups and compared across treatments during decomposition using ANOVA (Table 3.8). In the clearcut A treatment (current 1/3 BMP), the proportion of di-O-alkyl-C was significantly less (9.3%) at 12 month decomposition compared to time zero (13.4%) and 6 month decomposition (12.5%). However, the proportion of carbonyl-C was significantly greater (8.3 %) at 12 month decomposition compared to time zero (5.6%) and 6 month decomposition (6.3%).

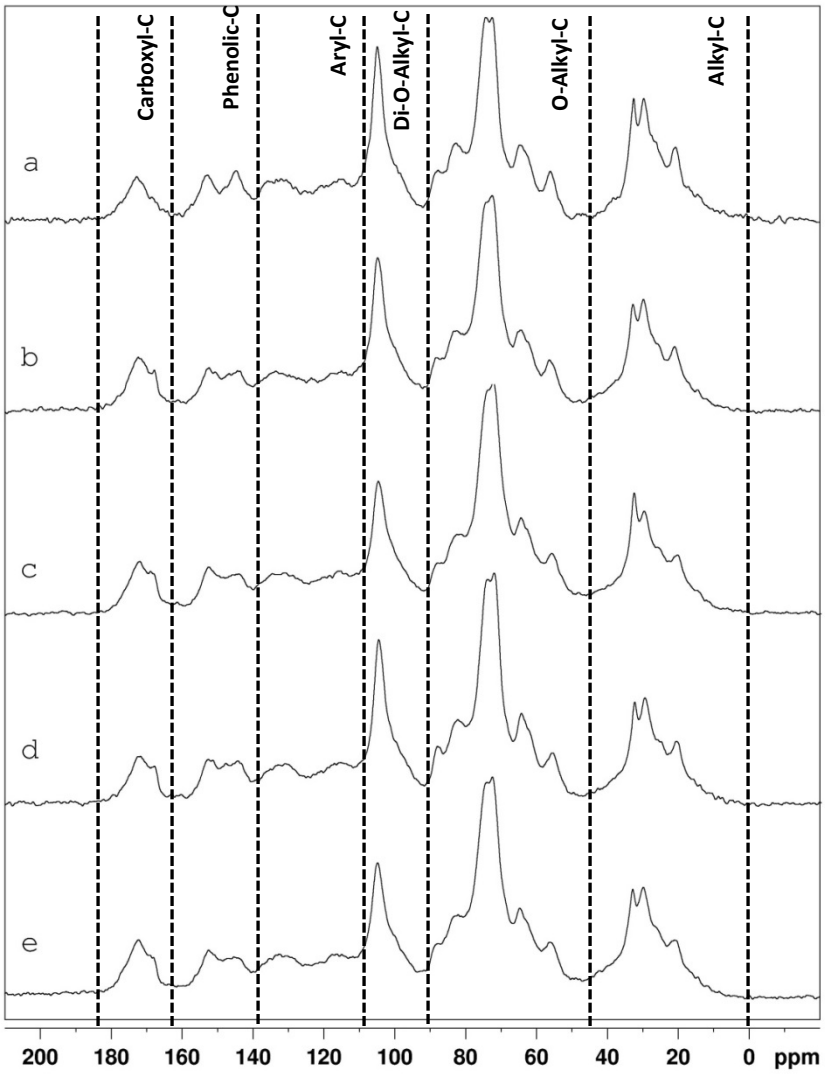


Figure 3.6. Representative ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectra of leaf litter material: (a) field blank from time zero, (b) control treatment (site 5) from 6 month burial period, (c) control treatment (site 5) from 12 month burial period, (d) clearcut B treatment (site 9) from 6 month burial period, (e) and clearcut B treatment (site 9) from 12 month burial period.

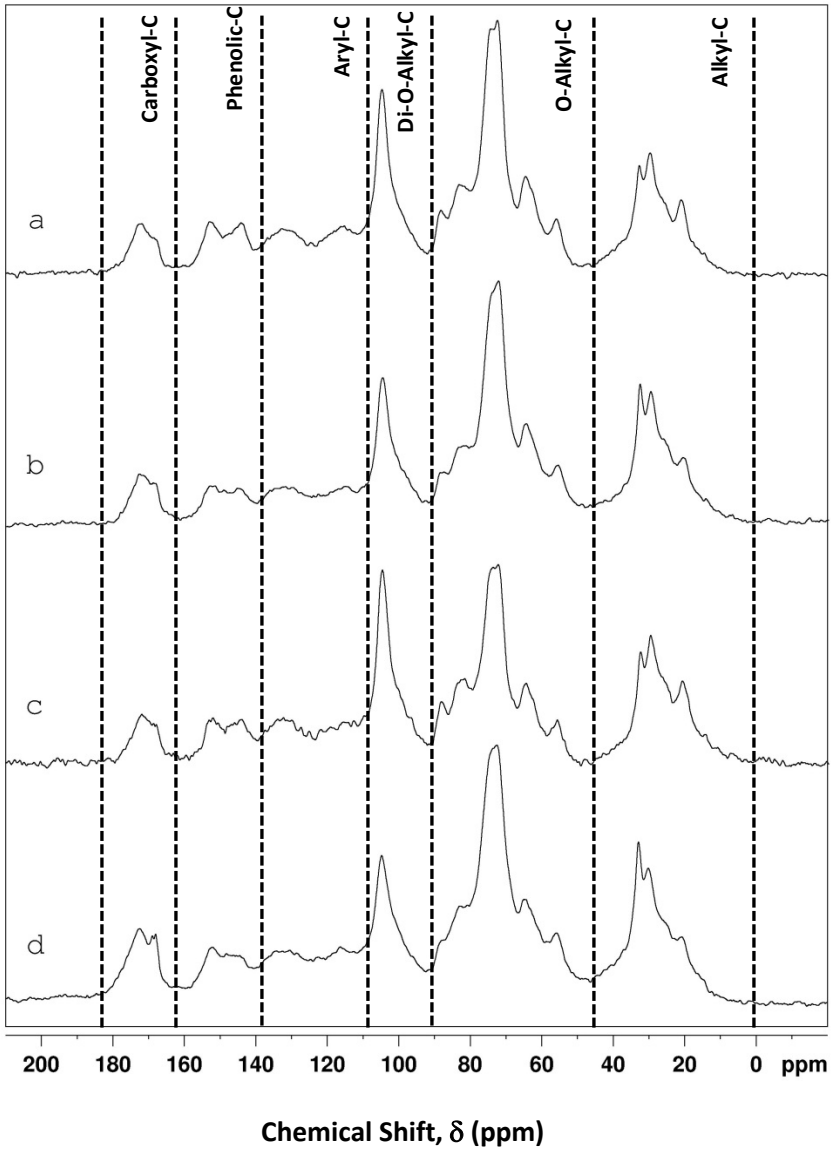


Figure 3.7. Representative ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra of leaf litter material: intermediate A treatment (site 12) at 6 month burial period (a), intermediate A treatment (site 12) from 12 month burial period (b), clearcut A treatment (site 4) from 6 month burial period (c), and clearcut A treatment (site 4) from 12 month burial period (d).

Table 3.7. Type 3 Tests of Fixed Effects, evaluating treatment (Trt), time, and the interaction effect on leaf litter properties. Dependent variable include proportions and concentrations of the six carbon functional groups studied (alkyl, o-alkyl, di-o-alkyl, aromatic, phenolic, and carbonyl). Significant values (p-values <0.05) are placed in bold.

	p-values		
	Source		
Analyte	**Trt**	**Time**	**Trt*Time**
Proportion			
Alkyl	0.1743	**<0.0001**	0.2026
O-Alkyl	0.0842	**<0.0001**	**0.0278**
DI-O-Alkyl	0.1016	**<0.0001**	0.2811
Aromatic	0.2757	**<0.0001**	**0.0007**
Phenolic	0.7905	**<0.0001**	0.5355
Carbonyl	0.0638	**<0.0001**	**0.0482**
Concentration			
Alkyl	**0.0411**	**<0.0001**	**0.0053**
O-Alkyl	0.0525	**<0.0001**	**0.0098**
DI-O-Alkyl	0.0684	**<0.0001**	0.0971
Aromatic	**0.0071**	**0.0019**	**0.0126**
Phenolic	0.3005	**<0.0001**	0.2432
Carbonyl	0.3005	**<0.0001**	0.2432

Table 3.8. Proportions of each ^{13}C NMR functional groups by treatment as determined by dividing the integration of each functional group by the sum of the integrated functional groups. Time represents the burial period in months of the leaf litter bags. Time zero represents leaf litter material that was kept in the lab and is used as a reference of the starting leaf material. Values followed by a different lowercase letter for a given functional group were significantly different among treatments (using Tukey's HSD) at $\alpha = 0.05$. Standard error is stated in parentheses. For treatment descriptions, refer back to Table 3.1.

		Treatment							
		Control	**Intermediate A**	**Intermediate B**	**Intermediate C**	**Clearcut A**	**Clearcut B**	**Clearcut C**	**Clearcut D**
Funtional Group	**Time**								
Alkyl	T= 0	0.25 (0.00) abc	0.25 (0.00) abc	0.25 (0.00) abc	0.25 (0.00) abc	0.25 (0.00) abc	0.25 (0.00) abc	0.25 (0.00) abc	0.25 (0.00) abc
	T= 6	0.23 (0.01) c	0.23 (0.01) abc	0.25 (0.01) abc	0.23 (0.01) c	0.24 (0.01) abc	0.22 (0.01) c	0.22 (0.00) c	0.23 (0.01) bc
	T= 12	0.24 (0.01) abc	0.25 (0.02) abc	0.25 (0.01) abc	0.26 (0.01) abc	0.27 (0.01) a	0.26 (0.01) abc	0.27 (0.01) ab	0.26 (0.01) abc
O-Alkyl	T= 0	0.42 (0.00) b	0.42 (0.00) b	0.42 (0.00) b	0.42 (0.00) b	0.42 (0.00) b	0.42 (0.00) b	0.42 (0.00) b	0.42 (0.00) b
	T= 6	0.44 (0.01) ab	0.45 (0.01) ab	0.44 (0.01) b	0.45 (0.01) ab	0.43 (0.02) b	0.48 (0.01) a	0.45 (0.01) ab	0.44 (0.00) b
	T= 12	0.45 (0.01) ab	0.45 (0.01) ab	0.43 (0.00) b	0.44 (0.01) b	0.42 (0.00) b	0.42 (0.01) b	0.43 (0.00) b	0.43 (0.01) b
DI-O-Alkyl	T= 0	0.13 (0.00) a	0.13 (0.00) a	0.13 (0.00) a	0.13 (0.00) a	0.13 (0.00) a	0.13 (0.00) a	0.13 (0.00) a	0.13 (0.00) a
	T= 6	0.13 (0.01) ab	0.12 (0.00) ab	0.13 (0.00) a	0.13 (0.00) a	0.13 (0.01) ab	0.12 (0.01) ab	0.12 (0.01) ab	0.13 (0.00) ab
	T= 12	0.12 (0.00) abc	0.11 (0.01) abc	0.12 (0.00) abc	0.11 (0.00) abc	0.09 (0.00) c	0.10 (0.00) bc	0.11 (0.00) bc	0.10 (0.00) bc
Aromatic	T= 0	0.07 (0.00) ab	0.07 (0.00) ab	0.07 (0.00) ab	0.07 (0.00) ab	0.07 (0.00) ab	0.07 (0.00) ab	0.07 (0.00) ab	0.07 (0.00) ab
	T= 6	0.07 (0.01) ab	0.07 (0.01) ab	0.06 (0.01) b	0.07 (0.00) ab	0.07 (0.00) ab	0.06 (0.00) b	0.08 (0.00) a	0.08 (0.01) a
	T= 12	0.07 (0.00) ab	0.08 (0.00) ab	0.07 (0.00) ab	0.07 (0.00) ab	0.08 (0.00) a	0.08 (0.00) a	0.07 (0.00) ab	0.08 (0.00) ab
Phenolic	T= 0	0.07 (0.00) a	0.07 (0.00) a	0.07 (0.00) a	0.07 (0.00) a	0.07 (0.00) a	0.07 (0.00) a	0.07 (0.00) a	0.07 (0.00) a
	T= 6	0.07 (0.00) ab	0.07 (0.00) ab	0.06 (0.00) b	0.06 (0.00) ab	0.07 (0.00) ab	0.06 (0.00) ab	0.07 (0.00) ab	0.07 (0.01) ab
	T= 12	0.06 (0.01) ab	0.05 (0.00) b	0.06 (0.00) ab	0.06 (0.00) ab	0.06 (0.00) ab	0.06 (0.00) ab	0.06 (0.01) ab	0.06 (0.00) ab
Carbonyl	T= 0	0.06 (0.00) c	0.06 (0.00) c	0.06 (0.00) c	0.06 (0.00) c	0.06 (0.00) c	0.06 (0.00) c	0.06 (0.00) c	0.06 (0.00) c
	T= 6	0.06 (0.00) bc	0.06 (0.00) bc	0.06 (0.00) bc	0.06 (0.00) bc	0.06 (0.00) bc	0.06 (0.00) bc	0.06 (0.01) bc	0.06 (0.00) bc
	T= 12	0.06 (0.00) bc	0.06 (0.00) bc	0.07 (0.00) abc	0.07 (0.00) abc	0.08 (0.00) a	0.07 (0.00) ab	0.66 (0.00) bc	0.07 (0.01) abc

According to the Tukey-Kramer analysis, treatment type had a significant effect on the alkyl-C ($p = 0.0411$) and aromatic-C ($p = 0.0071$) concentrations (Table 3.7). The total Alkyl-C concentration of leaf litter material for each treatment type during the one year decomposition period is shown in Figure 3.8. The alkyl-C concentration for clearcut B treatment is significantly less than the control, intermediate A, intermediate B, intermediate C, and clearcut C treatments. The total aromatic-C concentration of leaf litter material for each treatment type during the one year decomposition period is shown in Figure 3.9. The aromatic-C concentration for clearcut B treatment is significantly less than the control, intermediate A, intermediate B, and clearcut C treatments. Time had a significant effect on all of the six carbon functional group concentrations (Table 3.7). Furthermore, a significant interactive effect of treatment type and decomposition time was found for the concentrations of the alkyl-C ($p = 0.0053$), O-alkyl-C ($p = 0.0098$), and aromatic-C ($p = 0.0126$) functional groups (Table 3.7).

The concentrations of the ^{13}C NMR functional groups relative to the total organic C content were determined by multiplying the proportion of each functional group by the total soil organic C content and compared across treatments (Table 3.9). For all four of the clearcut treatments, the di-o-alkyl-C concentration is significantly lower at 12 month decomposition compared to time zero, with clearcut B (removal of all biomass) exhibiting the largest difference (62.015 g kg^{-1} at time zero and 29.323 g kg^{-1} at 12 month decomposition). There was also a significant decrease in the di-o-alkyl-C concentration relative to time zero and 12 month decomposition for the intermediate C treatment (62.015 g kg^{-1} to 41.090 g kg^{-1}, respectively). In the clearcut B treatment, the o-alkyl concentration significantly decreased from time zero to 12 month decomposition,

195.184 g kg^{-1} to 121.090 g kg^{-1}, respectively. Similarly, this pattern occurs within the clearcut B treatment for the alkyl-C (116.243 g kg^{-1} to 73.596 g kg^{-1}), phenolic-C (34.144 g kg^{-1} to 16.954 g kg^{-1}), and carbonyl-C (25.831 g kg^{-1} to 21.083 g kg^{-1}). While the di-o-alkyl-C concentration decreased in the intermediate treatments, there was a greater decrease over decomposition time among the clearcut treatments. This pattern can be seen with the other functional groups expect for aromatic-C (Table 3.9). The di-o-alkyl-C region (90-110ppm) comes mainly from carbohydrates. Tannins and lignins are the main contributors in the aromatic and phenolic regions, thus explaining the small decrease in concentrations among all treatments.

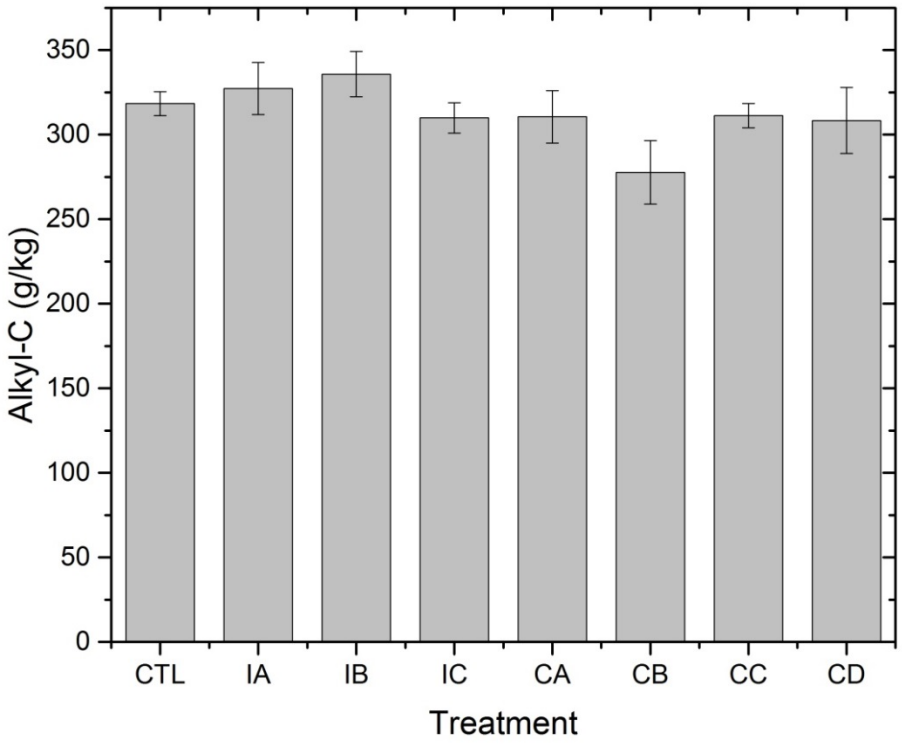


Figure 3.8. Total Alkyl-C concentrations of leaf litter material for each treatment type during the one year decomposition period. Refer back to Table 3.1 for treatment descriptions. Error bars represent standard error.

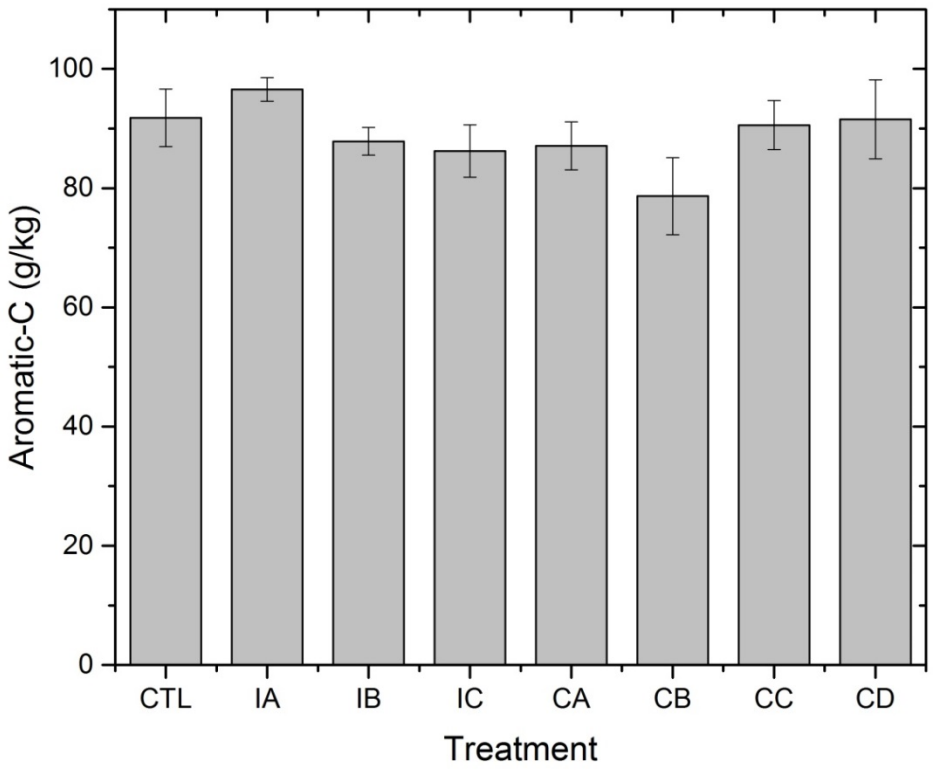


Figure 3.9. Total Aromatic-C concentrations of leaf material for each treatment type during the one year decomposition period. Refer back to Table 3.1 for treatment descriptions. Error bars represent standard error.

Table 3.9. Mean concentration of ^{13}C NMR functional groups (g kg^{-1} soil) by treatment as determined by multiplying the proportion of each functional group by the total leaf organic C content. Time represents the burial period in months of the leaf litter bags. Time zero represents leaf litter material that was kept in the lab and is used as a reference of the starting leaf material. Values followed by a different lowercase letter for a given functional group were significantly different among treatments (using Tukey's HSD) at $\alpha = 0.05$. Standard error is stated in parentheses. For treatment descriptions, refer back to Table 3.1.

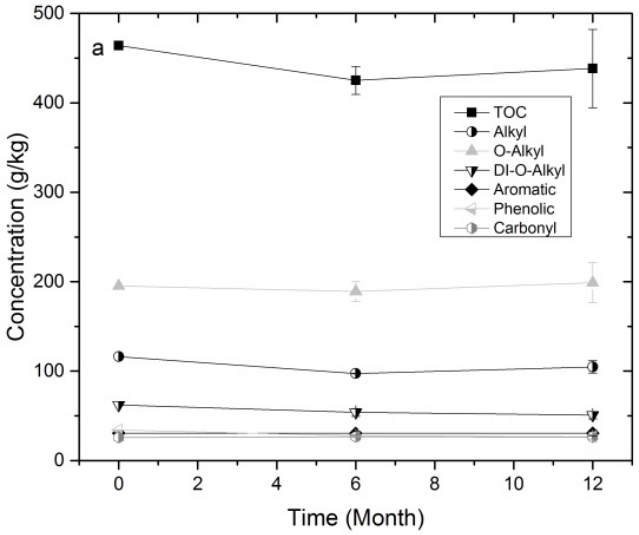
		Treatment							
		Control	Intermediate A	Intermediate B	Intermediate C	Clearcut A	Clearcut B	Clearcut C	Clearcut D
Funtional Group	**Time**								
Alkyl	T= 0	116.24 (0.00) a	116.24 (0.00) a	116.24 (0.00) a	116.24 (0.00) a	116.24 (0.00) a	116.24 (0.00) a	116.24 (0.00) a	116.24 (0.00) a
	T= 6	97.32 (0.18) abc	104.64 (3.52) abc	110.22 (7.84) ab	99.53 (3.30) abc	97.06 (10.31) abc	87.89 (7.80) bc	90.64 (3.46) abc	97.24 (8.57) abc
	T= 12	104.76 (6.89) ab	106.35 (11.88) ab	109.30 (5.53) ab	94.12 (5.62) abc	97.26 (5.20) abc	73.60 (10.95) c	104.41 (3.74) abc	94.85 (10.91) abc
O-Alkyl	T= 0	195.18 (0.00) a	195.18 (0.00) a	195.18 (0.00) a	195.18 (0.00) a	195.18 (0.00) a	195.18 (0.00) a	195.18 (0.00) a	195.18 (0.00) a
	T= 6	188.95 (11.00) ab	200.42 (2.54) a	192.16 (5.52) a	193.55 (3.53) a	169.18 (10.99) ab	195.49 (14.14) a	184.48 (14.00) ab	181.67 (8.70) ab
	T= 12	198.93 (22.59) a	189.99 (4.07) ab	185.44 (6.04) ab	161.04 (15.65) ab	150.37 (8.79) ab	121.09 (25.18) b	167.73 (5.79) ab	158.38 (25.51) ab
DI-O-Alkyl	T= 0	62.02 (0.00) a	62.02 (0.00) a	62.02 (0.00) a	62.02 (0.00) a	62.02 (0.00) a	62.02 (0.00) a	62.02 (0.00) a	62.02 (0.00) a
	T= 6	53.85 (4.42) abc	55.08 (1.91) abc	58.23 (3.41) ab	55.90 (1.55) abc	50.06 (8.10) abcd	50.74 (5.88) abcd	49.37 (4.23) abcd	52.46 (3.88) abcd
	T= 12	50.74 (3.96) abcd	47.03 (0.19) abcd	49.36 (2.83) abcd	41.09 (4.64) bcd	33.41 (1.40) d	29.32 (4.33) d	41.22 (2.63) bcd	38.65 (7.09) cd
Aromatic	T= 0	30.58 (0.00) a	30.58 (0.00) a	30.58 (0.00) a	30.58 (0.00) a	30.58 (0.00) a	30.58 (0.00) a	30.58 (0.00) a	30.58 (0.00) a
	T= 6	30.49 (2.00) a	33.20 (1.73) a	26.71 (1.66) a	31.20 (1.36) a	28.16 (2.53) a	24.27 (2.21) a	32.65 (1.88) a	32.93 (3.08) a
	T= 12	30.73 (2.84) a	32.77 (0.26) a	30.57 (0.67) a	24.45 (3.02) a	28.34 (1.49) a	23.79 (4.25) a	27.35 (2.26) a	28.02 (3.53) a
Phenolic	T= 0	34.14 (0.00) a	34.14 (0.00) a	34.14 (0.00) a	34.14 (0.00) a	34.14 (0.00) a	34.14 (0.00) a	34.14 (0.00) a	34.14 (0.00) a
	T= 6	27.73 (1.17) abc	30.41 (1.88) ab	25.06 (1.45) bc	27.03 (1.36) abc	27.24 (2.31) abc	25.25 (4.04) bc	27.34 (1.52) abc	27.23 (2.63) abc
	T= 12	26.67 (4.954) abc	23.24 (1.40) bc	26.64 (2.81) abc	21.97 (2.18) bc	21.71 (1.46) bc	16.95 (3.20) c	23.25 (2.02) bc	22.79 (3.85) bc
Carbonyl	T= 0	25.83 (0.00) a	25.83 (0.00) a	25.83 (0.00) a	25.83 (0.00) a	25.83 (0.00) a	25.83 (0.00) a	25.83 (0.00) a	25.83 (0.00) a
	T= 6	26.77 (0.94) abc	26.36 (0.98) ab	27.96 (2.96) bc	24.68 (0.99) abc	24.80 (0.37) abc	23.81 (2.15) bc	24.53 (1.28) abc	26.36 (1.58) abc
	T= 12	26.51 (2.44) abc	27.04 (1.35) bc	29.47 (1.83) abc	25.34 (1.74) bc	30.02 (2.53) bc	21.08 (2.59) c	25.61 (1.08) bc	25.80 (2.67) bc

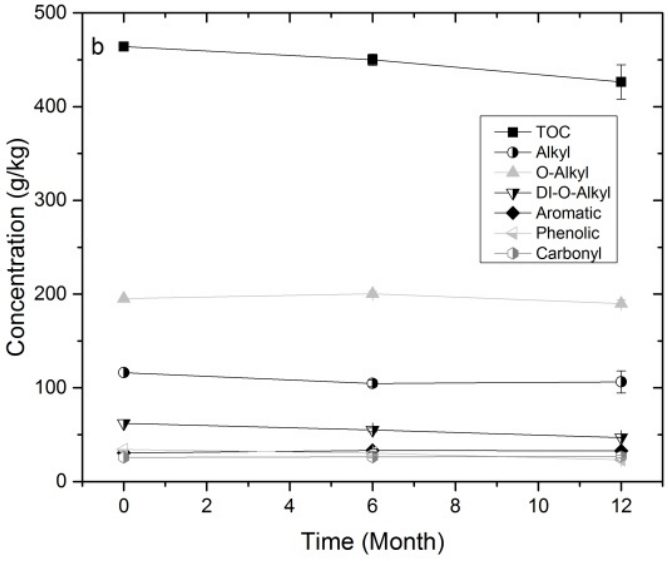
3.5 Discussion

Changes in different C fractions during litter decomposition

The changes in the total organic carbon (TOC) and the ^{13}C-NMR functional group concentrations (g kg^{-1}) showed similar trends during decomposition amongst treatments (Figure 3.10). Since the concentrations of the ^{13}C-NMR functional groups were determined by multiplying the proportion of each functional group by the total organic C content, it can be observed which functional groups contributed the most to changing TOC concentrations. The largest changes occur in the O-alkyl-C and the di-O-alkyl-C fractions. The o-alkyl-C region (45-90ppm) is mainly associated with sugars and polysaccharides, thus making decomposition fairly rapid since they are easily broken down and energy rich molecules (Bonanomi et al., 2013 and Wang et al., 2013). However, since the alkyl-C region (0-45ppm) is characteristically made up of lipid, waxes, and cutins; it takes longer periods to degrade due to their large, complex molecular structures. The large changes in the O-alkyl-C and di-O-alkyl-C, and the small changes in the alkyl-C are noticeable in Figure 3.10 c and d, which represent clearcut A and clearcut B respectively. As the TOC concentration decreases over time in the two clearcut treatments, the three aliphatic carbon fractions decrease more over time as well, thus contributing more to the changes seen in TOC. The concentrations of TOC and the functional groups only decreased slightly in the control and intermediate A treatments (Figure 3.10a and b); thus, indicating that the intermediate harvesting treatments did not have as much of an impact on the concentration values as the clearcut treatments did. Changes in litter chemistry along with increased sunlight and soil temperature may have

stimulated litter decay on harvested sites where more removal of biomass occurred, suggesting the importance of careful analysis of different harvesting techniques.


a
TOC
Alkyl
O-Alkyl
DI-O-Alkyl
Aromatic
Phenolic
Carbonyl
Concentration (g/kg)
Time (Month)
0
100
200
300
400
500
0
2
4
6
8
10
12


b
TOC
Alkyl
O-Alkyl
DI-O-Alkyl
Aromatic
Phenolic
Carbonyl
Concentration (g/kg)
Time (Month)
0
100
200
300
400
500
0
2
4
6
8
10
12

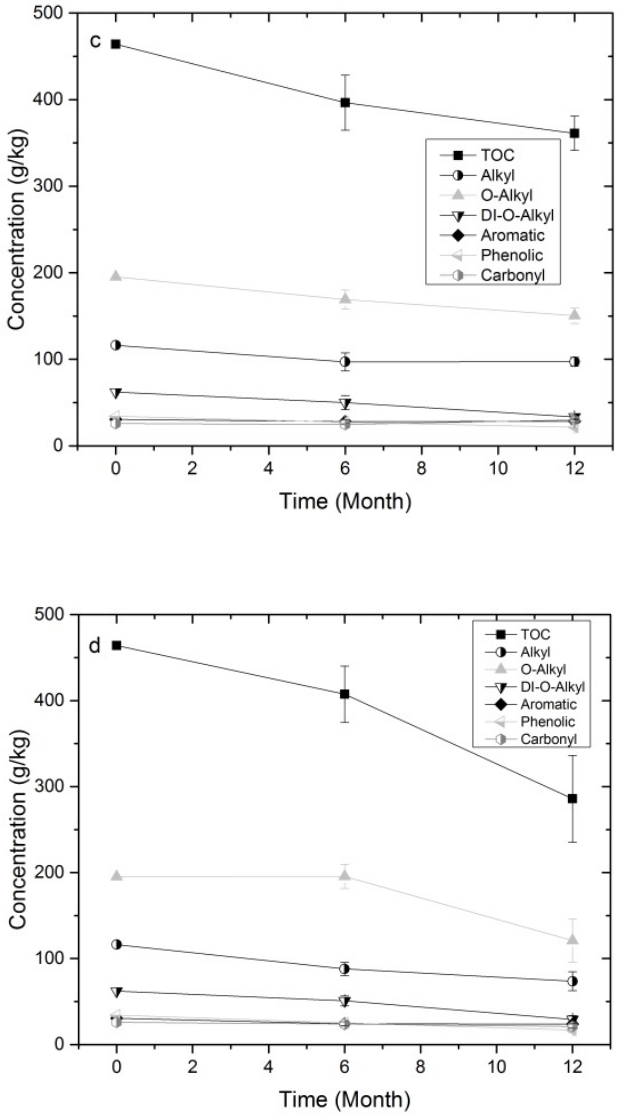


Figure 3.10. Concentrations of leaf litter C fractions and total organic C (TOC) of control treatment (a), intermediate A (b), clearcut A (c), and clearcut B (d) during decomposition. Error bars are the standard errors. Refer back to table 1 for treatment descriptions.

Litter decomposition

In this 1-year litterbag study, there was a loss of 9.1-32.5% of litter mass. The intense leaching and high mass loss during the first 3 months of decomposition can partly be explained by the high precipitation and snow fall on site. Similarly, a strong influence of winter precipitation in year 1 of decomposition of ten foliar litters was reported by Trofymow et al. (2002). Since each treatment type would produce different microclimate environments due to the difference in slash remaining on the ground, these variables could explain the differences in decay rate. Greater retention of slash occurred on clearcut A (Missouri BMP) and clearcut C (alternative BMP) than where no BMPs were applied. This along with greater nitrogen concentrations (as seen with the PRS probe data in chapter 2) provides ideal environments for microbial decomposition, thus indicating greater decay rates in these treatments. Nitrogen concentrations and C-N ratios are known predictors of litter decay rate (Bonanomi et al., 2013). In this study, TN was positively correlated to the mass percent loss ($r = 0.72$), while C/N ratio was negatively correlated to the mass percent loss ($r = -0.56$). The increase of N concentration during decomposition in all of the eight treatments is consistent with previous findings from a range of environments and litter types (Berg and McClaugherty, 2008; Q. Li et al., 2009). However, it is also known that N content has a dual, contrasting effect on litter decomposition, enhancing the decay rate during the early stages and limiting it thereafter (Berg and Matzner, 1997).

Differences of C compositional changes during decomposition

Factors controlling initial mass loss rates have been related to the loss of soluble compounds including soluble carbohydrates, phenolics, and tannins (Berg and Tamm, 1991). The decrease in the O-alkyl-C proportion and the increase in the carbonyl-C proportion were observed during leaf litter decomposition (Table 3.8), which are consistent with previous NMR studies using litterbags (Quideau et al., 2005; Lemma et al., 2007; Osono et al., 2008; Preston et al., 2010). The decrease in the proportion of O-alkyl-C may be mostly due to preferential decomposition of labile cellulosic compounds by soil microorganisms (Baldock et al., 1997). The strong decrease in O-alkyl-C concentrations, associated with carbohydrates, in the clearcuts compared to the intermediates and the control is evidence of greater decomposition rates. Since the spectra of the leaf litter material indicated a decrease in the relative proportions of the carbohydrate signals, this reveals that the first stages of decomposition were ongoing (Hopkins et al., 2007). Similar NMR studies have shown increases in methyl and alkyl-C in the early phases of decomposition (Hopkins and Chudek, 1997; Almendros et al., 2000). In clearcuts A and C, the alkyl-C concentrations increased from 6 months to 12 months of decomposition, whereas clearcut B and D decreased (Table 3.8). The slight increase in the proportion of alkyl-C that occurs between the 6 month and 12 month decomposition times could be caused by the accumulation of resistant leaf waxes, cutins, and other contributions from microbial growth during decomposition (Quideau et al., 2005). Such an accumulation of alkyl material has also been described in highly decomposed materials and it is considered to be due not to selective preservation, but

rather to an increase in cross-linking of the long-chain alkyl material occurring during humification (Skjemstad et al., 1997).

An increase in the proportion of carbonyl-C, seen in Table 3.9, may be attributed to formation by hydrolysis and oxidation processes during decomposition, as these processes are common in decomposition processes on forest floors (Ono et al., 2012). The carbonyl-C fraction was positively correlated with the mass percent loss (Table 3.4). The carbonyl-C concentration increased significantly over the decomposition period for intermediate A, intermediate C, and all of the clearcut treatments. Previous findings (Baldock et al., 1997; Osono et al., 2006; Wang et al., 2013) found that the increase in the proportion of aromatic-C may be partly due to relative accumulation of lignin structures during litter decomposition. This increase was also noted in the current study (Table 3.8). However, since there were no significant changes in the aromatic-C concentrations among treatments, the increase in aromaticity is not the dominant process (Table 3.9).

3. 6 Conclusions

Although our overall results are largely consistent with expected patterns of litter decay, based on initial litter chemistry, they add to the growing base of data exploring the effects of both timber harvesting and mixing litter types on subsequent decomposition patterns. Additionally, changes in litter chemistry resulting from harvest treatment may have stimulated litter decay on harvested sites, suggesting the importance of analyzing stand-specific litter characteristics as well as nutrient cycles. The mass losses in this 1-year decomposition study were positively related to changes in total nitrogen concentrations (Table 3.4). The accumulation of the alkyl-C and decreases in the O-alkyl-C revealed that the first stages of decomposition were ongoing. Therefore, the NMR spectra ^{13}C CPMAS NMR spectroscopy turned out to be a very powerful technique for the molecular characterization of leaf litter. The limitations of both NMR and chemical analysis indicate the need for molecular-level analysis to obtain a more complete understanding of the organic composition of litter and its decay. Overall, the findings of leaf litter C compositional decomposition in this study could contribute to developing an appropriate forest management strategy for maximizing soil C stock and enhancing soil C stability.

In general, the greatest differences between the treatments arose between the clearcuts and the intermediate/control treatments. Since the concentrations of TOC and the functional groups only decreased slightly in the control and intermediate treatments, the intermediate harvesting treatments did not have as much of an impact on the concentration values as the clearcut treatments did. However, treatment type did not have a significant effect on the percent mass loss in the leaf litter material. Since greater

amounts of biomass harvested occurred in clearcuts relative to the intermediates and control treatments, and thus residual woody debris on the forest floor was greater in the clearcut treatments as compared to the intermediate and control treatments, future work will need to include an expansion of the time required to replace the removed nutrients through woody debris decomposition.

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Chapter 4: Conclusions

This study provides an assessment of residue and nutrients remaining on site and short-term changes in soil nutrient flux and soil chemistry in thinning and clearcut treatments where MDC's current BMP for woody biomass harvest and an alternative BMP were utilized; treatments where no BMPs were implemented, traditional sawlog only removal, and control sites were also studied. In general, the greatest differences between the treatments occurred between the clearcut and the intermediate/control treatments.

Although nutrient flux was greater under the alternative BMP (clearcut C) compared to MDC's current BMP (clearcut A) for most nutrients, an overall view of all data collected indicates that practicing MDC's current BMP or the alternative BMP for woody biomass harvesting has no greater effect on short-term soil nutrient flux and concentrations than a traditional sawlog only harvest. Since the concentrations of TOC and the functional groups only decreased slightly in the control and intermediate treatments, the intermediate harvesting treatments did not have as much of an impact on the concentration values as the clearcut treatments did. However, treatment type did not have a significant effect on the percent mass loss in the leaf litter material. Since greater amounts of biomass harvested occurred in clearcuts relative to the intermediates and control treatments, and thus residual woody debris on the forest floor was greater in the clearcut treatments as compared to the intermediate and control treatments, future work will need to include an expansion of the time required to replace the removed nutrients through woody debris decomposition.

To ensure long-term sustainability and forest productivity, it is recommended to use the current Missouri BMPs or the alternative BMP (retain tops of all cut trees ≥ 20 cm dbh; remove boles, tops and limbs of all cut trees ≤ 20 cm dbh). Overall, the biomass guidelines supplement existing forestry rules and guidelines, encourage forest health and productivity, and enhance the full suite for ecological values. The current BMP and alternative BMP provide an opportunity to suggest alternative harvesting techniques, besides the traditional sawlog harvest, to high grading and damaging practices on the long-term health of the forest ecosystem.

Appendix

A. PRS-Probe Sampling Dates

Sample Period	Date
1	July 2, 2012 – July 31, 2012
2	September 9, 2012 – October 7, 2012
3	November 8, 2012 – December 11, 2012
4	January 9, 2013 – February 8, 2013
5	March 20, 2013 – April 21, 2013
6	May 27, 2013 – June 29, 2013
7	August 12, 2013 – September 11, 2013
8	October 22, 2013 – November 25, 2013

B. SAS Statistical Models

B.1 Code for spatially-repeated split-plot generalized linear mixed model in SAS software for analysis of soil data and nutrient flux data; each block split by harvest treatment (trt) and depth and repeated by collection (time). *Distribution codes must be changed for each dependent variable.

```
Proc glimmix data=WORK.ALLg plots=residualpanel;
      class Trt Time Block Depth;
      model Dependent Variable = Trt|Time|Depth/dist= normal
link=identity;
      random Trt/ subject=Block;
      random Depth/type=sp(pow)(Depth) subject=Trt*Block;
      random Time/type =arh(1) subject=Trt*Block;
      lsmeans Trt|Time|Depth / pdiff adjust=tukey ilink lines cl;
      run;
```

B.2 Code for repeated measures randomized complete block generalized linear mixed model in SAS software for analysis of repeated measures of leaf litter bags; each block split by harvest treatment (trt) by repeated measures (time).

```
Proc glimmix data=WORK.NMRg plots=residualpanel;
      class Trt Time Block;
      model Dependent Variable = Trt Time Trt*Time/dist= normal
link=identity;
      random Trt/ subject=Block;
      random time/type = arh(1) subject=Trt*Block;
      lsmeans Trt Time Trt*Time/ pdiff adjust=tukey ilink lines cl;
      run;
```

C. Pearson linear correlation coefficients for soil chemical properties.

Coefficients for exchangeable cations Ca^{2+}, Mg^{2+}, K^{+}, sum of exchangeable cations (sum), effective cation exchange capacity (ECEC), total percentage of base saturation by weight (BS), extractable acidity (EA), total percentage aluminum saturation (Al sat), soil pH (PH), total organic carbon (TOC), and total nitrogen (TN) with p-values stated in parentheses. (N=192)

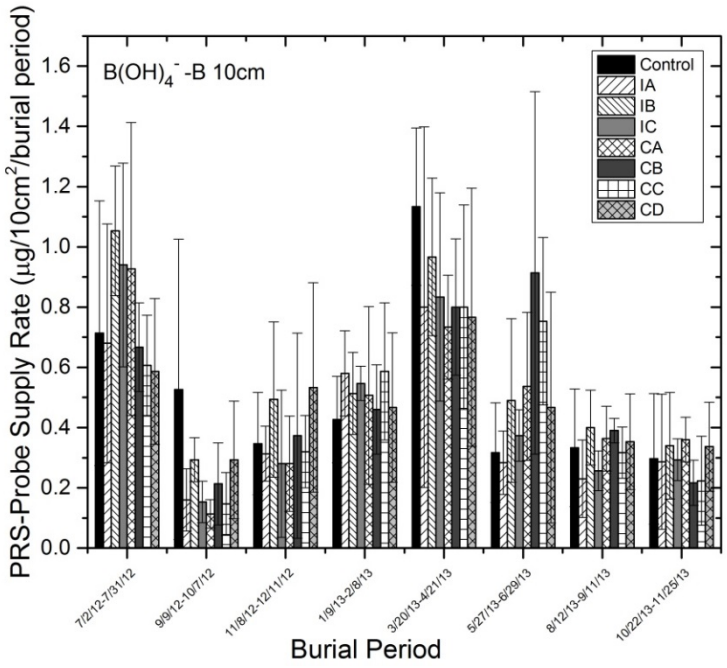
Analyte	Ca	Mg	K	Sum	EA	ECEC	AL	BS	TOC	PH	TN
Ca		0.74509	0.35859	0.94791	0.16729	0.58889	-0.81944	0.90405	0.25671	0.65869	0.3061
		(<.0001)	(<.0001)	(<.0001)	(0.0204)	(<.0001)	(<.0001)	(<.0001)	(0.0003)	(<.0001)	(<.0001)
Mg			0.33854	0.91502	0.42121	0.87001	-0.50391	0.77858	-0.17173	0.27335	-0.13268
			(<.0001)	(<.0001)	(<.0001)	(<.0001)	(<.0001)	(<.0001)	(0.0172)	(0.0001)	(0.0666)
K				0.4063	0.38129	0.4194	-0.30972	0.32162	0.19096	0.16752	0.26654
				(<.0001)	(<.0001)	(<.0001)	(<.0001)	(<.0001)	(0.008)	(0.0202)	(0.0002)
Sum					0.30293	0.76443	-0.7282	0.90676	0.07728	0.51976	0.12659
					(<.0001)	(<.0001)	(<.0001)	(<.0001)	(0.2867)	(<.0001)	(0.0802)
EA						0.72145	0.08469	0.04489	0.17938	-0.35191	0.20968
						(<.0001)	(0.2428)	(0.5364)	(0.0128)	(<.0001)	(0.0035)
ECEC							-0.22232	0.55393	-0.1808	-0.00005	-0.11535
							(0.0019)	(<.0001)	(0.0121)	(0.9995)	(0.1111)
AL								-0.85811	-0.3877	-0.77834	-0.41523
								(<.0001)	(<.0001)	(<.0001)	(<.0001)
BS									0.07892	0.68269	0.13392
									(0.2766)	(<.0001)	(0.064)
TOC										0.25043	0.92935
										(0.0005)	(<.0001)
PH											0.30269
											(<.0001)

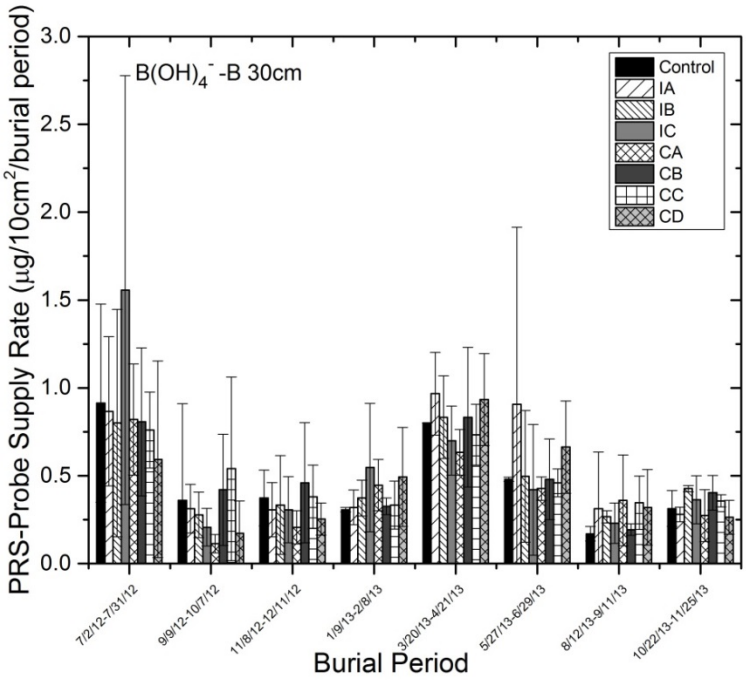
D. Pearson linear correlation coefficients for PRS-Probe analytes.

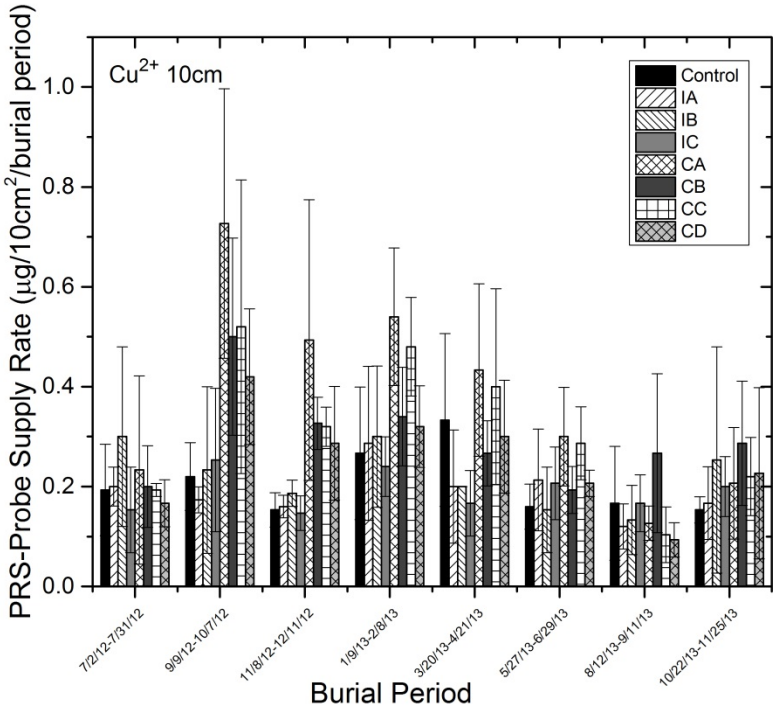
Coefficients for total N, NO_3^- -N, NH_4^+ -N, Ca, Mg, K, P, Fe, Mn, S, and Al with p-values stated in parentheses. (N=384)

Analyte	total N	NO3	NH4	Ca	Mg	K	P	Fe	Mn	S	Al
total N		0.98874	0.24124	0.35579	0.35797	0.28644	0.02302	0.1688	0.69564	0.47707	0.5804
		(<.0001)	(<.0001)	(<.0001)	(<.0001)	(<.0001)	(0.6529)	(0.0009)	(<.0001)	(<.0001)	(<.0001)
NO3			0.09328	0.38463	0.39394	0.25266	-0.01557	0.17597	0.68608	0.48029	0.60121
			(0.0679)	(<.0001)	(<.0001)	(<.0001)	(0.761)	(0.0005)	(<.0001)	(<.0001)	(<.0001)
NH4				-0.12719	-0.17301	0.26721	0.25412	-0.01814	0.17902	0.05935	-0.03728
				(0.0126)	(0.0007)	(<.0001)	(<.0001)	(0.723)	(0.0004)	(0.2459)	(0.4663)
Ca					0.72266	-0.18296	-0.00296	0.35349	0.31063	0.42582	0.26763
					(<.0001)	(0.0003)	(0.954)	(<.0001)	(<.0001)	(<.0001)	(<.0001)
Mg						-0.27236	-0.12856	0.34995	0.32341	0.41637	0.63045
						(<.0001)	(0.0117)	(<.0001)	(<.0001)	(<.0001)	(<.0001)
K							0.23783	-0.09288	0.15969	0.18868	-0.08611
							(<.0001)	(0.069)	(0.0017)	(0.0002)	(0.092)
P								0.07389	0.06743	-0.03768	-0.06507
								(0.1484)	(0.1873)	(0.4616)	(0.2033)
Fe									0.23175	0.17662	0.22145
									(<.0001)	(0.0005)	(<.0001)
Mn										0.32762	0.41869
										(<.0001)	(<.0001)
S											0.26488
											(<.0001)

E. Mean analyte flux by PRS probe for boron (B), copper (Cu), lead (Pb), and zinc (Zn) for all harvest treatments over time at 10cm and 30cm depth. Error bars represent 95% confidence intervals.






Cu2+ 10cm
Control
IA
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CA
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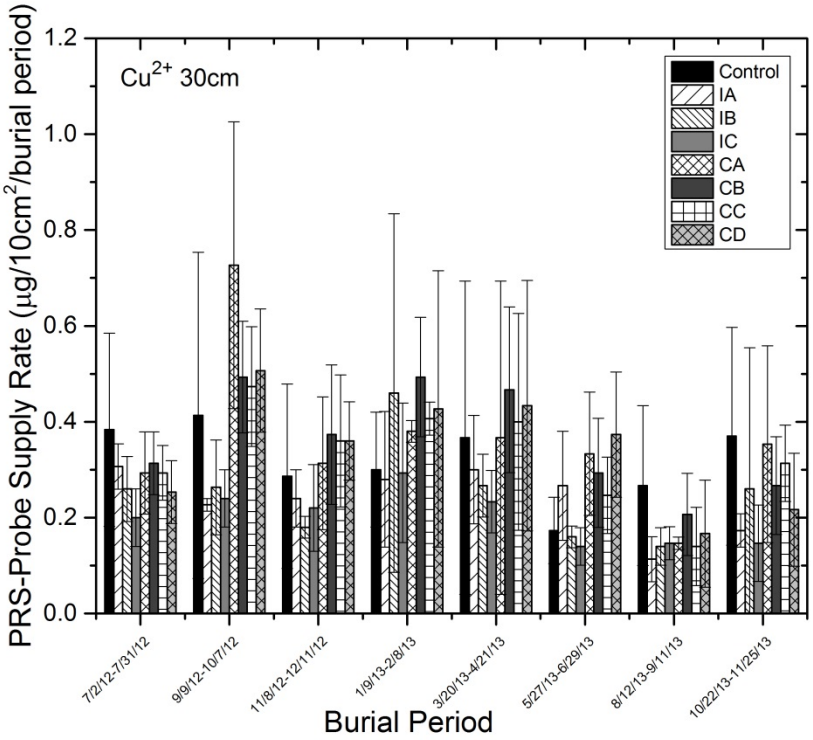
PRS-Probe Supply Rate (μg/10cm2/burial period)
0.0
0.2
0.4
0.6
0.8
1.0
7/2/12-7/31/12
9/9/12-10/7/12
11/8/12-12/11/12
1/9/13-2/8/13
3/20/13-4/21/13
5/27/13-6/29/13
8/12/13-9/11/13
10/22/13-11/25/13
Burial Period


Cu2+ 30cm
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PRS-Probe Supply Rate (μg/10cm2/burial period)
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0.4
0.6
0.8
1.0
1.2
7/2/12-7/31/12
9/9/12-10/7/12
11/8/12-12/11/12
1/9/13-2/8/13
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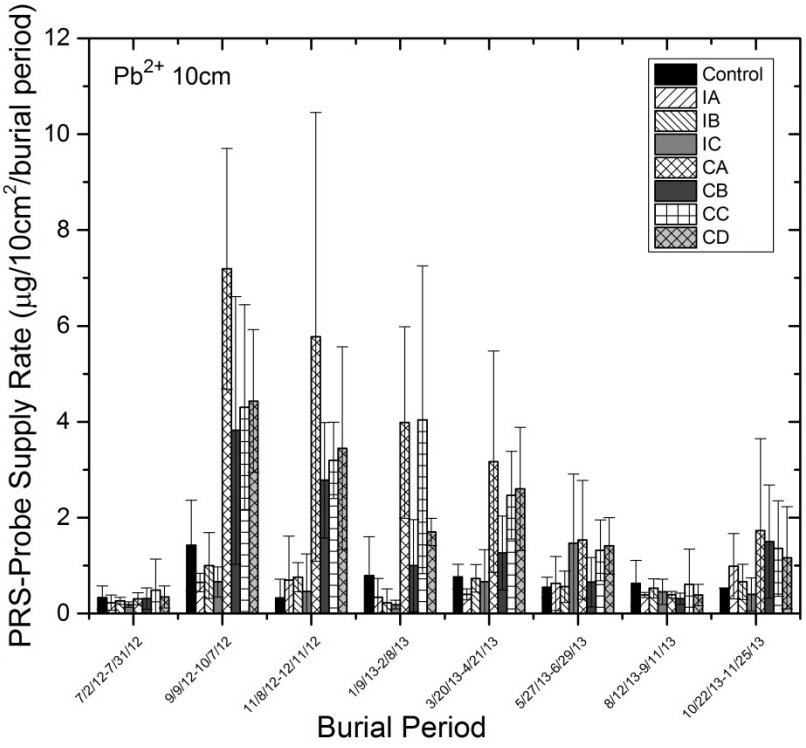
10/22/13-11/25/13
Burial Period


Pb2+ 10cm
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PRS-Probe Supply Rate (μg/10cm2/burial period)
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7/2/12-7/31/12
9/9/12-10/7/12
11/8/12-12/11/12
1/9/13-2/8/13
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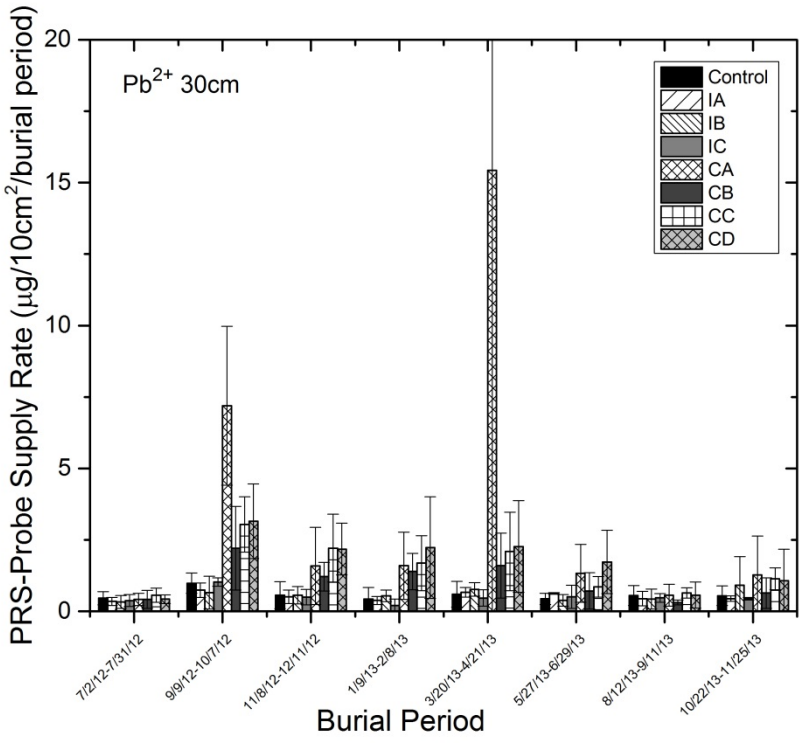
8/12/13-9/11/13
10/22/13-11/25/13
Burial Period


Pb2+ 30cm
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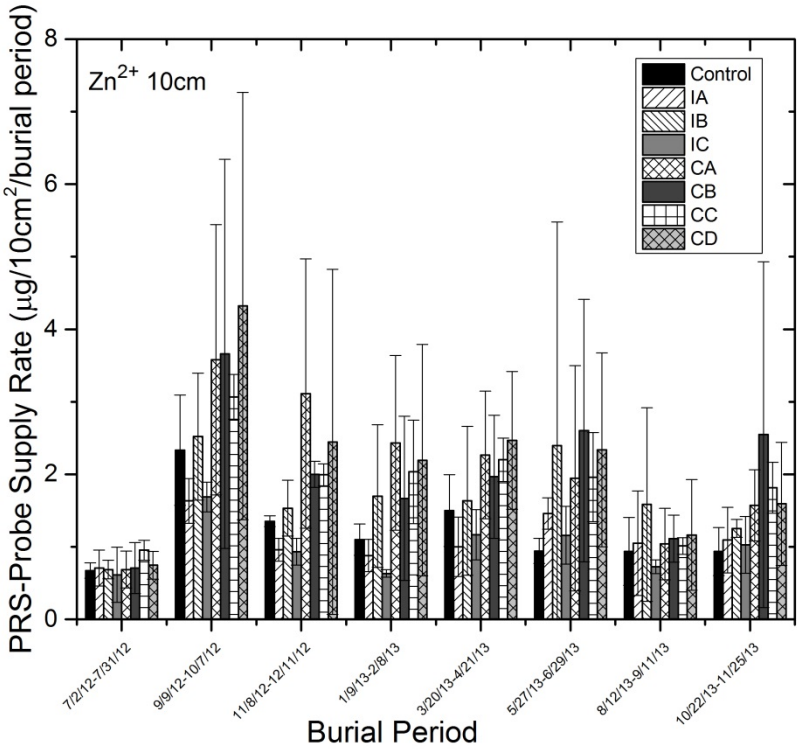
10/22/13-11/25/13
Burial Period


Zn2+ 10cm
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PRS-Probe Supply Rate (μg/10cm2/burial period)
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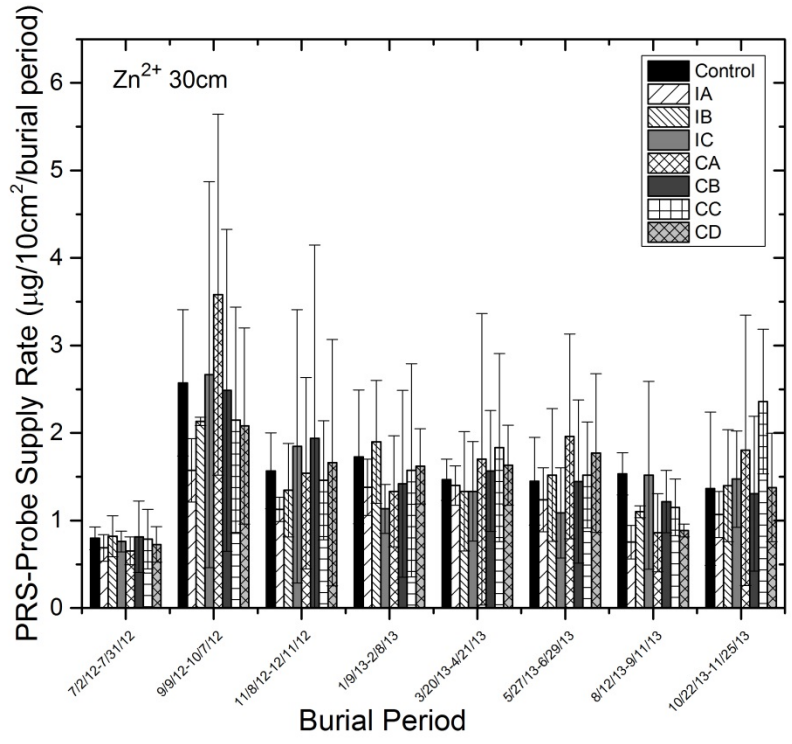
10/22/13-11/25/13
Burial Period


Zn2+ 30cm
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PRS-Probe Supply Rate (μg/10cm2/burial period)
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7/2/12-7/31/12
9/9/12-10/7/12
11/8/12-12/11/12
1/9/13-2/8/13
3/20/13-4/21/13
5/27/13-6/29/13
8/12/13-9/11/13
10/22/13-11/25/13
Burial Period