

An analysis of solute transport on a harvested hillslope in the southern Appalachian Mountains

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An analysis of solute transport on a harvested hillslope in the southern Appalachian Mountains

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(ABSTRACT)

Interest in transport of dissolved nitrogen (N) and carbon (C) in forested ecosystems is growing because of potential effects of these solutes on streamwater quality and implications for C sequestration. Additional research will further the understanding about the dynamics of these soil solutes, particularly in response to harvesting of forests. Also, the purported role of riparian buffers, where logging is restricted along stream channels, in retaining soil solutes is not well studied in the steeply sloping terrain of the southern Appalachian Mountains. I examined solute transport in a first-order watershed in the Nantahala National Forest in North Carolina that was harvested in February 2006 with retention of a 10-m riparian buffer.

To quantify the movement of dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), and dissolved organic carbon (DOC), four transects of lysimeters, approximately 30 m apart, were installed perpendicular to the stream on one hillslope. Porous ceramic cup (2-bar) lysimeters were installed in each transect 1, 4, 10, 16, 30, and 50 m from the stream in the A horizon and B horizon, and 4, 16, and 50 m from the stream in the saprolite layer. Samples were removed from the lysimeters 24 hr after 50 centibars of tension were placed on them, and riparian groundwater well and stream samples were collected at the same time as lysimeter samples. Collection of samples from the lysimeters, wells, and stream occurred every four to six weeks for one calendar year beginning March 2007. A 16-wk laboratory N mineralization study was conducted on A horizon soils.

Mean nitrate values in the soil solution of the A horizon in the spring were 1.53mg-N/L and decreased through the growing season to 0.030mg-N/L. Mean soil solution nitrate values in the B horizon and saprolite layer were 0.40mg-N/L in the spring and summer and decreased to 0.031mg-N/L in the winter. Mean soil solution ammonium concentrations were higher in the A horizon (0.090mg-N/L) than the B horizon and saprolite layer (0.034mg-N/L) and were lowest during the summer and fall. Dissolved organic C was significantly higher in the A horizon, with values ranging from 2.3mg/L to 599mg/L, than in the relatively stable B horizon and saprolite (1.9mg/L to 36.6mg/L). Dissolved organic C was logarithmically correlated to DON ($r^2 = 0.64$),

and DON values were highest in the A horizon (0.70mg/L). Cumulative N mineralization potential ranged from 48.1mg-N/kg to 75.6mg-N/kg and was not a useful predictor for nitrate soil solution values.

Nitrate leached vertically, and a large percentage of nitrate was stored in the B horizon and saprolite. Ammonium, DON, and DOC did not appear to leach vertically because they did not increase in the B horizon or saprolite layer. Ammonium, DON, and DOC are less mobile in soil solution than nitrate. The 10-m riparian zone had little impact on nitrate, ammonium, DON, and DOC removal. Nitrate remaining in the A horizon was likely removed through plant uptake in the harvested area before reaching the riparian zone. There was no detectable difference between ammonium concentrations in the harvested area and riparian zone likely because of limited mobility. The riparian zone did not remove excess DON or DOC, and in some transects was a source of DON and DOC. Nitrate and DOC concentrations were highly variable among transects and locations within transects. This may be caused by sensitivity of these solutes to site heterogeneity. This suggests that a large number of lysimeters should be used to account for this variability in future studies to ensure accuracy.

This study observed limited vertical leaching of ammonium, DON, and DOC through the profile. However, excess nitrate was observed moving from the A horizon into the B horizon and saprolite layer, suggesting the potential for delivery to the stream via subsurface transport and the need for attenuation of nitrate by the riparian zone. Because of low concentrations of nitrate entering the riparian zone during this study, the capacity for riparian attenuation of nitrate was not demonstrated.

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An analysis of solute transport on a harvested hillslope in the southern Appalachian Mountains

1 Introduction

1.1 INTRODUCTION

Nonpoint source pollution, such as increased sediment loads and nutrient fluxes, often associated with silvicultural practices can degrade stream ecosystems by impairing aquatic habitat and water quality. In 1972 the United States enacted the Federal Water Pollution Control Act to protect “the biological, chemical, and physical, integrity of the nation’s water ways.” This act, along with its associated amendments, required that states develop and enact Best Management Practices (BMPs) for silvicultural operations to alleviate and reduce the impact of nonpoint source pollution on waterways. Forestry BMPs, which provide guidelines ranging from road building to harvesting, are designed to allow silvicultural treatments to continue with a minimum impact on stream quality (Lynch and Corbett 1990).

Although nitrogen (N), a federally regulated pollutant, is naturally found in stream water, excess N can enter waterways in response to harvesting through nonpoint sources. Riparian zones have been shown to remove up to 90% of nitrate entering from upslope sources (Peterjohn and Correll 1984). Both plant uptake and denitrification reduce nitrate in riparian zones (Vitousek and Melillo 1979), although the percentage removed by each varies from site to site (Sabater et al. 2003).

A large amount of research has been dedicated to nitrate removal by riparian zones in agricultural systems, particularly in the Coastal Plain (Lowrance et al. 1984, Peterjohn and Correll 1984, Lowrance et al. 1985, Vought et al. 1995). It has been well documented that BMPs with riparian zones greatly reduce the amount of N entering streams due to silvicultural activities (Lynch and Corbett 1990, Hubbard and Lowrance 1997, Arthur et al. 1998, Wynn et al. 2000, Sabater et al. 2003). However, relatively few studies have examined nitrate removal laterally and/or vertically in the riparian zone (Cooper 1990, Nelson et al. 1995, Hubbard and Lowrance 1996). The impact of riparian zones on nitrate removal in the vadose zone laterally and vertically, particularly in deeper soil horizons, is still relatively unexplored.

Increases in water yield after harvesting not only cause increased leaching, but coupled with temperature increases, can cause accelerated nitrification from organic matter decomposition (Vitousek and Melillo 1979, Wynn et al. 2000). The increases in N mineralization and available N can cause soil nitrate concentrations to remain elevated for several years in disturbed systems (Waide et al. 1988, Yeakley et al. 2003). After harvesting, decreased plant uptake can also cause nitrate levels in the stream and soil solution to increase

(Swank and Vose 1997, Wynn et al. 2000). Soil nitrate levels after harvesting have been shown to peak in March and decrease during the summer months, most likely because of plant uptake during the growing season (Pardo et al. 1995), and stream nitrate levels have shown the same seasonal response (Likens and Bormann 1995, Swank and Vose 1997, Kaushal and Lewis 2003, Dittman et al. 2007).

Harvesting does not always increase ammonium concentrations and riparian zones may not be necessary for lowering ammonium concentrations (Blackburn and Wood 1990, Hubbard and Lowrance 1997). Ammonium concentrations increased and remained elevated for several years after harvesting in the top 10cm of soil in the Southern Appalachians (Waide et al. 1988). However, the study design did not account for the effectiveness of riparian zones for removal of ammonium. Additionally, Gallardo (2003) found that soil water ammonium concentrations in Spain were not highly variable because ammonium cations are not very mobile and tend to be retained.

Additional research will further our understanding about the impact of harvesting and disturbance on dissolved organic nitrogen (DON), which will leach from N-limited ecosystems despite demands for nitrate and ammonium (Perakis and Hedin 2002), and can be the dominant form of N leaching (Lovett et al. 2000). Labile DON can be taken up by plants (Neff et al. 2003), but DON losses from ecosystems can be biologically independent, especially if the DON consists of a large recalcitrant fraction (Campbell et al. 2000, Neff et al. 2003). Riparian buffer removal of DON is variable, with buffers acting as either sinks or sources of DON (Bedard-Haughn et al. 2004).

Sustained pulses of dissolved organic carbon (DOC) in streams can negatively impact the limnology of receiving lakes by increasing acidity and controlling transport, solubility, and toxicity of metals (Carignan et al. 2000, McGlynn and McDonnell 2003). After harvesting, DOC concentrations increased and remained elevated for up to 15 years in the northern Appalachians (Dai et al. 2001). However, in the southern Appalachians studies have shown that harvesting and disturbances do not cause significant increases in soil water DOC concentrations (Meyer and Tate 1983, Yeakley et al. 2003). Dai et al (2001) observed that increased levels of DOC in soil did not result in increased levels in the stream.

The steep mountain slopes of the southern Appalachians have been harvested for timber beginning in the late 1800's. However, with growing interest in retention of N and C in forested

watersheds, there is an increasing need to understand the impact of contemporary forest harvesting on DIN, DON, and DOC dynamics within these watersheds. This study focuses on the movement of dissolved N and C through the soil solution at multiple depths and locations over the course of one year on a harvested hillslope with a 10-m riparian buffer located in the southern Appalachian Mountains of southwestern North Carolina.

1.2 LITERATURE REVIEW

1.2.1 Nonpoint Source Pollution from Forest Management

Silvicultural operations can degrade water quality because of increases in water yields, stream temperature, sediment loading, and nutrient concentrations (Corbett et al. 1978, Wynn et al. 2000). Potentially harmful silvicultural practices include road construction, harvesting, and site preparation for regeneration (Binkley and Brown 1993). Often, the two biggest sources of stream impairment from silvicultural operations are excess sediment and nitrate loading (Lowrance et al. 1983, Binkley and Brown 1993, Wynn et al. 2000).

After harvesting, water yields can greatly increase because of decreases in evapotranspiration (Arthur et al. 1998). Higher water yields can alter stream hydrology and can also increase erosion, nutrient leaching, and biogeochemical cycling of nutrients (Lynch and Corbett 1990). In the Ridge and Valley province, water yields can dilute stream solutes such as calcium, magnesium, and sodium (Lynch and Corbett 1990) while in the Cumberland Plateau province water yields increase leaching, which can override dilution effects (Arthur et al. 1998).

Erosion can increase because of forest road construction, harvesting, and site preparation, although the amount of increase varies from site to site (Binkley and Brown 1993, Arthur et al. 1998). Increases in fine sediment particles can alter stream substrate and block light, both of which can have detrimental impacts on stream organisms (Hesser et al. 1975). Sediment increases are also damaging to drinking water sources because of the higher cost and time associated with removing sediments from water (Corbett et al. 1978). Not only can sediment physically impair water quality, but nutrients are often attached to the sediment particles, which can chemically impair streams (Wynn et al. 2000).

Removal of trees from riparian zones can cause thermal pollution in waterways and bank destabilization. Increases in stream temperature negatively affect fish by influencing metabolic rates, hatching, development, and migration patterns (Hesser et al. 1975). Stream temperature

increases can also cause a decrease in oxygen availability (Binkley and Brown 1993). Additionally, the removal of trees along channels can lead to bank destabilization, which can cause in-stream channel erosion and bank failure.

Silviculture operations in the Appalachians can cause an increase in nutrients released into streams, such as phosphate and nitrate (Corbett et al. 1978, Arthur et al. 1998). These nutrients can be detrimental to organisms living in streams because they increase algae growth, alter foodwebs, and can lead to eutrophication (Binkley and Brown 1993). However, most increases in phosphorus levels due to forestry practices are not substantial enough to critically impair streams (Binkley and Brown 1993). Nitrate is a federally regulated drinking water pollutant, and excess nitrate in streams and lakes can also lead to eutrophication (Nelson et al. 1995). Increases in water yield associated with harvesting can not only cause increased leaching, but coupled with temperature increases, can cause accelerated nitrification from organic matter decomposition (Vitousek and Melillo 1979, Wynn et al. 2000). Soil nitrate and ammonium levels can remain elevated for several years following disturbances and harvesting in the southern Appalachians, most likely because of an increase in available nitrate and an increase in N mineralization rates from increases in soil temperature and moisture (Waide et al. 1988, Yeakley et al. 2003). Nitrogen mineralization rates vary widely from forest to forest, but rates are generally higher in hardwoods than in conifers. In undisturbed forests much of the nitrified N does not reach the stream because plants act as a nitrate sink (Vitousek and Melillo 1979).

1.2.2 Harvesting Impacts on Nitrogen

After harvesting, increased nitrification and decreased plant uptake can cause nitrate levels in the stream and soil solution to increase (Swank and Vose 1997, Wynn et al. 2000). Soil nitrate levels after harvesting have been shown to peak in March and decrease during the summer months, most likely because of plant uptake during the growing season (Pardo et al. 1995). Stream nitrate responses in recently disturbed watersheds can also be seasonal. Lower nitrate levels in summers are attributed to seasonal plant uptake and microbial demand (Likens and Bormann 1995, Swank and Vose 1997, Kaushal and Lewis 2003, Dittman et al. 2007). Nitrate can also be removed from stream water via biotic uptake and denitrification in streambed sediment (Mulholland et al. 2008). In watersheds with mature forest communities in the southern Appalachians that have stable N mineralization levels and nitrate output, stream

concentrations have been shown to be higher during summer and drought years when the dilution impact is moderated (Swank and Vose 1997).

Soil nitrate levels, stream nitrate levels, and *in-situ* N mineralization are often strongly correlated and frequently increase after disturbance (Dittman et al. 2007). However, soil nitrate concentrations can be extremely variable within a small range because of variability in plant uptake, soil leaching, nitrification, and denitrification (Gallardo 2003). In contrast, ammonium concentrations are often less variable in the soil because ammonium is less mobile and tends to be retained as cations (Gallardo 2003). Post-disturbance increases in N levels are most often observed near the soil surface and diminish at lower horizons (Yeakley et al. 2003).

Currently, little is known about the impact of harvesting and disturbance on DON. Dissolved organic N will leach from N-limited ecosystems despite demands for nitrate and ammonium (Perakis and Hedin 2002) and can be the dominant form of N leaching in the Northern Appalachians (Lovett et al. 2000). However, labile DON can be taken up by plants in addition to the N produced from microbial mineralization (Neff et al. 2003). Still, DON losses from ecosystems can be less biologically dependent, especially if the DON in the system consists of a large recalcitrant fraction (Campbell et al. 2000, Neff et al. 2003).

1.2.3 Harvesting Impacts on Organic Carbon

After harvesting, dissolved organic carbon (DOC) concentrations in soil solution can increase and remain elevated for up to 15 years in the northern Appalachians (Dai et al. 2001). However, in the southern Appalachian forests increases in soil water DOC concentration were statistically insignificant after harvesting (Meyer and Tate 1983) or even decreased after disturbance (Yeakley et al. 2003). Furthermore, high concentration variability among porous cup lysimeters can make it difficult to determine effects of harvesting (Meyer and Tate 1983). Increase in DOC in Canada after harvesting can be caused by large quantities of easily leached decomposed organic material that, coupled with higher temperature and water yield, can lead to increases of DOC (Carignan et al. 2000). However, lower leaf litter inputs after harvesting could decrease DOC leaching into the soil water in successive years (Meyer and Tate 1983).

In systems with sustained DOC export, DOC can negatively impact limnology properties by increasing stream acidity and altering nutrient availability (Carignan et al. 2000). However, Dai et al. (2001) observed that increased levels of DOC in soil did not result in increased DOC in the stream, and Meyer and Tate (1983) found that DOC concentrations were lower in a harvested

stream than a non-harvested stream. Elevated stream DOC concentrations in mountain streams may be a result of increased precipitation and increased microbial activity, (McGlynn and McDonnell 2003, Dittman et al. 2007). In Coastal Plain regions, 63% of the DOC leached into streams came from riparian wetlands, which only contributed 6% of the area (Dosskey and Bertsch 1994).

1.2.4 Forestry Best Management Practices

Silvicultural operations must be managed to minimize movement and delivery of excessive sediment and nutrients to streams and to maintain stream temperature dynamics. Forestry BMPs became a necessary part of forest management practices when the United States enacted the Federal Water Pollution Control Act in 1972 (FWPCA) and its subsequent amendments. Section 208 of the FWPCA recognized silvicultural activities as sources of nonpoint source pollution and required states to develop management plans to reduce nonpoint source pollution of water associated with forestry. In addition, section 304 granted the EPA authority to issue guidelines to states for identifying and evaluating the specific sources of nonpoint source pollution resulting from silviculture and appropriate methods to manage the sources of pollution.

State BMPs outline practices for building roads, harvesting, site preparation, and riparian buffers that maintain the integrity of the streams by preventing excessive erosion and minimizing nutrient fluxes. The BMPs issued by each state are methods that have been found to best reduce pollution and site degradation so that water quality meets state and federal guidelines (Corbett et al. 1978). Besides differences among states, the BMPs implemented vary because of slope, soils, and water quality needs of a specific site (Corbett et al. 1978).

Best management practices have been found to alleviate and minimize water quality degradations that could arise due to harvesting, such as sediment loading and nutrient pollution (Lynch and Corbett 1990, Wynn et al. 2000). In addition, BMPs help maintain stream temperature and prevent channel erosion (Lynch and Corbett 1990). The amount of phosphorus and N entering streams is lessened when forestry BMPs are in place on a site (Arthur et al. 1998, Wynn et al. 2000).

1.2.5 Riparian Buffer Zones

Riparian buffer zones, also called streamside management zones (SMZs), are areas adjacent to streams or wetlands where management is focused on retaining riparian structure and

function. An essential component of most BMPs, SMZs serve as buffers between intensive upland management and waterways (Lowrance et al. 1983). Their biological and physical attributes help ameliorate upslope practices by filtering sediment and retaining and/or transforming nutrients (Nutter and Gaskin 1988). Sources of sediment entering streams include alluvial sediment from accelerated stream bank erosion, colluvial sediment from adjacent hillslope erosion, and from roads and skid trails (Arthur et al. 1998). Riparian zones reduce the amount of sediment entering streams through increased filtration and infiltration (Binkley and Brown 1993). Forested riparian zones also provide habitat for wildlife, provide coarse woody debris to streams, control stream temperature by providing shade, and stabilize the stream bank.

Riparian zones have been shown to reduce the amount of N, P, Ca²⁺, Mg²⁺, K⁺ and Cl⁻ entering streams in mountain and coastal areas (Lowrance et al. 1983, Arthur et al. 1998). Paired watershed studies in Appalachian sites have shown that stream nitrate concentrations are significantly lower in sites with intact riparian zones (Arthur et al. 1998). The riparian zones can also remove as much as 80% of phosphorus originating from adjacent agricultural fields in the Coastal Plain (Peterjohn and Correll 1984). Biotic processes, such as denitrification and nutrient assimilation, along with abiotic processes including volatilization and adsorption, lead to the retention or removal of nutrients within the riparian zones. Dissolved nutrients in surface runoff can also be retained through sediment deposition (Lowrance et al. 1984). The ability of riparian zones to effectively remove nutrients and sediments depends on soil and vegetation properties of the riparian zone along with the topography (Comerford 1992).

Although riparian zones can reduce the concentrations of sediment and nutrients entering streams, they do not fully prevent impairment of water quality. During high precipitation events and in steep sites, overland flow can occur that allows sediment to reach the stream (Arthur et al. 1998). When channelized flow occurs, riparian zones are unable to reduce flow rates and allow for suspended sediment and associated nutrients to fall out of suspension (Nutter and Gaskin 1988). Additionally, riparian zones do not have infinite sink potential and can be overloaded by upslope sources (Nutter and Gaskin 1988), and it has been suggested that mature trees should be harvested from the riparian zone to remove nutrients from the system and allow for new growth and increased plant uptake (Lowrance et al. 1983).

Movement of subsurface flow in the riparian zone and how it impacts filtration and nutrient uptake is poorly understood (Bosch et al. 1994). It has been shown though that

preferential flow paths can impact the remediation capabilities of riparian zones (Angier et al. 2005). Additionally, because of the complex nature of the biological and physical components in riparian zones, it is often difficult to determine which and to what extent certain processes are functioning on sites because of riparian zone heterogeneity (Nutter and Gaskin 1988).

The appropriate width of the riparian buffer is often debated, and needs to be sufficient to maintain the riparian functions and to meet management goals (Vought et al. 1995). When managing for wetland birds or animals, large riparian buffers of up to 100m may be needed. However, sediment management may only require a 10m buffer which has been shown to reduce the input of sediment into a stream by up to 99% (Castelle et al. 1994). Overall, riparian buffers of 15m have been found to be effective for nonsource pollution control at most sites. However, the necessary width is still site-dependent and determined by management objectives (Castelle et al. 1994). At sites with easily erodable soil or steep slopes, a riparian buffer of up to 30m may be necessary to prevent most nonsource point pollution (Corbett et al. 1978).

1.2.6 Nitrogen Removal in Riparian Zones

Paired watershed studies have shown that riparian zones can significantly reduce the amount of N entering streams by effectively retaining and/or transforming nitrate and ammonium in the soil solution (Hubbard and Lowrance 1996, Arthur et al. 1998, Sabater et al. 2003). Effectiveness of riparian zones is variable, and neither climate nor vegetation appear to be an overriding factor in the N removal ability of the riparian zones (Sabater et al. 2003), although it has been shown that forested riparian zones are much more efficient than grass riparian zones at removing nitrate (Hubbard and Lowrance 1997). Riparian zones remove nitrate through plant uptake, denitrification, and microbial immobilization (Simmons et al. 1992). Ammonium is removed through immobilization by decomposers or by plant assimilation (Vitousek and Melillo 1979). Streams can also remove N through biological assimilation (Cooke and Cooper 1988, Mulholland et al. 2008). However, nitrate, rather than ammonium, is the primary form of N removed from soil solution in riparian zones (Martin et al. 1984, Cooper 1990). Ammonium concentrations in soil solution do not generally increase after harvesting, explaining the lack of riparian effects on ammonium removed from systems (Blackburn and Wood 1990, Hubbard and Lowrance 1997). Riparian buffer removal of dissolved organic N is variable, with some buffers attenuating sources of DON and others providing a source of DON, most likely due to differences in concentrations of labile and recalcitrant forms (Bedard-Haughn et al. 2004).

Riparian buffers have been shown to reduce nitrate by up to 90% in coastal areas (Peterjohn and Correll 1984). In these areas, which have high organic matter and are seasonally flooded, denitrification is the main source of nitrate removal (Lowrance et al. 1984). The anaerobic conditions in these soils have high denitrification potential and are actually underutilized for nitrate removal (Cooper 1990). Because of the high amount of denitrification in these areas, plant uptake may account for less than 33% of nitrate removal (Peterjohn and Correll 1984).

Both wetland riparian zones and drier riparian zones have been shown to have a high capacity of nitrate removal during the growing season, while during the dormant season transition zones may only remove a third of the amount of nitrate as the wetland zones (Simmons et al. 1992). Nitrate loading in streams has also been found to be highest in riparian zones with low microbial activity (Cooper 1990). The wetland riparian areas dominated by hydric soils not only remove nitrate more efficiently year round, but remove the nitrate uniformly throughout the extent of the riparian zone (Nelson et al. 1995). In a study by Simmons et al. (1992) it was reported that in non-hydric riparian soils there is minimal removal of groundwater nitrate, less than 36%, compared to hydric riparian soil with a high removal of groundwater nitrate, up to 86%. These consistent removal rates in riparian zones with hydric soils indicate that denitrification is a major cause of nitrate loss (Nelson et al. 1995). Additionally, studies have found that riparian zones with higher water tables were more effective at removing groundwater nitrate, most likely because the high water table had more contact with the root zones and allowed for a larger amount of plant uptake (Cooper 1990, Nelson et al. 1995).

Although riparian zones can reduce the amount of N reaching waterways from upslope disturbances, they do not retain or transform all N from the system (Lynch and Corbett 1990, Arthur et al. 1998). Nitrate levels in streams can still become elevated immediately after harvesting and typically remain elevated for several years before decreasing as vegetation is reestablished. Nitrate released from upslope activities can take several years to move to the riparian zone, and most of this movement occurs during rainy seasons in the Coastal Plain (Hubbard and Lowrance 1996). However, because of the ability of the riparian zones to effectively retain or transform N, the nitrate levels rarely exceed EPA drinking water quality standards of 10mg-N/L and levels typically remain below 0.5mg-N/L in North America (Binkley and Brown 1993).

Preferential flow paths, such as macropore systems, can discharge soil solutes directly to streams (Angier et al. 2005). Because of the rapid rate of movement, the nitrate that moves through these preferential flow paths is not likely to be subjected to denitrification or plant uptake, making these sources responsible for a large portion of nitrate entering streams (Simmons et al. 1992). These spatial variations, along with seasonal variations, influence the movement and fate of nitrate in groundwater (Simmons et al. 1992). However, Hubbard and Lowrance (1996) showed that 7m within a riparian zone in the Coastal Plain most nitrate that entered the edge of the riparian zone had been removed.

1.2 RESEARCH OBJECTIVES

The overall goal of this project is to quantify the transport of DIN, DON, and DOC on a recently logged mountainside hillslope with a 10-m streamside management zone in place. It has been well documented that riparian zones can limit the amount of sediment and nutrients entering stream channels by a variety of physical, biological, and chemical processes including filtration, plant uptake, and denitrification. However, movement and pathways of soil solute are still poorly understood, especially in response to silvicultural operations on steep slopes. Monitoring of this site will further the understanding of dissolved N and C transport on harvested hillslopes by examining the following specific objectives:

1. Determine the relationship of N mineralization potential to patterns of dissolved N in the A horizon.
2. Determine if DN or DOC leaches into the saprolite layer and the relationship between DN and DOC in the saprolite layer and DN and DOC in the upper soil horizons.
3. Quantify patterns of DN and DOC within the soil solution from the harvested upslope area through the riparian buffer.
4. Explore relationships between levels of DN and DOC in soil solution and levels of DN and DOC in near-stream groundwater and in the stream.

1.3 NOTES ABOUT CHAPTER 2 AND APPENDICES

Publication of research findings in peer-reviewed journals is an important part of the scientific process. Virginia Tech and the Department of Forestry encourage publication in a peer-reviewed journal and recommend that the thesis body of work conform to scientific journal

formats. For that purpose, Chapter 2 of this paper has been written as a draft manuscript describing the study design and findings that will later be submitted to a peer-reviewed journal for publication.

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2 An analysis of solute transport on a harvested hillslope in the southern Appalachian Mountains

2.1 INTRODUCTION

Nonpoint source pollution, such as increased sediment loads and nutrient fluxes, sometimes associated with silvicultural practices can degrade stream ecosystems by impairing aquatic habitat and water quality. Silviculture operations, particularly forest harvesting and associated building and maintenance of logging roads, can impair water quality because of increases in water yields, sediment loading, and nutrient concentrations (Corbett et al. 1978, Wynn et al. 2000). Potentially damaging silvicultural practices include road construction, harvesting, and site preparation for regeneration (Binkley and Brown 1993). Two of the largest sources of stream impairment from silvicultural operations are sediment and nitrate loading (Lowrance et al. 1983, Binkley and Brown 1993, Wynn et al. 2000).

Increases in water yield after harvesting not only can cause increased leaching, but coupled with temperature increases, can cause accelerated nitrification from organic matter decomposition (Vitousek and Melillo 1979, Wynn et al. 2000). Increases in nitrogen (N) mineralization rates and available N can cause nitrate concentrations to remain elevated for several years in disturbed systems in the southern Appalachians (Waide et al. 1988, Yeakley et al. 2003). Ammonium concentrations can also remain elevated in the top 10cm of soil for several years in the southern Appalachians (Waide et al. 1988), whereas several Coastal Plain studies showed no increases in ammonium after harvesting (Blackburn and Wood 1990, Hubbard and Lowrance 1997). Decreased plant uptake after harvesting can cause nitrate levels in streams and soil solution to increase (Swank and Vose 1997, Wynn et al. 2000). Soil nitrate levels after harvesting have been shown to peak in March and decrease during the summer months, most likely because of plant uptake during the growing season (Pardo et al. 1995), and stream nitrate levels have shown a similar pattern of response (Likens and Bormann 1995, Swank and Vose 1997, Kaushal and Lewis 2003, Dittman et al. 2007).

Riparian zones have been shown to remove up to 90% of nitrate entering from upslope sources in the Coastal Plain (Peterjohn and Correll 1984). Both plant uptake and denitrification reduce nitrate in riparian zones (Vitousek and Melillo 1979), although the percentage removed by each varies from site to site (Sabater et al. 2003).

A large amount of research has been dedicated to studying nitrate removal in riparian systems in agricultural systems and Coastal Plain areas (Lowrance et al. 1984a, Peterjohn and Correll 1984, Lowrance et al. 1985, Vought et al. 1995). Most research examining nitrate

pollutants in silvicultural operations has been broader in scope. It has been well documented that BMPs with streamside management buffer zones can greatly reduce the amount of N entering streams due to silvicultural activities (Lynch and Corbett 1990, Hubbard and Lowrance 1997, Arthur et al. 1998, Wynn et al. 2000, Sabater et al. 2003). Relatively few studies have examined nitrate removal laterally and/or vertically in the riparian zone, and then only in groundwater (Cooper 1990, Nelson et al. 1995, Hubbard and Lowrance 1996). This study will further our knowledge about the impact of riparian zones on nitrate removal in the vadose zone laterally and vertically.

Less research is available on the impact of harvesting on dissolved organic nitrogen (DON) and dissolved organic carbon (DOC). Recent studies have shown that DON is an important part of N cycling in forest ecosystems, and further investigations will help explain how harvesting impacts DON transport in soil solution (Neff et al. 2003). Rapidly expanding interest in global carbon (C) cycling has created a need to understand how forest management affects C dynamics, including C sequestration in forest soils and movement of DOC in response to forest harvesting.

It has been reported that DON leaches from N-limited ecosystems in South America despite demands for nitrate and ammonium (Perakis and Hedin 2002) and can be the dominant form of N leaching in North America (Lovett et al. 2000). Even though labile DON can be taken up by plants along with the N produced from microbial mineralization (Neff et al. 2003), DON losses from ecosystems can be biologically independent, due to a large recalcitrant fraction of DON in many systems (Campbell et al. 2000, Neff et al. 2003). Riparian buffer removal of DON is variable, with some buffers attenuating sources of DON and others leaking DON, most likely due to differences in concentrations of labile and recalcitrant forms (Bedard-Haughn et al. 2004).

Sustained inputs of DOC to streams can negatively impact limnological properties (Carignan et al. 2000). After harvesting, DOC concentrations in soil solution can increase and remain elevated for up to 15 years in the northern Appalachians (Dai et al. 2001). Increases in DOC after harvesting in Canada were attributed to large quantities of easily leached decomposed organic material that, coupled with the higher temperatures and water yields, can lead to increased delivery of DOC to stream channels (Carignan et al. 2000). However, Dai et al. (2001) observed that the increased levels of DOC in soil did not result in increased DOC in the stream.

In the southern Appalachians, studies have shown that increases of soil solution DOC concentration can be statistically insignificant after harvesting (Meyer and Tate 1983) or can even decrease after disturbance (Yeakley et al. 2003), and stream DOC concentrations can be lower in a harvested stream than a non-harvested stream (Meyer and Tate 1983). Decreases in DOC after harvesting can be caused by decreased leaf litter inputs that could reduce DOC leaching into the soil solution in successive years (Meyer and Tate 1983).

The steep mountain slopes of the southern Appalachians have been harvested for timber beginning in the late 1800's. However, with growing interest in retention of N and C in forested watersheds, there is an increasing need to understand the impact of contemporary forest harvesting on DIN, DON, and DOC dynamics within these watersheds. This study focused on the movement of dissolved N and C through the soil solution on a hillslope of a harvested watershed located in the southern Appalachian Mountains of southwestern North Carolina and the role of a streamside management zone (SMZ) in attenuating delivery of DIN, DON, and DOC to a first-order stream.

2.2 OBJECTIVES AND HYPOTHESIS

The overall goal of this project was to quantify the transport laterally and vertically of DIN, DON, and DOC on a mountainside hillslope logged with a 10-m SMZ in place. Additionally, the project determined if there was a relationship between N mineralization potential in the surface 15cm of soil and patterns of *in situ* dissolved N. On harvested hillslopes, increased temperatures, increased organic matter from logging debris, and increased soil moisture can increase N mineralization and N leaching in the surface horizon (Carignan et al. 2000, Wynn et al. 2000). *In-situ* net N mineralization can be strongly correlated to soil nitrate levels in a watershed (Dittman et al. 2007). Therefore, it was hypothesized that pulses of dissolved N in the A horizon will correlate with areas of high N mineralization potential.

Excess N and C in the soil solution that is not immobilized, transformed, or taken up by plants can move laterally and vertically through the soil profile towards the stream and increase N and C loading to the stream (Adams et al. 2006). Nitrogen and C concentrations are greatest in the upper soil horizons and concentrations diminish as water percolates to lower horizons and into the stream (Yeakley et al. 2003, Dittman et al. 2007). Based on literature above, it was expected that storage and transport of dissolved N and C within the B horizon and saprolite layer

were negligible compared to the A horizon. Plant uptake and denitrification in riparian zones can lower excess N levels (Lynch and Corbett 1990, Hubbard and Lowrance 1997, Arthur et al. 1998, Sabater et al. 2003). However, DOC concentrations tend to remain consistent between upslope and riparian zones (Dai et al. 2001). It was expected that concentrations of dissolved N in the soil solute would decrease in the riparian zone, while dissolved organic C concentrations would not change between upslope locations and the riparian zone. Dissolved N and C patterns in the soil solution are expected to be similar to patterns in the stream, although seasonal patterns in the stream were often tempered compared to those in soil solution (Yeakley et al. 2003, Dittman et al. 2007).

2.3 METHODS

2.3.1 Site Description

The Ray Branch study site is located in southwestern North Carolina in the Nantahala Ranger District of the Nantahala National Forest (latitude 35°12'3''N, longitude 83°32'39''W; Figure 1). Vegetation in the area is a second-growth mixed-oak (*Quercus*) mature hardwood forest. Climate at the site is classified as marine-humid-temperate (Swift et al. 1988). The area receives approximately 237cm of precipitation annually (Figure 2), predominantly in the form of rainfall from the Gulf of Mexico, and the precipitation is evenly distributed throughout the year (Swift et al. 1988). The hillslope has a north aspect and a steep topography, averaging 30% in the riparian zone and 15% in the harvested area. The riparian soils are mapped as Cullasaja (Humic Dystrudepts), whereas soils on shoulder slope positions are mapped as Evard (Typic Hapludults). Pockets of Lithic Dystrudepts Chestnut and Edenyville soils are also present on the site (Soil Survey Staff 2008). The harvested site is small (1.36ha) and is drained by a first-order stream. The site was harvested as a shelterwood in February 2006. The trees were felled with a chainsaw and removed with a cable yarder and log skidder in February 2006. A 10-m-buffer was left adjacent the stream. No trees were removed from the buffer, although trees from the upslope area were felled into and then removed from the buffer. The study site is part of a larger study that consists of three other sites: an unharvested control, 30-m-buffer, and 0-m-buffer. Additional studies are currently being conducted by the U.S.D.A. Forest Service Coweeta Hydrologic Laboratory on the site, ranging from assessments of stream leaf litter inputs to vegetative re-growth.

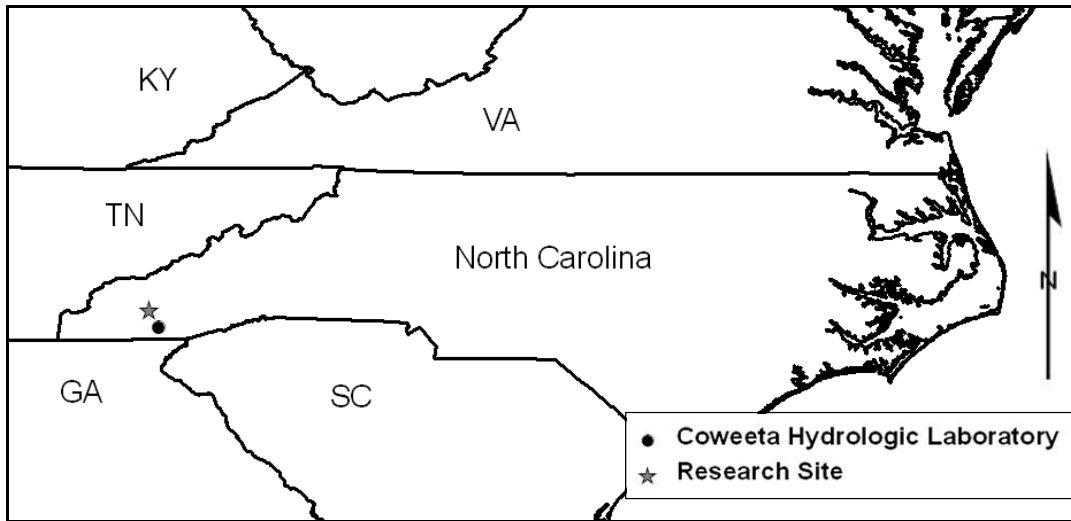


Figure 1. Ray Branch site location and Coweeta Hydrologic Laboratory location in Otto, North Carolina.

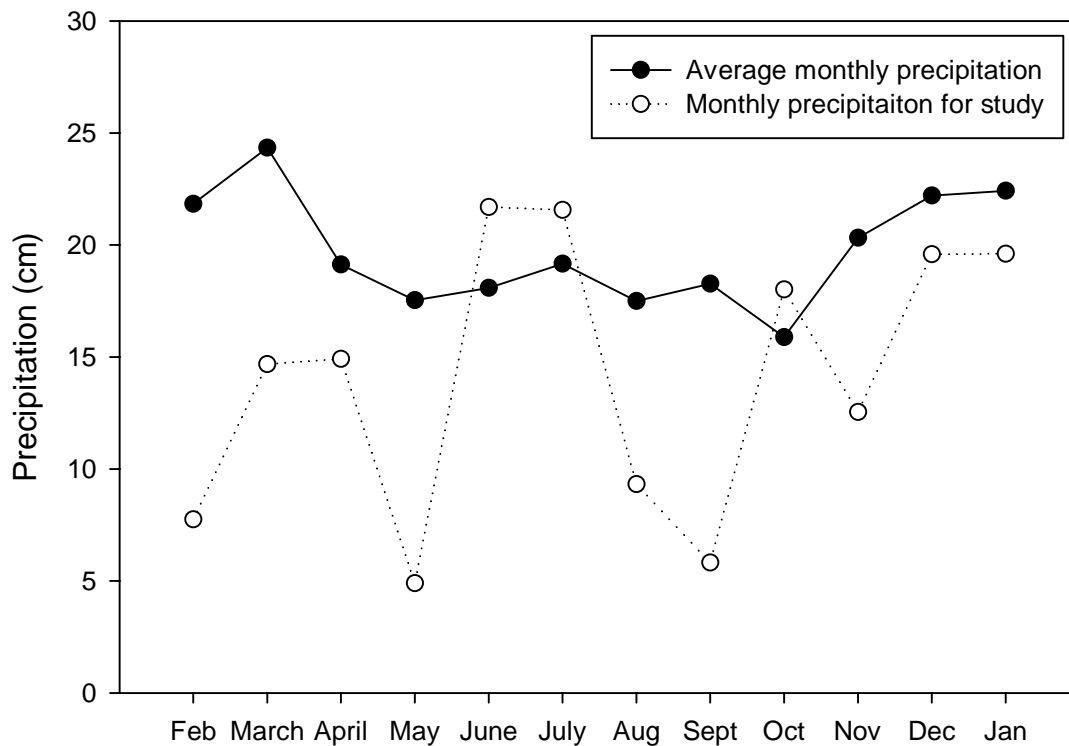


Figure 2. Average monthly precipitation at Coweeta Hydrologic Laboratory in North Carolina from August 1936 to April 2008 and monthly precipitation from February 2007 to January 2008. Data provided by Coweeta Hydrologic Laboratory, U.S.D.A. Forest Service.

2.3.3 Data Collection and Analysis

2.3.3.1 Dissolved Nitrogen and Carbon

To quantify the movement of DIN, DON, and DOC on the selected hillslope, four transects of tension lysimeters were installed perpendicular to the stream on one hillslope (Figure 2). The transects were separated from each other by a distance of 25-40m and were located in surface identified preferential flow paths. Porous ceramic cup (2-bar) lysimeters were installed in each transect 1, 4, 10, 16, 30, and 50 m from the stream (Figure 3). Each point location had two lysimeters installed: one located at a depth of 15cm (generally transition between A and B horizons) and the other located at a depth to the bottom of the Bt or B soil horizon (depths ranged from 38 to 70 cm below soil surface). Additional lysimeters were placed at least 30cm into the saprolite layer (depths ranged from 67 to 153 cm below soil surface) at transect locations 4, 16, and 50 m from the stream. In one transect, no lysimeters were installed 50-m from the stream because the point was located in a different watershed. A lysimeter was installed in the saprolite 30m away from the stream instead.

Lysimeters were installed by hand by augering holes to the desired depth. A slurry of deionized water, soil, and silicate powder was created to fill the bottom portion of the hole ensuring adequate contact between the porous cup of the lysimeter and the soil. The hole was then back filled with the augered soil. The lysimeters were then covered with 6in PVC pipe to protect from animal damage.

Wells from a concurrent study were installed within the 10-m-buffer site and are located at the bottom of two of the lysimeter transects (Figure 3). They were installed below the streambed and are screened for the bottom 15cm.

Samples were taken monthly from the lysimeters, wells, and stream for one calendar year beginning March 2007 to determine patterns of DIN, DON, and DOC in soil solution, riparian groundwater, and stream water. Samples were collected from the lysimeters twenty four hours after applying 50 centibars of tension. Well and stream samples were collected at the same time as lysimeter samples. The stream samples were collected at the bottom of each transect and above and below the harvested area.

Stream and well samples were filtered prior to analysis the same day they were collected using Whatman GF/G pre-ashed fiberglass filters. Lysimeter, well, and stream samples were

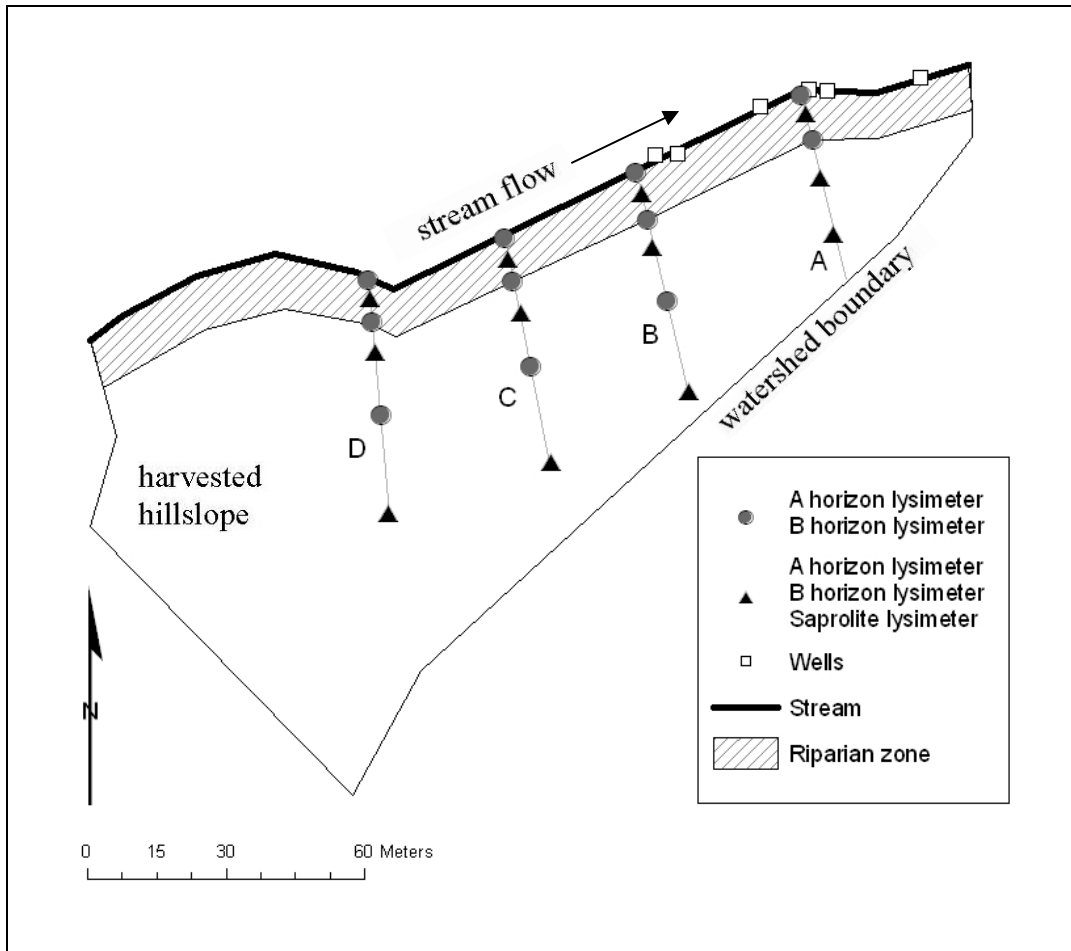


Figure 3. Lysimeter and well locations on a hillslope of the Ray Branch site within the Nantahala National Forest, North Carolina.

immediately frozen at -20°C until analysis was conducted. Concentrations of nitrate-N and ammonium-N were measured with a Seal AutoAnalyzer 3 that had detection limits of 0.002mg N/L (SEAL Analytical Inc., Mequon, Wyoming). Dissolved organic C concentrations were measured using an Elementar liquiTOC, which had a detection limit 1.8mg/L, and total dissolved nitrogen (TDN) was measured using the Elementar TNb, which had a detection limit of 0.85mg/L (Elementar Americas Inc., Mount Laurel, New Jersey). Dissolved organic N concentrations were determined by subtracting DIN (nitrate + ammonium) from TDN.

2.3.3.2 Soil Characterization

Soil samples for chemical and physical characterization were taken from the A horizon, B horizon, and saprolite layer at the six lysimeter locations within each transect. The soil samples were used to determine total C, total N, pH, available phosphorus, exchangeable cations, and particle-size distribution. Samples from the A horizon were also used to determine N mineralization potential based on a laboratory incubation. For the A horizon, five subsamples were collected from within 1m of each sampling point and composited for analysis. For the B horizon and saprolite layer, three sub-samples were taken from each and composited for analysis. Bulk density samples were also be collected at each transect point for the A horizon and at transect points 4, 16, and 50 for the B horizon and saprolite layer to minimize site disturbance.

Total soil C and total soil N were analyzed via dry combustion using the Elementar varioMax CNS (Elementar, Americas Inc., Mount Laurel, New Jersey). Available phosphorus was analyzed using a Mehlich extractable phosphorus method (Carter 1993) and measured using a spectrophotometric analysis using a Vista-MPX Inductively Coupled Plasma Spectrometer (Varion, Walnut Creek, California). Soil pH was be analyzed using a 1:1 soil:CaCl₂ dilution (Carter 1993) and measured using an Orion 3-Star Benchtop pH meter (Thermo Fisher Scientific, Waltham, Massachusetts). Exchangeable cations (Ca²⁺, K⁺, Mg²⁺, Na⁺) were analyzed using a double acid extraction (Carter 1993) and measured using a spectrophotometric analysis using a Vista-MPX ICP (Varion, Walnut Creek, California). Saturated hydraulic conductivity and porosity were measured on the bulk density samples using a hanging column procedure (Carter 1993). Bulk density, taken using a bulk density hammer and 5cm cores, was quantified by determining oven-dry weight (105°C) of soils from known volumes (Carter 1993).

2.3.3.3 Nitrogen Mineralization Potential

Soil samples from the A horizon were used to determine N mineralization potential in a laboratory incubation. For the A horizon, five subsamples were collected from within 1m of each transect point and composited for analysis. Potential N mineralization was measured using an aerobic incubation method (Burger 2007). The soil was air-dried to a constant percent moisture and 55g of air-dried soil was mixed with 160g of clean-washed sand to allow for greater surface area and to facilitate leaching. Soil-sand mixtures were incubated at 30°C for four months. The soil was leached using a 0.01M CaCl² solution at 1, 2, 4, 6, 9, 12, and 16 weeks and filtered through Whatman GF/F filters. Leachate was analyzed for nitrate-N and ammonium-N using a TRAACS 2000 AutoAnalyzer (Bran and Luebbe, Buffalo Grove, Illinois). Nitrogen mineralization potential was calculated as the sum of accumulated nitrate and ammonium over the 16 weeks.

2.3.3.4 Vegetation and Elevation Survey

A vegetation survey and an elevation survey were also conducted on the site. All woody stems within 1m of the lysimeters were counted and recorded for species and diameter size. A 1m sampling radius was used because vegetation within this proximity has the most influence on soil water concentrations because lysimeters have been shown to pull water from within 0.3m in sand (Wu et al. 1995). Using a compass, meter tape, and clinometer, the elevation survey recorded transect slopes and locations, and recorded the harvested area perimeter and slope.

2.3.3.5 Statistical Analysis

All statistical analyses were conducted using SAS 9.1 (SAS 2003). Statistical analysis for dissolved N and C dynamics on the hillslope was conducted using a repeated measures ANOVA. To meet the normal distribution assumptions, data that did not meet the Shapiro-Wilks test for normality were log transformed. Significantly different means were tested using Tukey's test, with significant differences occurring at $p < 0.05$. Only two-way interactions were examined because of model limitations due to the small number of samples and resultant limitations involving degrees of freedom. Additionally, distance from stream was treated as a continuous variable in the model because of the small number of samples. To test for differences within distance from stream, a separate ANOVA model was used. Simple and multiple regressions were used to determine correlations among soil solution, stream, and riparian

groundwater solute concentrations, and N mineralization potential, soil characteristics, and vegetation surveys.

Preliminary analysis indicated a strong seasonality trend, therefore analysis was done on a seasonal basis (Spring = March, April, May; Summer = June, July, August; Fall = September, October, November; Winter = December, January). Soil solution concentrations from the saprolite lysimeter 30m from the stream in Transect A were analyzed as 50m from the stream to allow for comparison with other saprolite lysimeters 50m from the stream. Dissolved organic concentrations 1m from the stream in Transect C were removed for analysis because concentrations were 10 to 100 times higher (concentrations as high as 600mg/L) than other soil solution DOC concentrations.

2.4 RESULTS

2.4.1 Soil Solution

2.4.1.1 Ammonium-N

Ammonium concentrations were relatively low throughout the year ($\bar{x} = 0.050\text{mg-N/L}$), with peak concentrations occurring in the spring ($\bar{x} = 0.092\text{mg-N/L}$). The spring transect concentrations were two to five times higher than the fall transect ammonium concentrations (Figure 4a). Additionally, Transects B and D spring ammonium concentrations were two to four times higher than their respective summer ammonium concentrations. Only in Transect C were mean winter concentrations significantly higher than mean fall concentrations with a difference of 0.027mg-N/L , and only in Transect D were mean spring concentrations significantly higher than mean winter concentrations with a difference of 0.116mg-N/L (Figure 4a).

Additionally, within each soil horizon, mean ammonium concentrations in the spring were two to five times higher than concentrations in summer and fall (Figure 4b). Mean A horizon ammonium concentration of 0.169mg-N/L in spring was also significantly higher than mean ammonium concentration of 0.057mg-N/L in winter, and mean summer concentration of 0.079mg-N/L in the A horizon was significantly higher than mean fall concentration of 0.047mg-N/L . The mean winter ammonium concentration of 0.044mg-N/L in the B horizon was two and five times greater than mean summer and fall ammonium concentrations, respectively. The mean winter saprolite ammonium concentration was also significantly higher than the mean

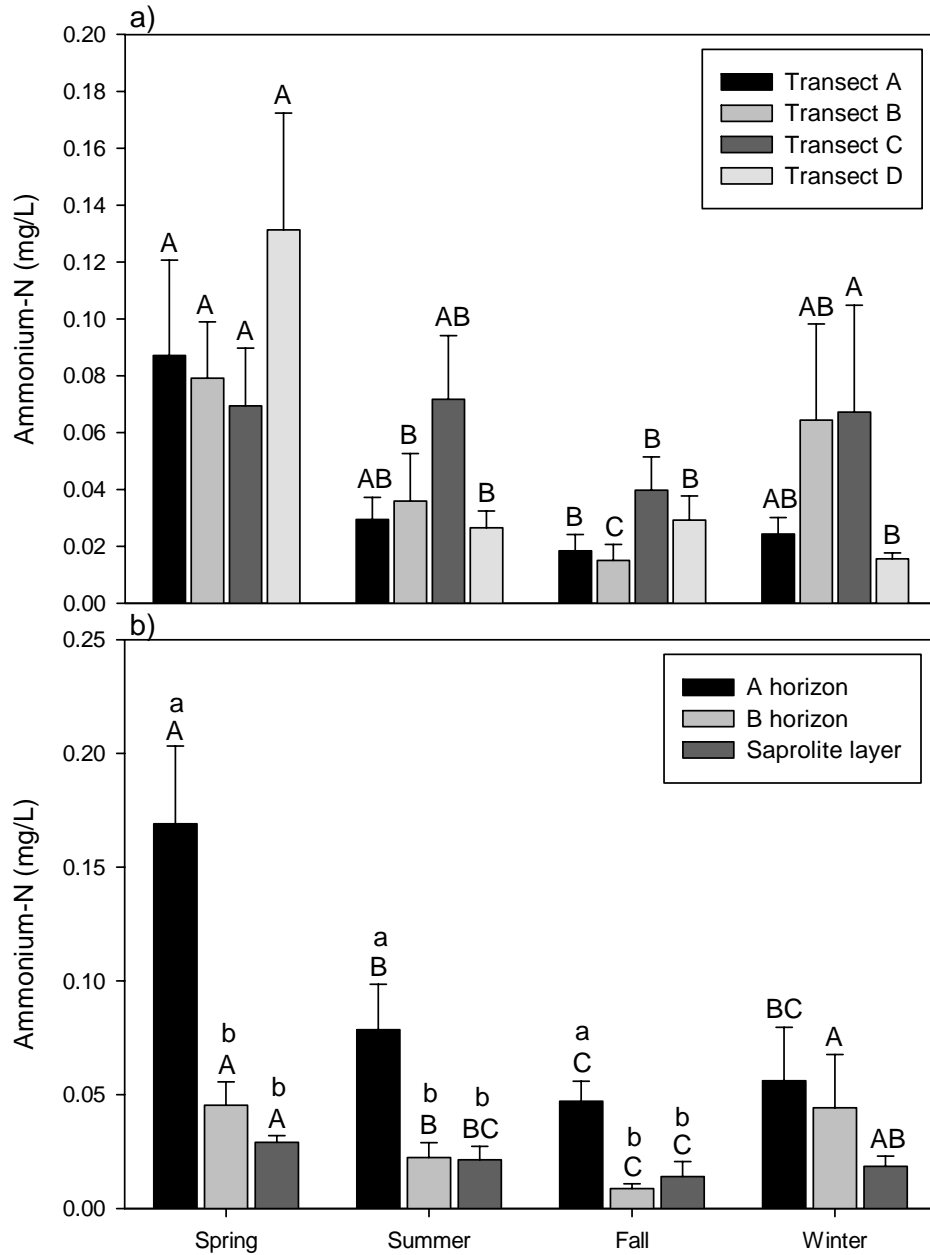


Figure 4. Mean seasonal transect ammonium concentrations (a) and mean seasonal horizon ammonium concentrations (b) for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each season, different lower case letters denote significant differences ($p < 0.05$) among horizons. For each transect or horizon, different upper case letters denote significant differences ($p < 0.05$) among seasons. Error bars represent one standard error.

summer saprolite ammonium concentration by 0.004mg-N/L. Ammonium concentrations in the A horizon were at least three times higher than B horizon and saprolite layer concentrations all seasons except winter (Figure 4b). However, this horizon trend was driven by significant differences among horizons in Transects C and D (Figure 5). There were no detectable differences for ammonium concentrations within locations for the three horizons (Figure 6).

Summer stream ammonium concentrations ($\bar{x} = 0.212\text{mg-N/L}$) were significantly higher than all other seasons ($\bar{x} = 0.016\text{mg-N/L}$) (Figure 7), and mean monthly stream ammonium concentrations were strongly correlated to riparian groundwater ammonium concentrations ($r^2 = 0.90$, $p < 0.0001$, Figure 8). Stream ammonium concentrations were not correlated to soil solution concentrations in the A horizon, B horizon, or saprolite layer (data not shown).

2.4.1.2 Nitrate-N

Mean soil solution nitrate was highly variable among transects within a season and within transects across seasons, ranging from a high in Transect D during spring of 2.003mg-N/L to a low in Transect B during fall of 0.008mg-N/L (Figure 9a). In the spring, nitrate concentrations in Transects B and D were over six times higher than nitrate concentration in Transects A and C. In the fall, nitrate concentrations in Transect D ($\bar{x} = 0.142\text{mg-N/L}$) were over seventeen times higher than nitrate concentrations in Transects A and B. Transects B and D in the spring were significantly higher than Transects B and D in the summer, fall, and winter. Additionally, Transect B concentrations in the summer were significantly higher than Transect B concentrations in the fall and winter. Mean spring and summer nitrate concentrations in Transect A of 0.247mg-N/L and 0.083mg-N/L, respectively, were ten to twenty times higher than mean fall and winter nitrate concentrations in Transect A. Summer nitrate concentrations in Transect C ($\bar{x} = 0.131\text{mg-N/L}$) were significantly higher than fall and winter nitrate concentrations in Transect C ($\bar{x} = 0.048\text{mg-N/L}$ and 0.084mg-N/L, respectively).

Typically, the highest nitrate concentrations occurred in the spring and summer (Figures 9a and 9b). Mean spring and summer nitrate concentrations, which ranged from 0.056mg-N/L to 1.531mg-N/L in each horizon, were significantly higher than mean fall and winter nitrate values, which ranged from 0.029mg-N/L to 0.118mg-N/L (Figure 9b). A horizon nitrate concentrations in the summer were also significantly higher than A horizon nitrate concentrations in the fall and winter. There were no detectable differences in nitrate concentrations among the A horizon, B

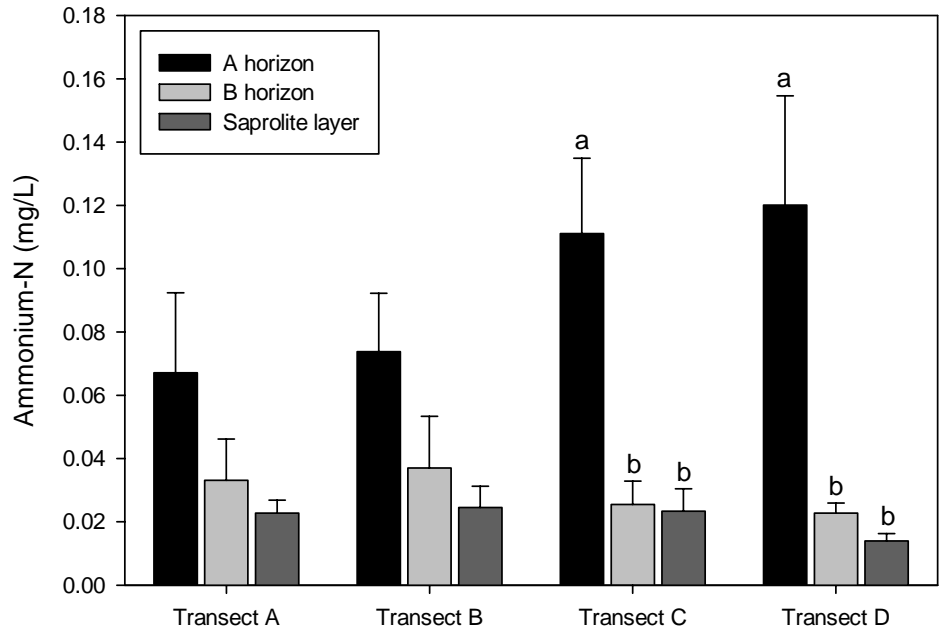


Figure 5. Mean soil horizon ammonium concentrations by transect for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each transect, different letters denote significant differences ($p < 0.05$) among soil horizons. Error bars represent one standard error.

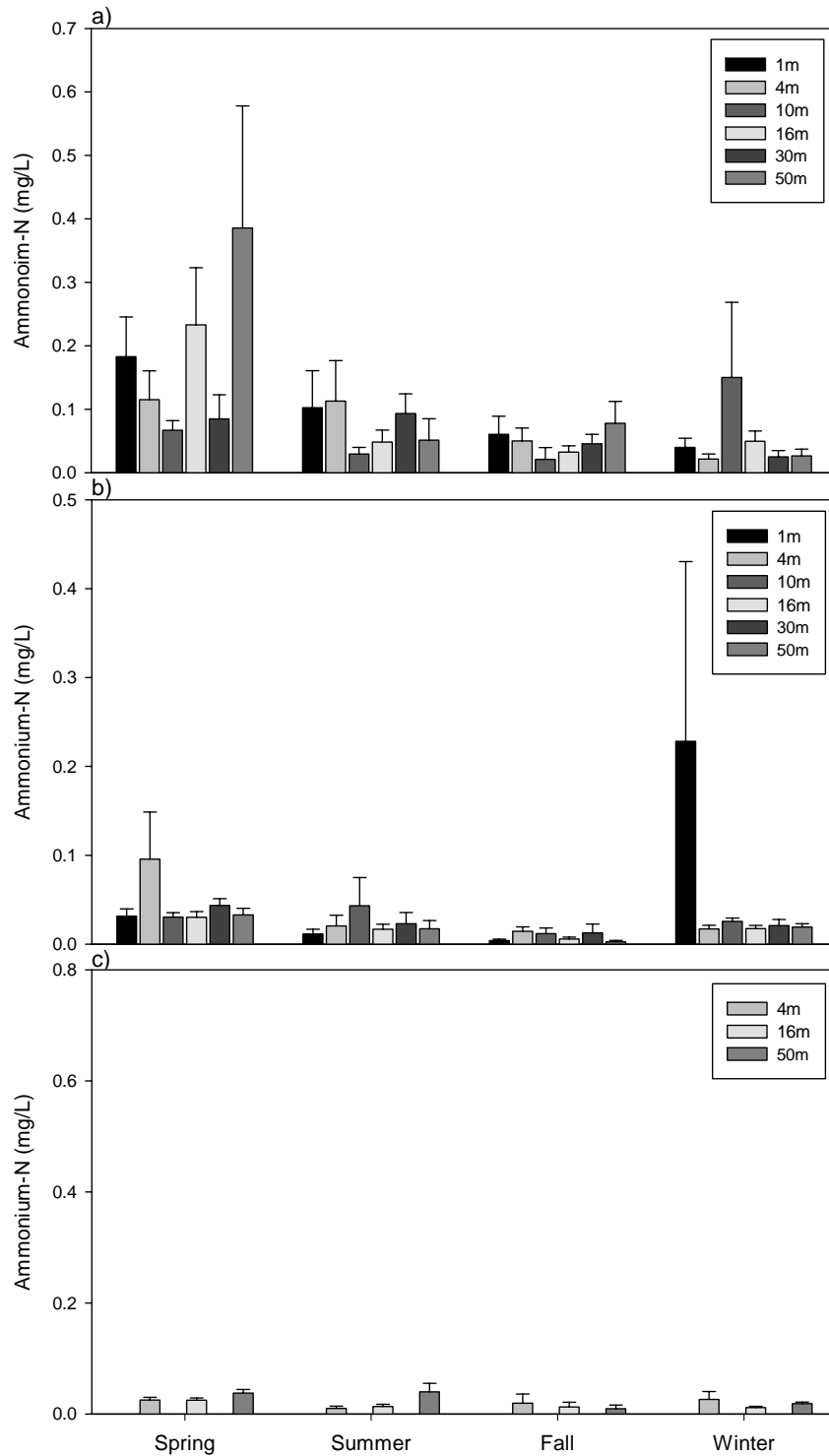


Figure 6. Mean seasonal A horizon ammonium concentrations (a), mean seasonal B horizon ammonium concentrations (b), and mean seasonal saprolite layer ammonium concentrations (c) at increasing distance from the stream channel for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. Error bars represent one standard error.

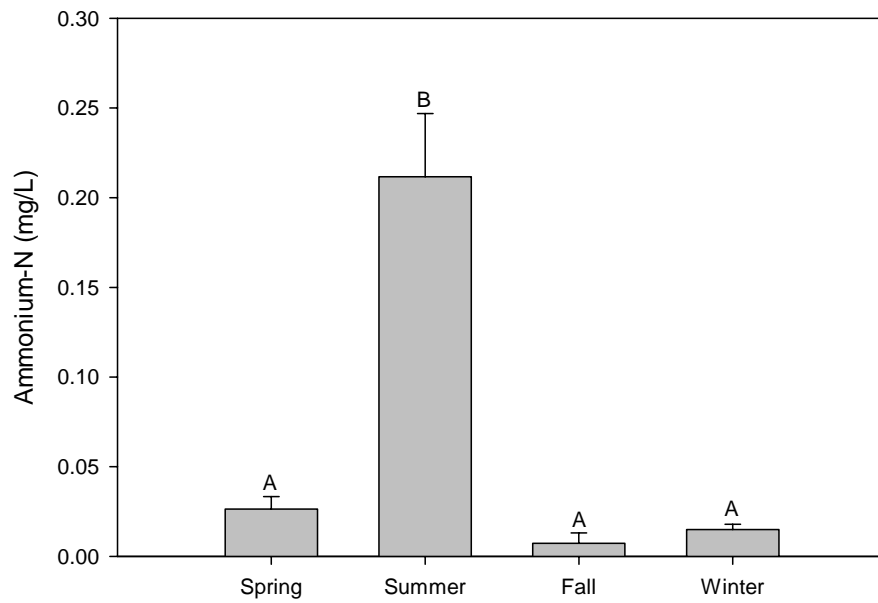


Figure 7. Mean seasonal stream ammonium concentrations for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. Different letters denote significant differences among seasons ($p < 0.05$). Error bars represent one standard error.

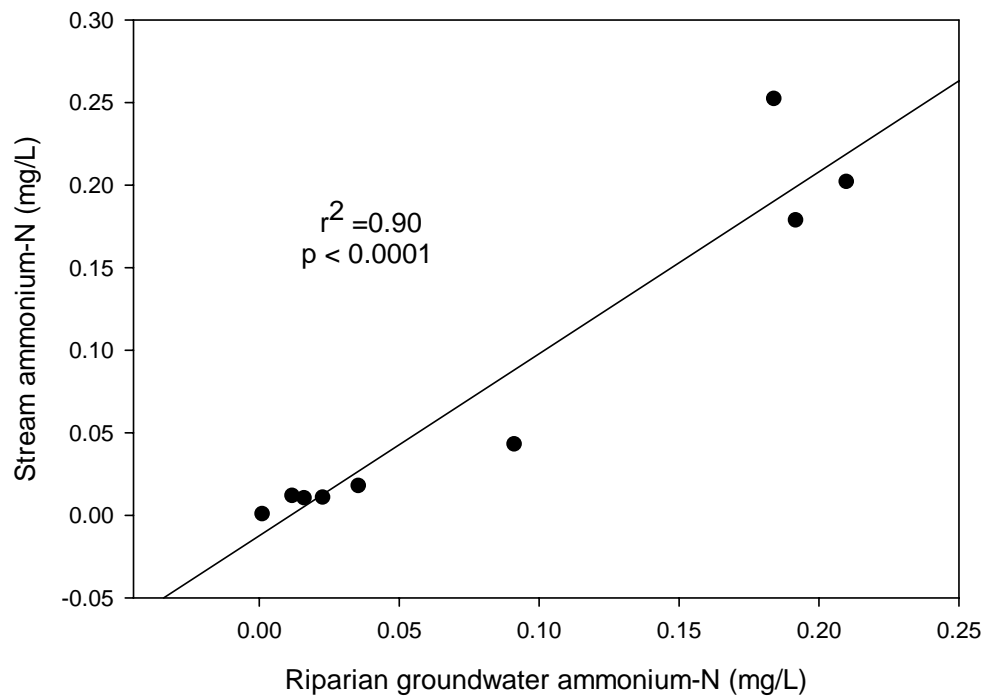


Figure 8. Ray Branch mean monthly riparian groundwater ammonium concentrations versus Ray Branch mean monthly stream ammonium concentrations for May 2007 through January 2008.

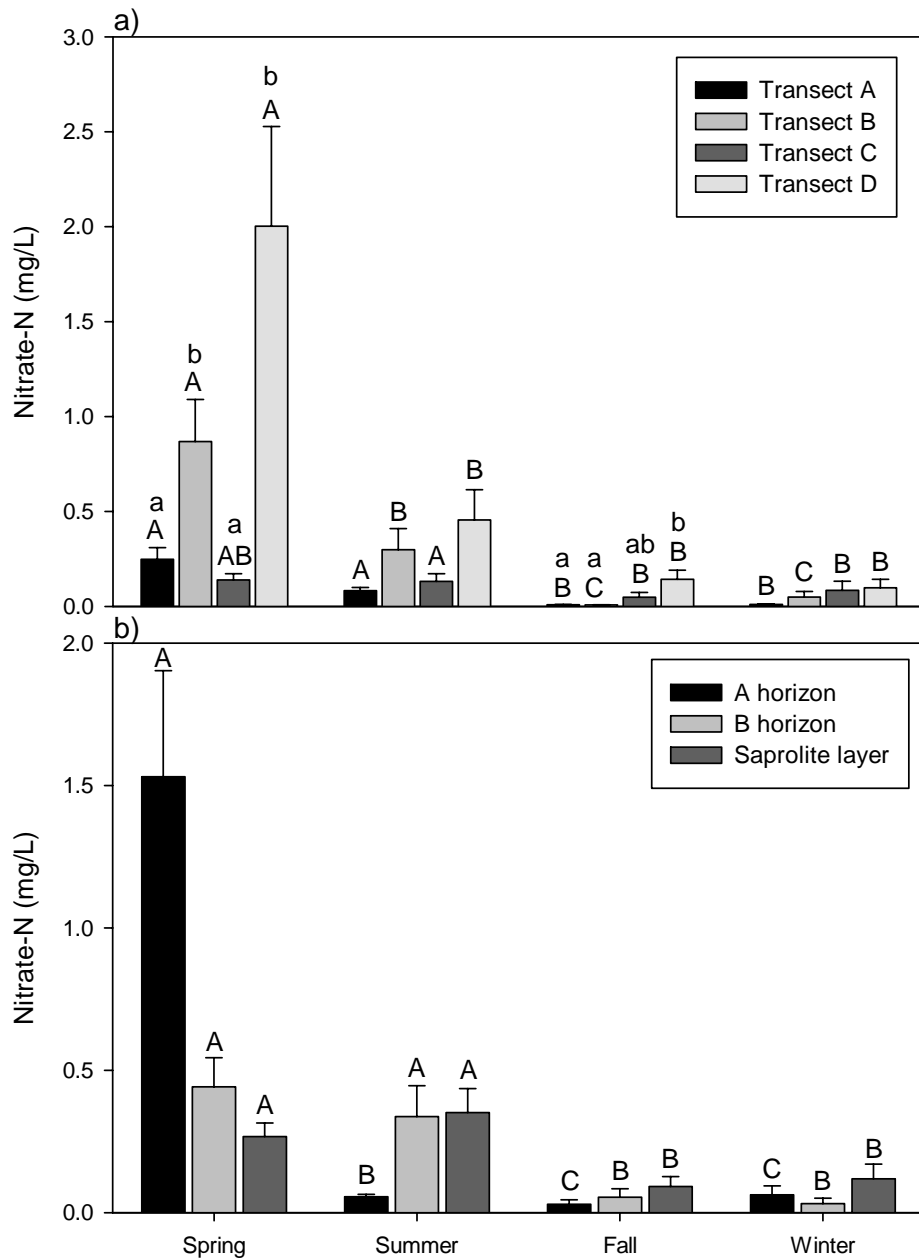


Figure 9. Mean seasonal transect nitrate concentrations (a) and mean seasonal horizon nitrate concentrations (b) for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each season, different lower case letters denote significant differences ($p < 0.05$) among transects. For each transect or horizon, different upper case letters denote significant differences ($p < 0.05$) among seasons. Error bars represent one standard error.

horizon, and saprolite layer within a transect, with the exception of Transect C where the mean saprolite layer nitrate concentration of 0.242mg-N/L was three times higher than mean A and B horizon nitrate concentrations (Figure 10). The mean nitrate concentration of 1.40mg-N/L in the A horizon in Transect D was significantly higher than mean nitrate concentrations of 0.121mg-N/L and 0.078mg-N/L in A horizon in Transects A and C, respectively. Additionally, nitrate concentrations in the B horizon in Transect D were ten times greater than nitrate concentrations in the B horizon in Transect C.

For each season, there were no detectable differences in nitrate concentrations among locations in the A horizon (Figure 11a). In the B horizon in the spring, the mean nitrate concentration of 0.027mg-N/L 1m from the stream was significantly lower than mean nitrate concentrations 10m, 16m, 30m, and 50m from the stream which ranged from 0.260mg-N/L to 1.092mg-N/L (Figure 11b). Additionally, in the B horizon in the summer, nitrate concentrations 1m and 4m from the stream were significantly lower than nitrate concentrations 50m from the stream. For both spring and summer in the saprolite layer, mean nitrate concentrations 50m from the stream of 0.408mg-N/L and 0.793mg-N/L, respectively, were significantly higher than nitrate concentrations 4m and 16m from the stream (Figure 11c).

The mean summer stream nitrate concentration of 0.591mg-N/L was significantly higher than mean nitrate concentrations in all other seasons (Figure 12). Stream nitrate concentrations were strongly correlated to riparian groundwater nitrate concentrations ($r^2 = 0.96$, $p < 0.0001$) (Figure 13). Stream nitrate concentrations were also correlated to mean saprolite layer nitrate concentrations ($r^2 = 0.41$, $p < 0.05$) (Figure 14) and saprolite layer nitrate concentrations 50m from the stream ($r^2 = 0.54$, $p < 0.01$) (Figure 14). Stream nitrate concentrations were not correlated to soil solution concentrations in the A or B horizon (data not shown).

2.4.1.3 Dissolved Organic Carbon

There was very little variability in DOC soil solution concentrations among transects or seasons (Figures 15a and 15b). Mean values ranged from 4.4mg/L to 8.0mg/L, with the exception of Transect C in the fall ($\bar{x} = 12.7$ mg/L). However, DOC concentrations in the A horizon were significantly higher than DOC B horizon and saprolite layer concentrations each season (Figure 15b) and within each transect (Figure 16). A horizon DOC concentrations were also significantly higher in the summer ($\bar{x} = 13.1$ mg/L) than in the spring ($\bar{x} = 8.8$ mg/L) (Figure

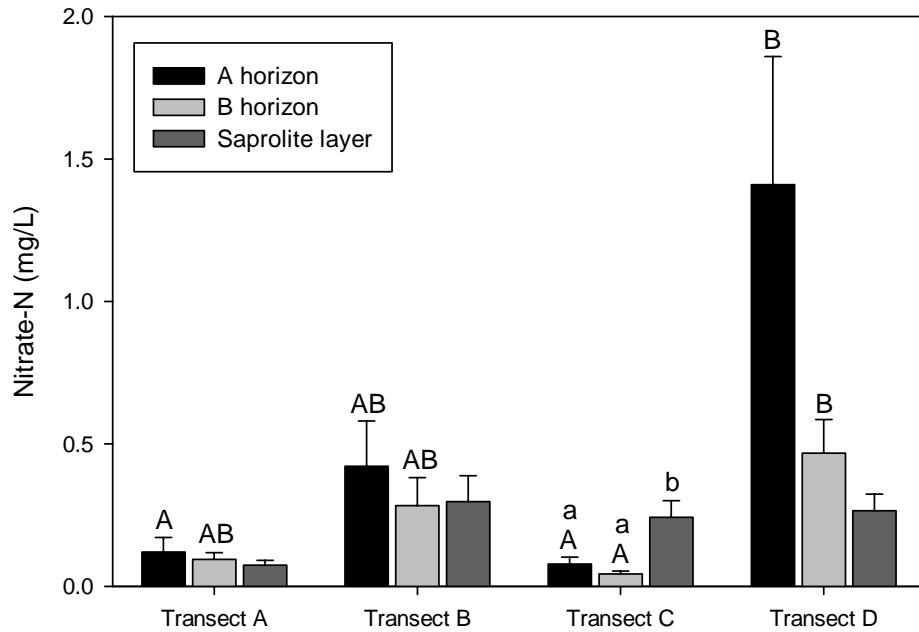


Figure 10. Mean soil horizon ammonium concentrations by transect for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each transect, different lower case letters denote significant differences ($p < 0.05$) among soil horizons. For each horizon, different upper case letters denote significant differences ($p < 0.05$) among transects. Error bars represent one standard error.

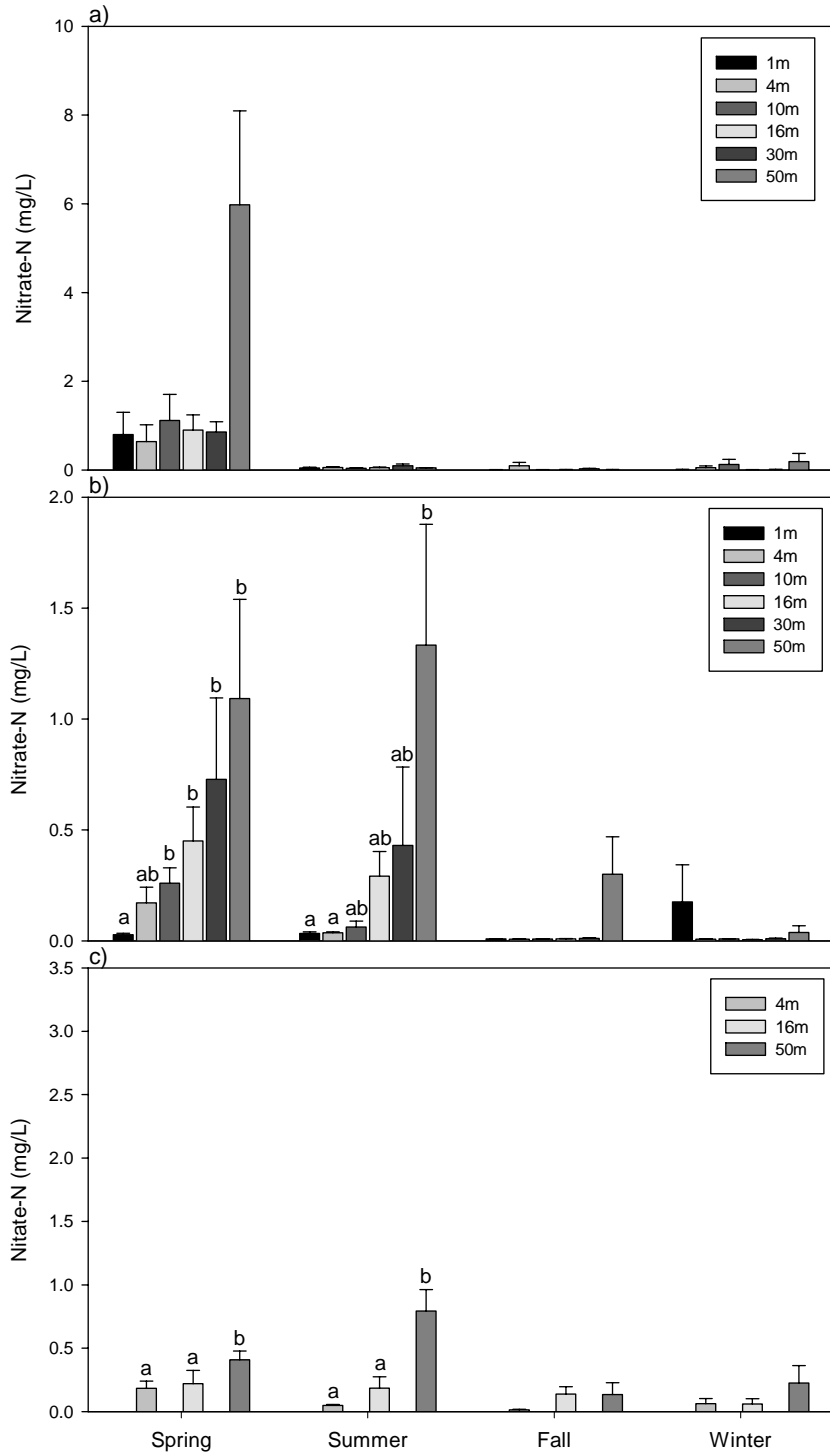


Figure 11. Mean seasonal A horizon nitrate concentrations (a), mean seasonal B horizon nitrate concentrations (b), and mean seasonal saprolite layer nitrate concentrations (c) at increasing distance from the stream channel for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each season, different letters denote significant differences ($p < 0.05$) among sampling distances from the stream channel. Error bars represent one standard error.

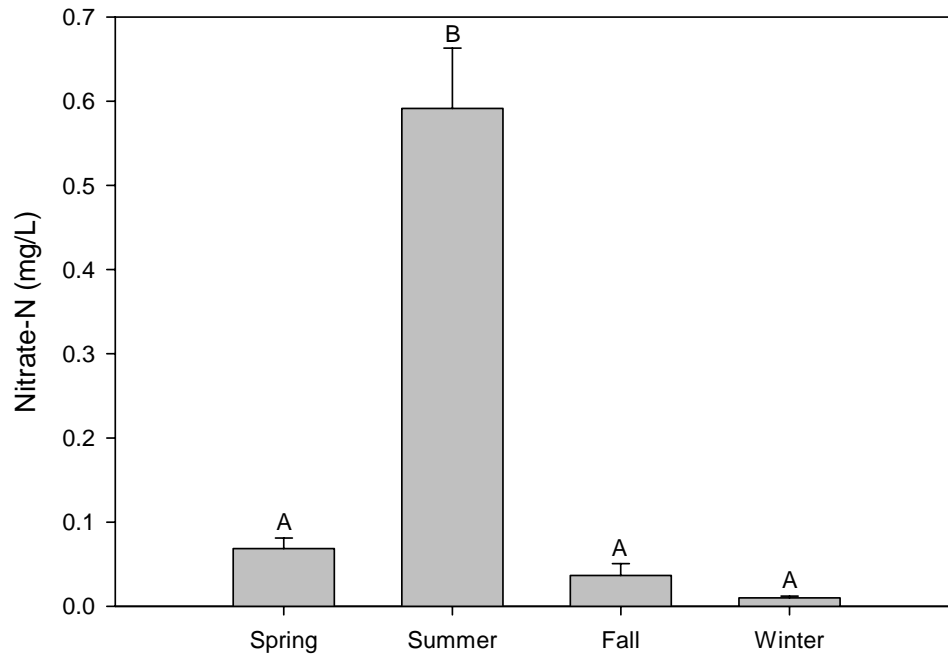


Figure 12. Mean seasonal stream nitrate concentrations for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. Different letters denote significant differences among seasons ($p < 0.05$). Error bars represent one standard error.

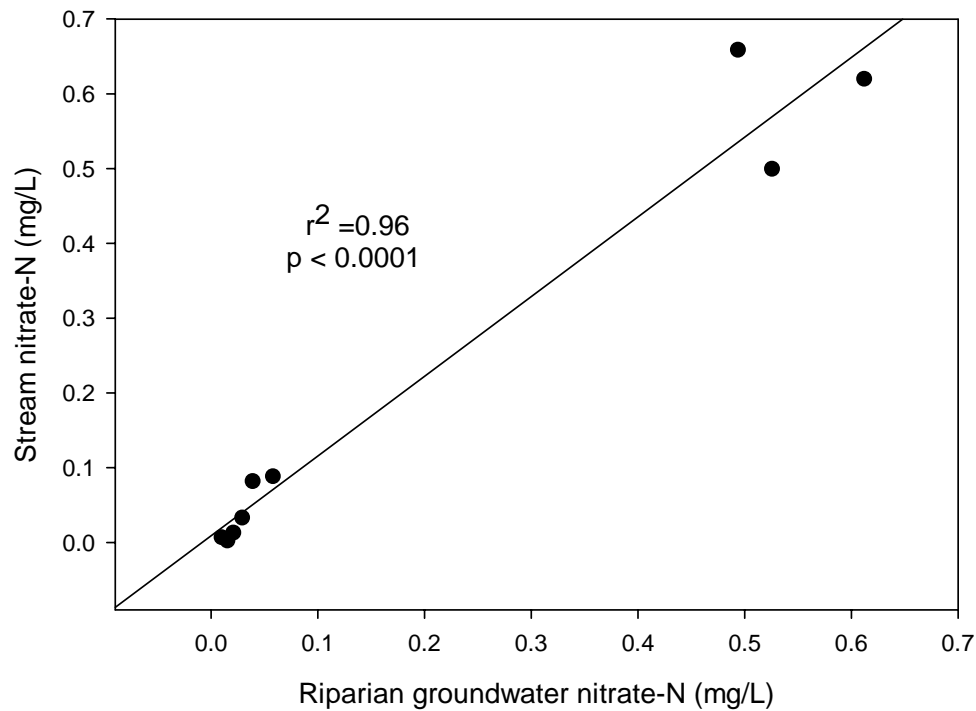


Figure 13. Ray Branch mean monthly riparian groundwater nitrate concentrations versus Ray Branch mean monthly stream nitrate concentrations for May 2007 through January 2008.

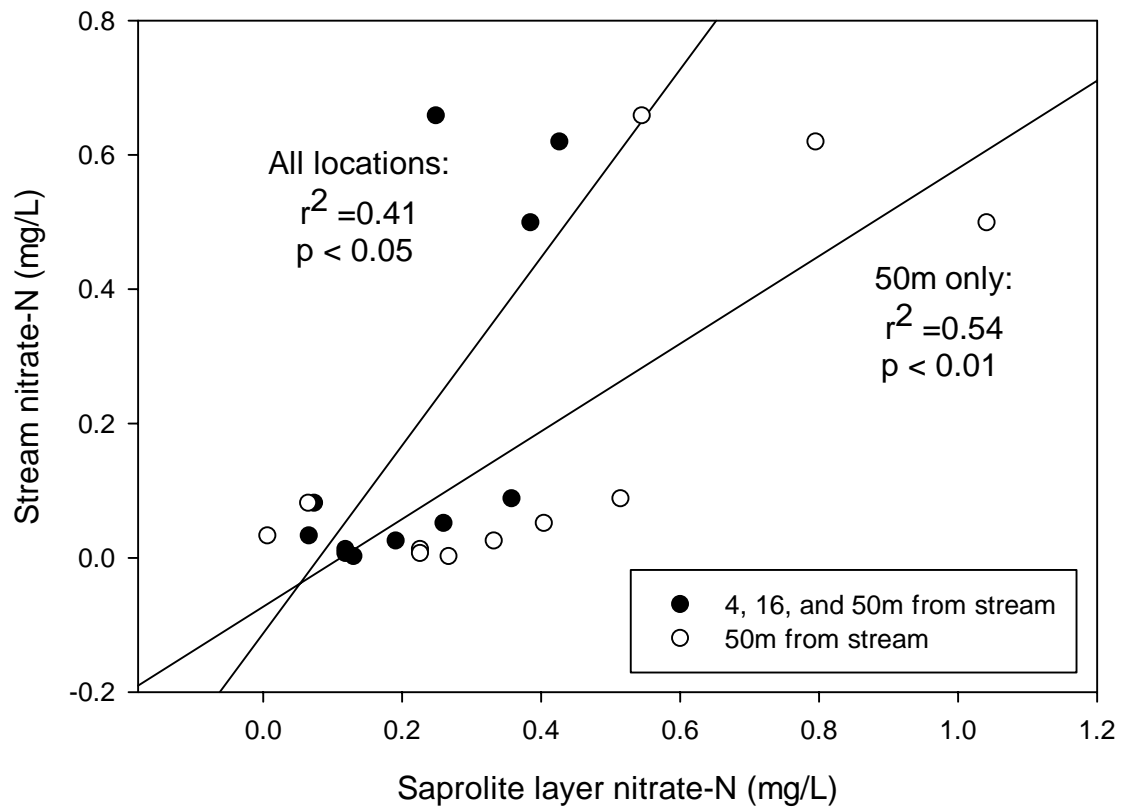


Figure 14. Ray Branch mean monthly saprolite nitrate concentrations versus Ray Branch mean monthly stream nitrate concentrations for May 2007 through January 2008.

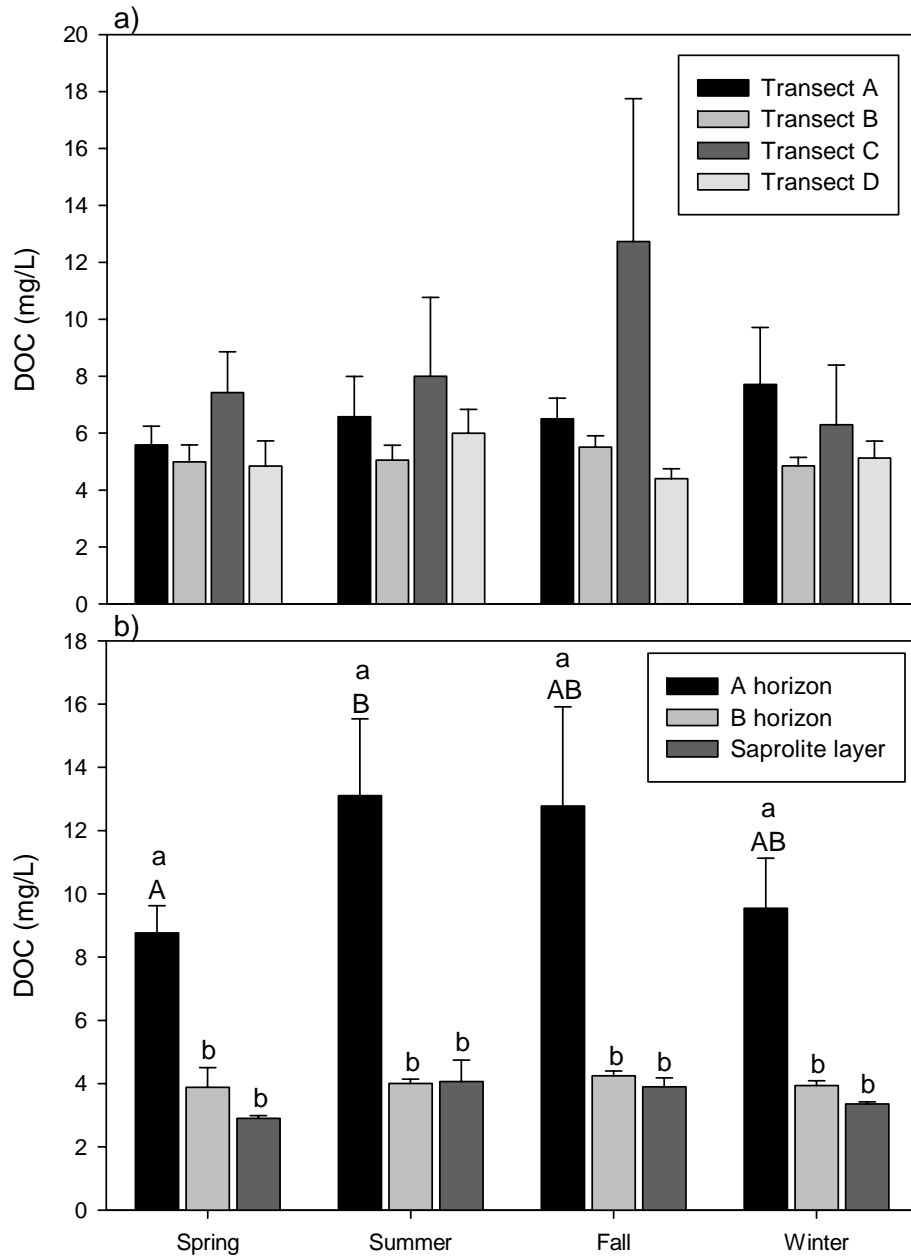


Figure 15. Mean seasonal transect DOC concentrations (a) and mean seasonal horizon DOC concentrations (b) for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each season, different lower case letters denote significant differences ($p < 0.05$) among horizons. For each horizon, different upper case letters denote significant differences ($p < 0.05$) among seasons. Error bars represent one standard error.

15b). The mean A horizon DOC concentration in Transect C was more than 10mg/L greater than mean A horizon concentrations in Transect B and D (Figure 16). For each season, there were no detectable differences among sampling distances from the stream channel in either of the two soil horizons or the saprolite layer (Figure 17).

Fall and winter stream DOC concentrations were significantly higher than spring and summer stream DOC concentrations (Figure 18). Stream DOC concentrations were not correlated to soil solution DOC concentrations (data not shown). However, stream and riparian groundwater concentrations of DOC were well correlated ($r^2 = 0.47$, $p < 0.05$) (Figure 19).

2.4.2.2 Dissolved Organic Nitrogen

Over three quarters of the DON values were below the detection limit of 0.85mg/L. Therefore, relationships between DOC and DON were explored to determine if DOC could be used to predict DON. Dissolved organic N correlated to DOC using a logarithmic curve ($r^2 = 0.64$, Figure 20). However, when the relationship was used to estimate DON values below the detection limit, 35% of the predicted A horizon values exceeded the detection limit (0.85mg/L). High DOC values ($> 75\text{mg/L}$) were removed to explore a linear relationship to estimate DON values ($r^2 = 0.29$) (Figure 21). The relationship was weak, and 15% of the predicted DON values in the A horizon still exceeded the detection limit when this linear relationship was used. Consequently, for analysis, DON values below the detection limit were estimated as 0.4mg/L (detection limit – $\text{DIN} / 2$).

For each season, DON concentrations were not affected by transects (Figure 22a). During spring, A horizon DON concentrations ($\bar{x} = 0.7\text{mg/L}$) were significantly higher than saprolite layer DON concentrations ($\bar{x} = 0.4\text{mg/L}$) (Figure 22b). Additionally, in Transect C, DON concentration in the A horizon ($\bar{x} = 1.2\text{mg/L}$) was more than double the B horizon and saprolite layer DON concentrations, and was more than double A horizon DON concentrations in all other transects (Figure 23). During the summer saprolite layer DON concentrations were twice as high 50m from the stream than concentrations 4 and 10m from the stream (Figure 24c). There were no other detectable differences within or among horizons, transects, seasons, or locations (Figures 22, 23, and 24).

Dissolved organic N was the predominant form of N in the soil solution in the summer, fall, and winter, making up between 35 and 85% of the total soil solution N each season, whereas

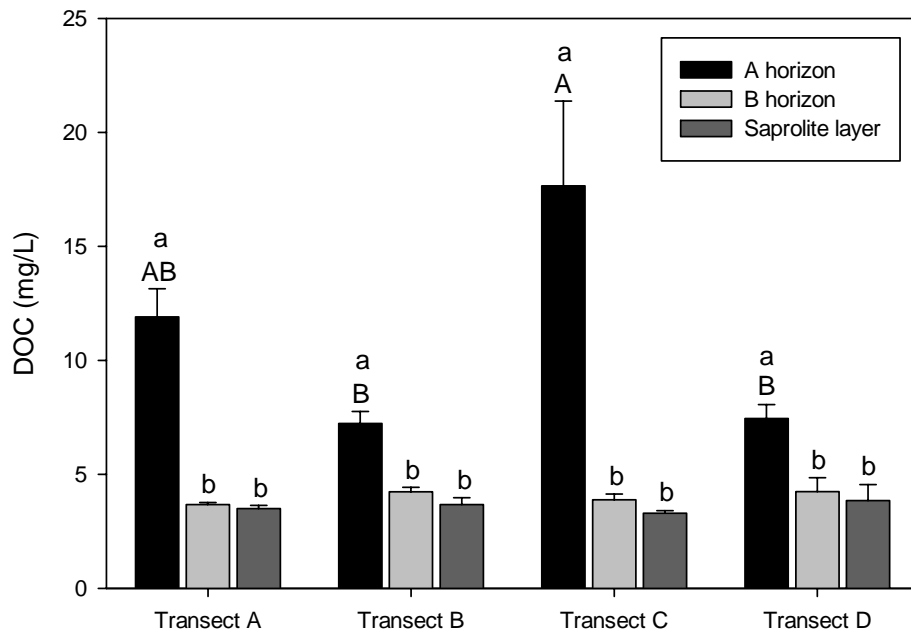


Figure 16. Mean soil horizon DOC concentrations by transect for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each transect, lower case letters denote significant differences ($p < 0.05$) among soil horizons. For each horizon, different upper case letters denote significant differences ($p < 0.05$) among transects. Error bars represent one standard error.

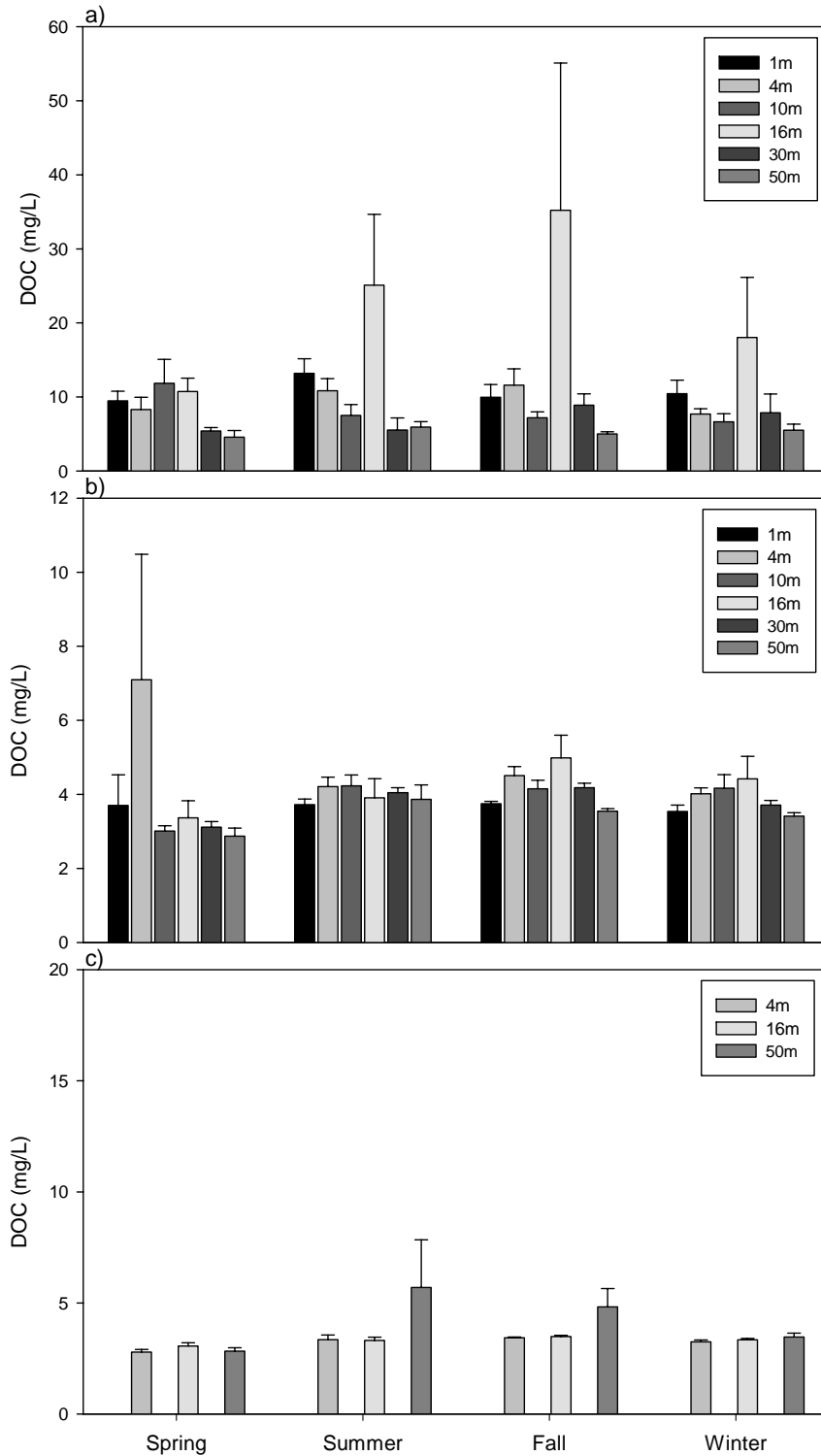


Figure 17. Mean seasonal A horizon DOC concentrations (a), mean seasonal B horizon DOC concentrations (b), and mean seasonal saprolite layer DOC concentrations (c) at increasing distance from the stream channel for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. Error bars represent one error.

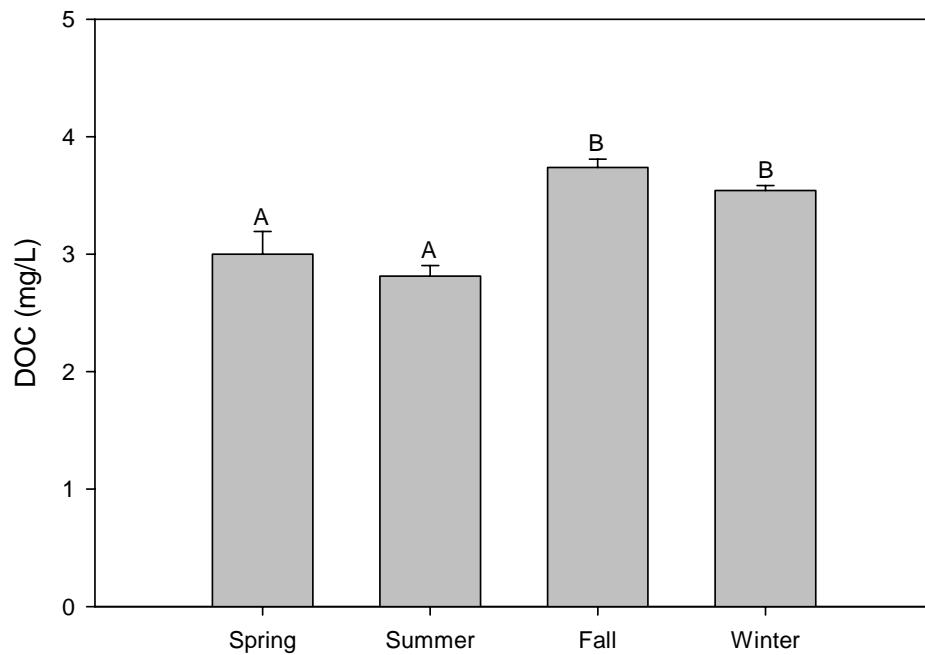


Figure 18. Mean seasonal stream DOC concentrations for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. Different letters denote significant differences among seasons ($p < 0.05$). Error bars represent one standard error.

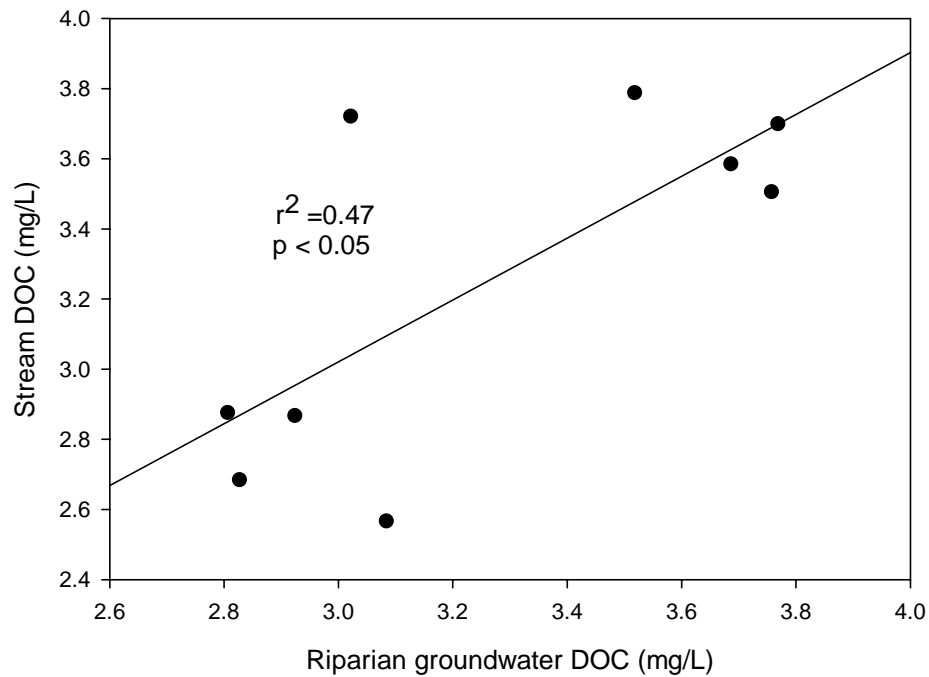


Figure 19. Ray Branch mean monthly riparian groundwater DOC concentrations versus Ray Branch mean monthly stream DOC concentrations for May 2007 through January 2008.

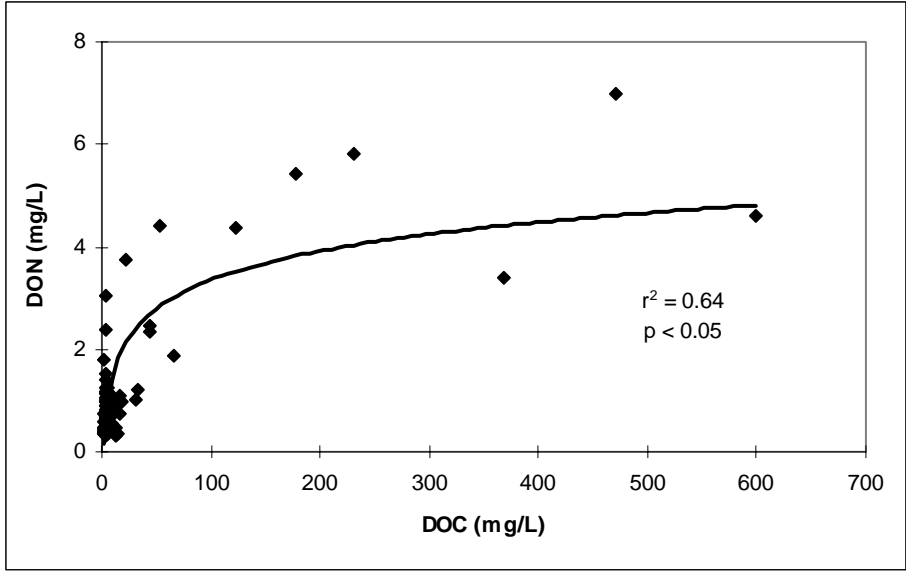


Figure 20. Ray Branch soil solution DOC concentrations versus Ray Branch soil solution DON concentrations for May 2007 through January 2008.

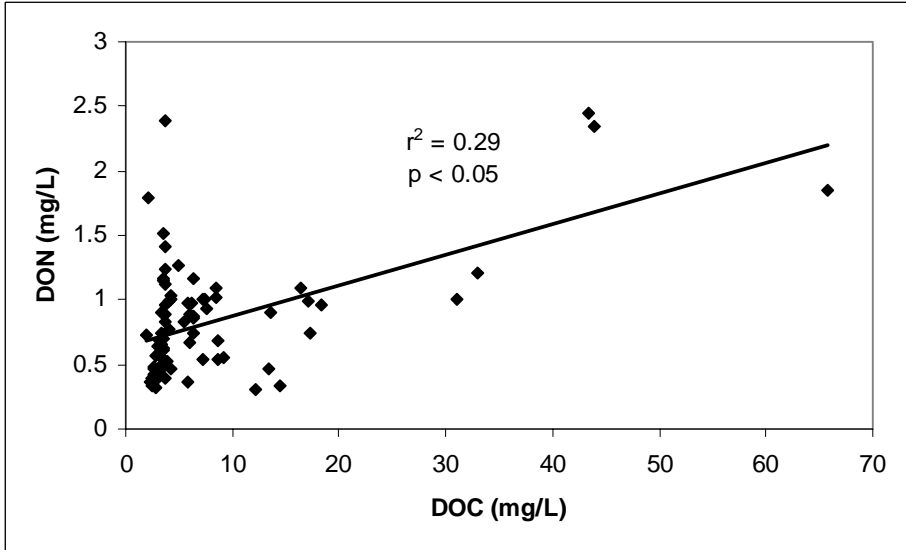


Figure 21. Ray Branch soil solution DOC concentrations versus Ray Branch soil solution DON concentrations for May 2007 through January 2008 with DOC values > 70mg/L removed.

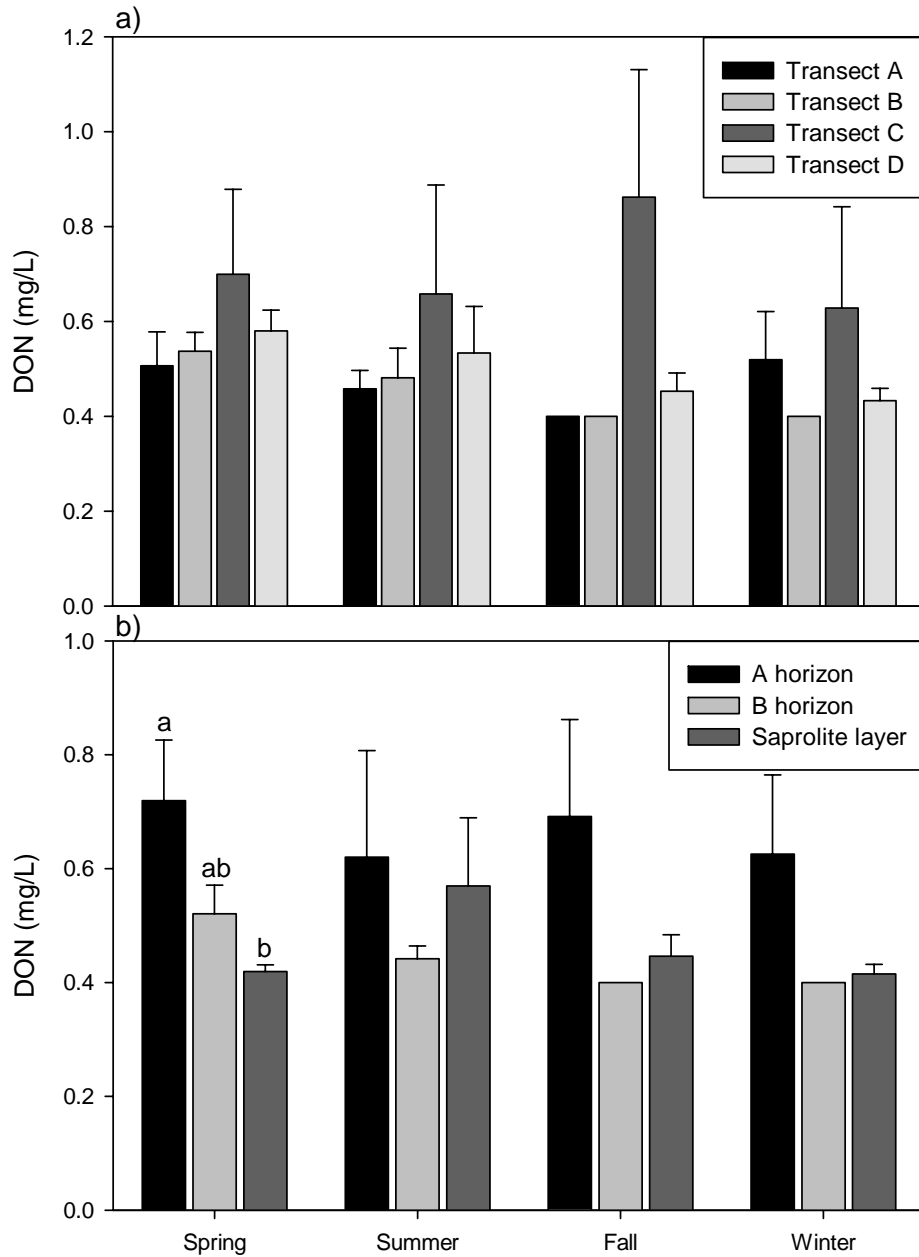


Figure 22. Mean seasonal transect DON concentrations (a) and mean seasonal horizon DON concentrations (b) for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each season, different letters denote significant differences ($p < 0.05$) among horizons. Error bars represent one standard error.

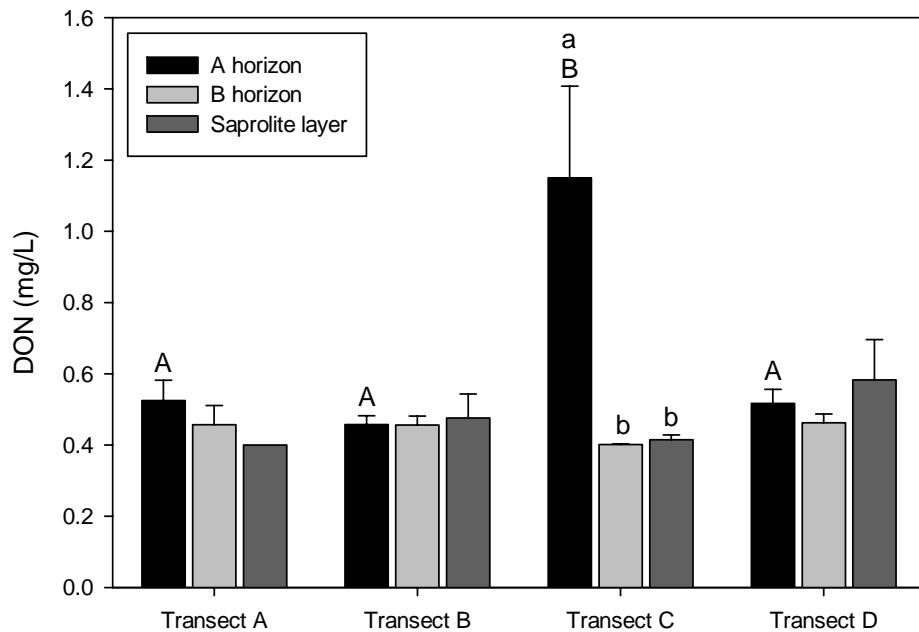


Figure 23. Mean soil horizon DON concentrations by transect for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each transect, different lower case letters denote significant differences ($p < 0.05$) among soil horizons. For each horizon, different upper case letters denote significant differences ($p < 0.05$) among transects. Error bars represent one standard error.

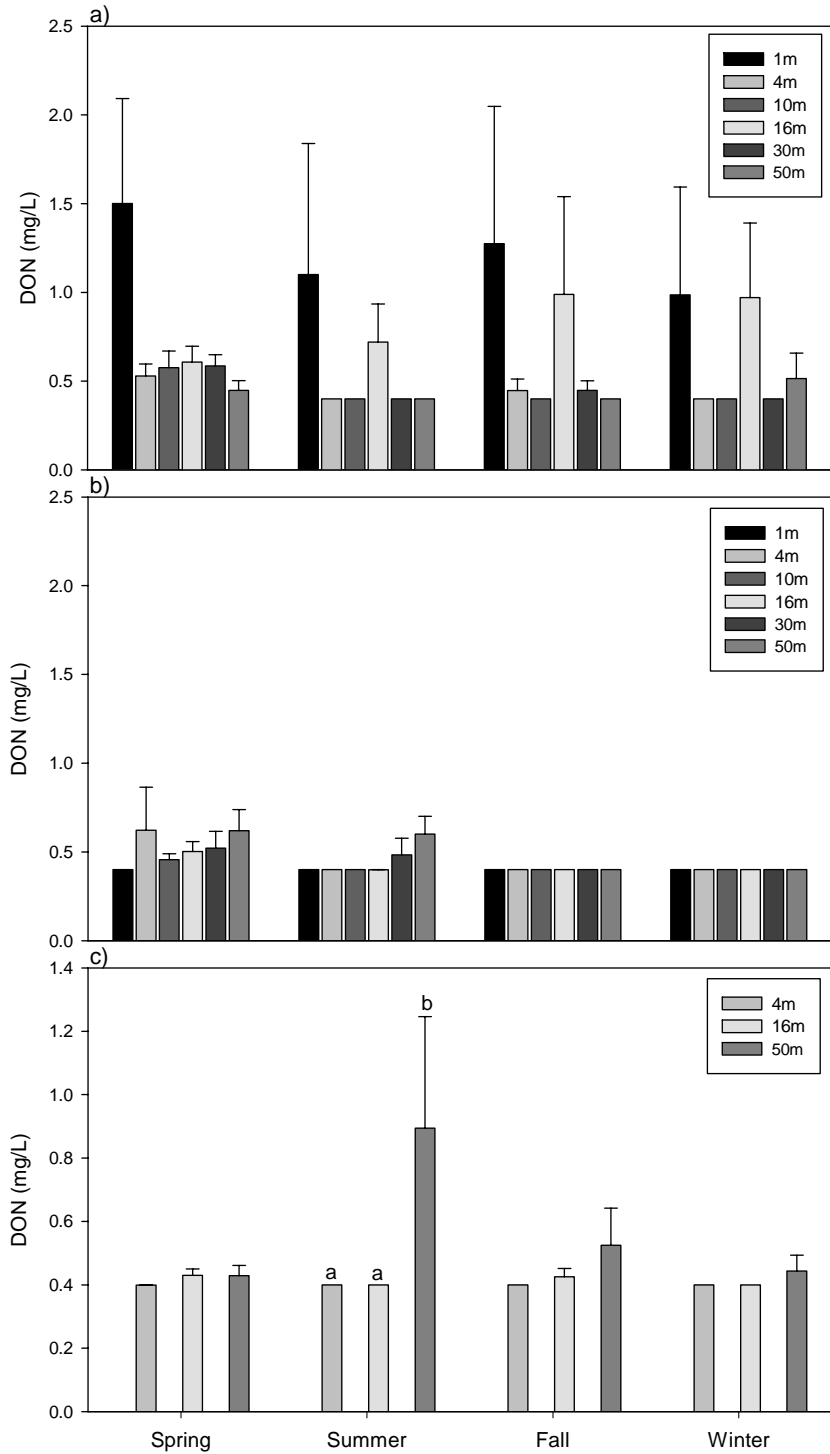


Figure 24. Mean seasonal A horizon DON concentrations (a), mean seasonal B horizon DON concentrations (b), and mean seasonal sapolite layer DON concentrations (c) at increasing distance from the stream channel for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each season, different letters denote significant differences ($p < 0.05$) among sampling distances from the stream. Error bars represent one standard error.

nitrate dominated in spring, comprising 58% (Figure 25). Additionally, no relationship was observed between DIN and DON ($r^2 = 0.034$, data not shown). Dissolved organic N was only detectable in the riparian groundwater and stream during May (data not shown).

2.4.2 Soil Analysis

2.4.2.1 Soil Characterization

Total soil N, total soil C, available soil phosphorus, and exchangeable cations were highest in the A horizon and decreased with depth in the soil profile (Table 1). Mean horizon values for pH ranged from 4.6 to 4.8 (Table 1). Bulk density increased with depth from 0.75 Mg/m³ to 1.1 Mg/m³, and total porosity decreased with depth from 72% to 60% (Table 1).

In the spring and summer, soil solution ammonium concentrations were positively correlated to total soil N ($r^2 = 0.20$ and 0.18 , respectively) (Figure 26). Soil solution DOC concentrations in the spring and winter were positively correlated to total soil C ($r^2 = 0.15$ and 0.14 , respectively) (Figure 27).

2.4.2.2 Nitrogen Mineralization Potential

Concentration of leached ammonium peaked in week 1 and was quickly depleted from the soil in subsequent leachings during the 16-wk laboratory incubation. Accumulated ammonium concentrations ranged from 27.5mg-N/kg to 69.0mg-N/kg (Table 2). Nitrification continued at a constant rate throughout the incubation. Accumulated nitrate concentrations ranged from 0.9mg-N/kg to 28.7mg-N/kg (Table 2). Final accumulated N mineralization concentrations were determined by adding accumulated ammonium and accumulated nitrate concentrations and ranged from 48.1mg-N/kg to 75.6mg-N/kg (Table 2).

There were no detectable differences in N mineralization potential or nitrification potential among transects or locations (data not shown). There were also no significant correlations between seasonal nitrate soil solution values in the A horizon and N mineralization potential (Figure 28) or nitrification potential (data not shown), nor were there significant correlations between seasonal ammonium soil solution values in the A horizon and N mineralization potential or nitrification potential (data not shown). Nitrogen mineralization potential was positively correlated to total soil N ($r^2 = 0.29$, $p < 0.05$, Figure 29). Nitrification potential was positively correlation to total soil N ($r^2 = 0.22$, $p < 0.01$, Figure 30) and to pH ($r^2 = 0.34$, $p < 0.005$, Figure 31).

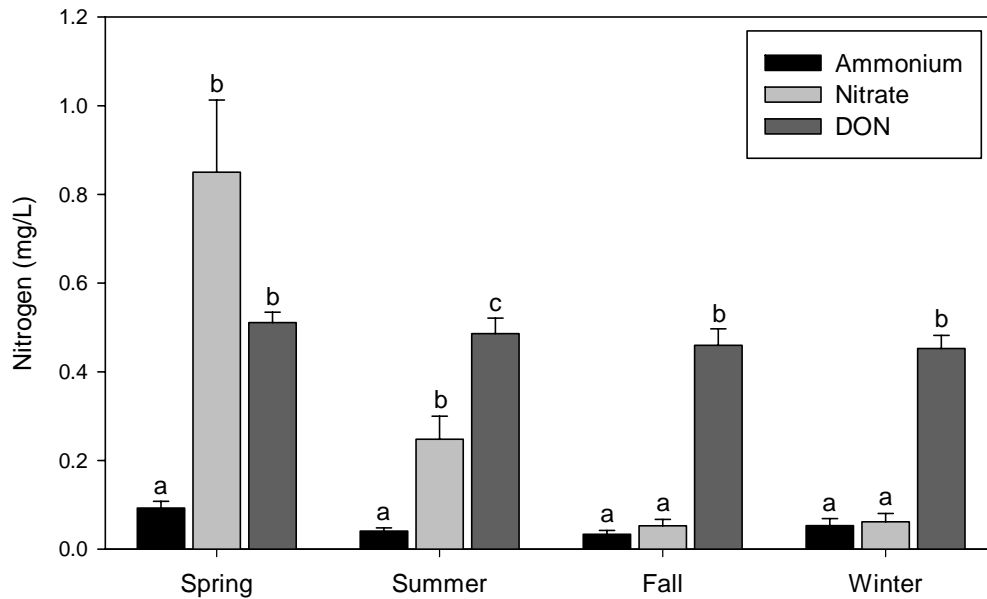


Figure 25. Mean seasonal N concentrations in soil solution, including A and B horizons and saprolite layer, for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008. For each season, different letters denote significant differences ($p < 0.05$) among N forms. Error bars represent one standard error.

Table 1. Soil characterization for the Ray Branch site within the Nantahala National Forest, North Carolina.

Horizon	Total Soil Nitrogen (mg/kg)	Total Soil Carbon (mg/kg)	Available Soil Phosphorus (mg/kg)	Exchangeable Cations (mg/kg)	pH	Bulk Density (g/cm ³)	Total Porosity (%)
A	0.32 (0.05) ¹	5.1 (0.8)	7.8 (2.2)	2279 (1006)	4.8 (0.2)	0.75 (0.14)	72 (5.3)
B	0.14 (0.03)	2.1 (0.7)	4.8 (1.0)	914 (765)	4.6 (0.2)	0.91 (0.13)	65 (4.8)
Saprolite	0.080 (0.01)	0.93 (0.2)	3.1 (0.6)	687 (302)	4.6 (0.2)	1.1 (0.17)	60 (6.4)

¹ Number in parenthesis represent one standard deviation.

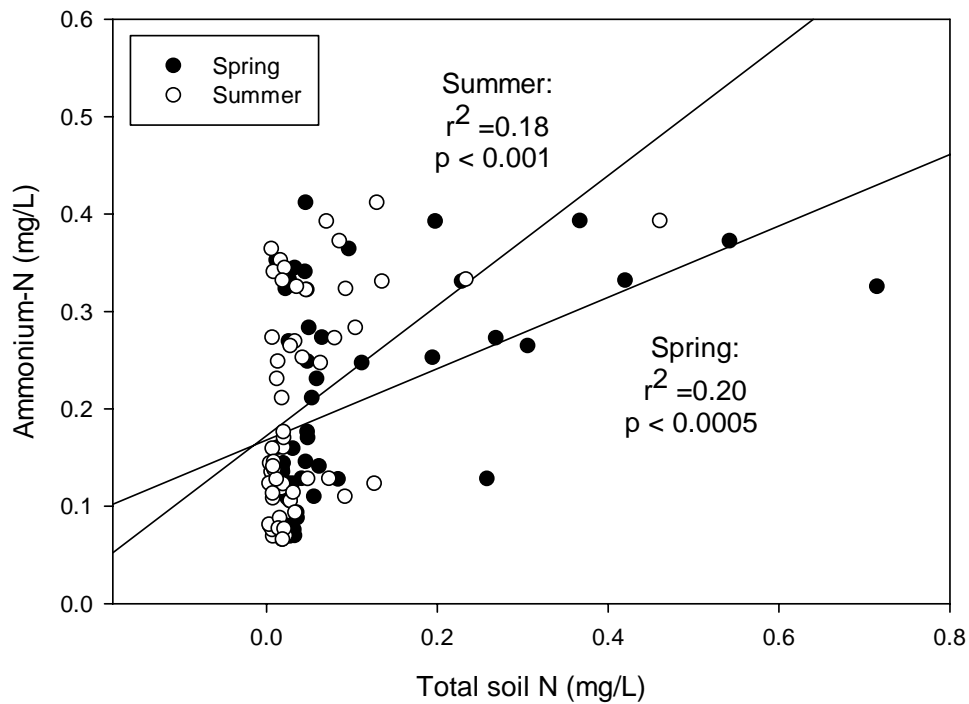


Figure 26. Ray Branch total soil N versus Ray Branch mean seasonal ammonium concentration in soil solution.

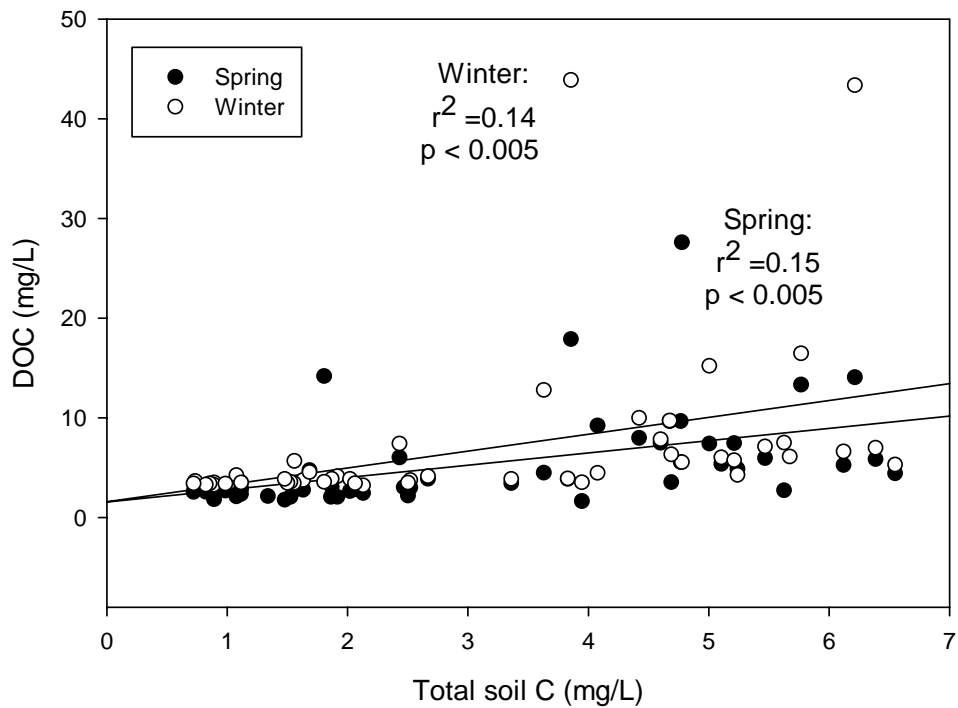


Figure 27. Ray Branch total soil C versus Ray Branch mean seasonal DOC concentration in soil solution.

Table 2. Results of 16-wk laboratory incubation to determine N mineralization potential in A horizon soils from Ray Branch site within the Nantahala National Forest, North Carolina.

Transect	Distance from stream (m)	Total ammonium-N (mg-N/kg)	Total nitrate-N (mg-N/kg)	Total N mineralization potential (mg-N/kg)
A	1	34.6	17.4	52.0
A	4	44.2	17.3	61.4
A	10	63.8	4.7	68.5
A	16	69.0	1.1	70.1
A	30	39.3	13.5	52.8
B	1	35.9	24.8	60.8
B	4	55.3	13.2	68.5
B	10	39.3	8.7	48.1
B	16	39.0	26.8	65.9
B	30	41.1	18.8	59.9
B	50	51.2	11.0	62.2
C	1	46.1	27.0	73.0
C	4	36.2	28.7	64.9
C	10	61.7	13.9	75.6
C	16	48.1	0.9	49.0
C	30	51.8	23.2	75.0
C	50	27.5	22.7	50.2
D	1	42.6	5.0	47.6
D	4	47.6	11.2	58.8
D	10	56.5	9.1	65.5
D	16	60.4	5.6	66.1
D	30	32.1	19.7	51.8
D	50	40.0	27.3	67.3

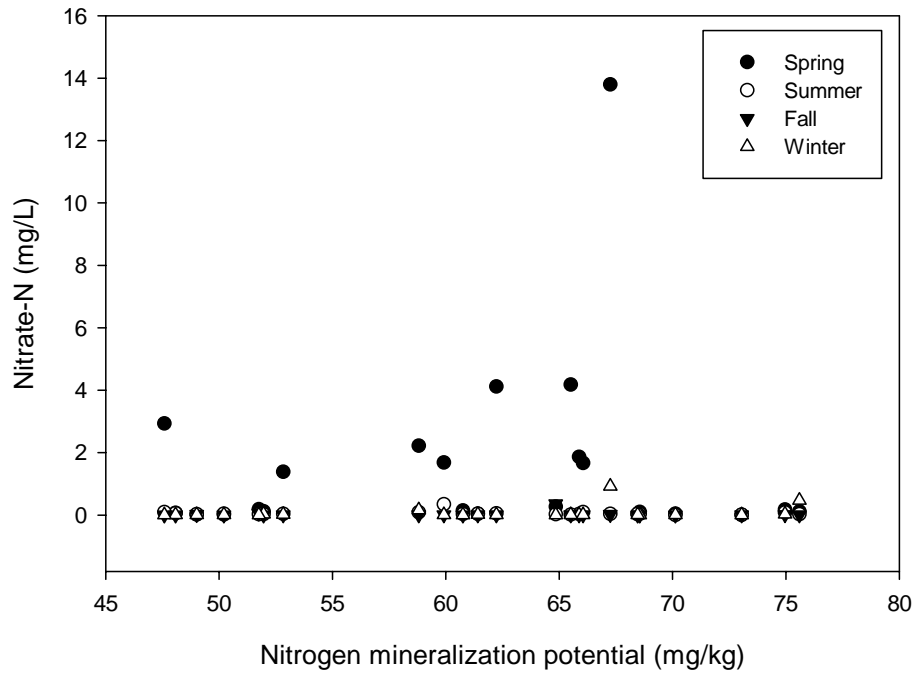


Figure 28. Ray Branch N mineralization potential concentrations versus Ray Branch mean seasonal A horizon soil solution nitrate concentrations for March 2007 through January 2008.

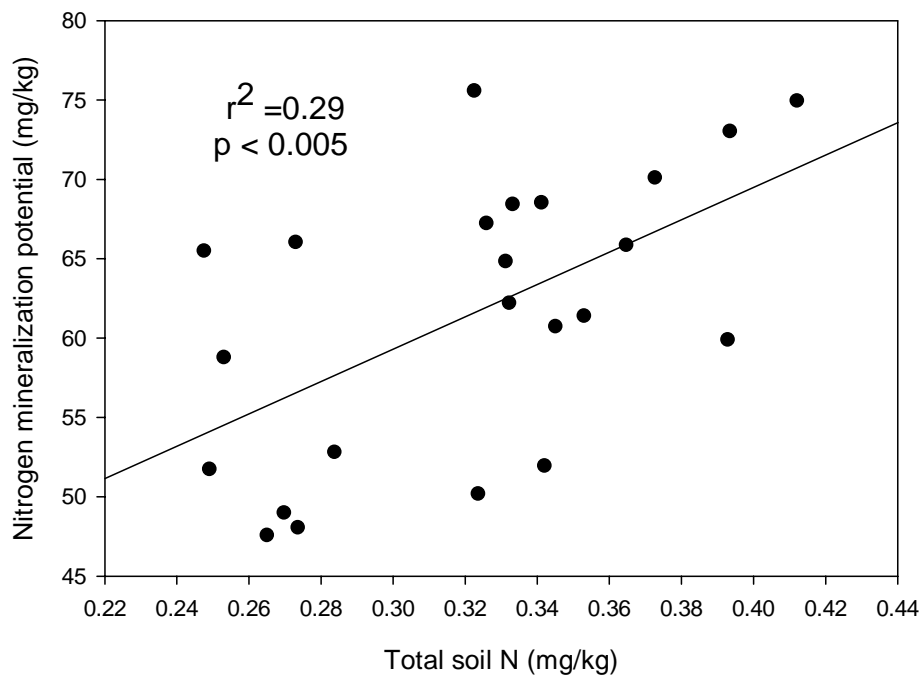


Figure 29. Ray Branch total soil N versus Ray Branch N mineralization potential in the A horizon.

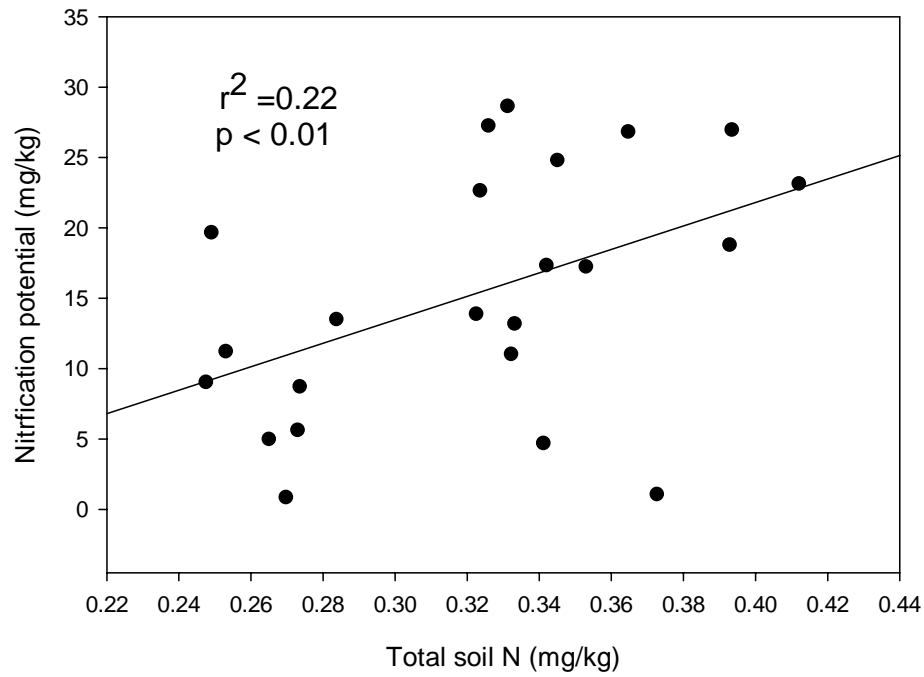


Figure 30. Ray Branch total soil N versus Ray Branch nitrification potential in the A horizon.

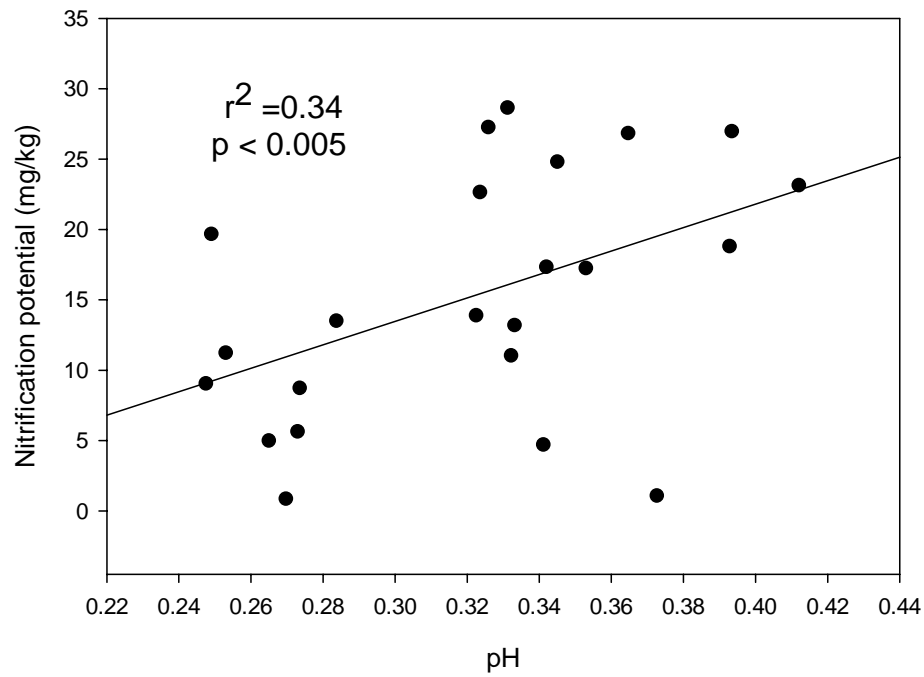


Figure 31. Ray Branch pH versus Ray Branch nitrification potential in the A horizon.

2.4.3 Vegetation

The number of stems/ha was variable among lysimeter locations, ranging from approximately 3,185 to 108,000 stems/ha (data not shown). Red maple (*Acer rubrum*) was the most abundant, with 32,401 stems/ha, and tulip poplar (*Liriodendron tulipifera*), red oaks (*Quercus spp.*), and green briar (*Smilax spp.*) were also abundant, each having > 1,080 stems/ha. Vegetation frequency (stems/ha) at each lysimeter location was not correlated to soil solution nitrate, ammonium, DOC, or DON, or to N mineralization potential (data not shown).

2.5 DISCUSSION

2.5.1 Ammonium-N

Ammonium concentrations were low and relatively stable throughout the year, slightly decreasing throughout the growing season. Ammonium concentrations are often low and show little variation over time in the Nantahala National Forest (Swank and Vose 1997). Nitrification most likely caused the decrease in ammonium concentrations, a process that transforms ammonium and keeps it from accumulating in mountain systems, although plant uptake and immobilization can also decrease ammonium concentrations (Burns and Murdoch 2005). Although increases in ammonium were not significant towards the end of winter, the slight increase I observed may have been caused by decreased nitrification because of cold weather and low microbial activity.

Ammonium in the A horizon was significantly higher than the B horizon and saprolite layer, indicating that the limited mobility of ammonium prevented it from being transported or leached into lower horizons (Waide et al. 1988). There were no significant differences in ammonium between transects and between the harvested and riparian areas, a finding that also was reported in Coastal Plain studies (Lowrance et al. 1984a). Because ammonium concentrations were low and ammonium has limited mobility, the 10m riparian buffer zone appeared to have little influence on ammonium concentrations on this harvested hillslope.

Ammonium concentrations in the stream were correlated to ammonium concentrations in the riparian groundwater indicating that the hyporheic zone is mixing with the stream. Both stream and riparian groundwater ammonium concentrations were significantly higher during the summer than the other seasons. However, these concentrations did not correlate with saprolite

ammonium concentrations as was observed with nitrate, nor were correlations observed between stream water and A horizon or B horizon ammonium concentrations.

2.5.2 Nitrate-N

Soil water nitrate concentrations have been shown to peak in early spring after forest harvesting (Pardo et al. 1995), and the high spring nitrate values I observed were most likely caused by high *in-situ* N mineralization and nitrification rates, which can be strongly correlated with levels of nitrate in the soil solution (Dittman et al. 2007). After site disturbance, increased N mineralization and nitrification along with decreased plant uptake can lead to higher soil nitrate concentrations (Waide et al. 1988). In my study, it appears that plant uptake may have contributed to a significant decline in nitrate in the A horizon beginning with the onset of the growing season in April. Plant uptake is a major cause of nitrate removal in non-riparian areas (Gallardo 2003) and causes decreasing nitrate values during the growing season (Pardo et al. 1995). Although denitrification is often an important mechanism for nitrate removal (Lowrance et al. 1984a, Nelson et al. 1995), there was no evidence that the well-drained soils in the harvested and riparian areas were saturated frequently enough for denitrification to play a large role. Additionally, leaching into lower horizons that I observed most likely contributed to declining nitrate values in the A horizon.

Not only are nitrate dynamics variable across climate gradients (Sabater et al. 2003), nitrate concentrations and removal can be highly variable within much smaller ranges because of variability in plant uptake, soil leaching, nitrification, and denitrification (Gallardo 2003). The four transects in my study, spaced 25m to 40m apart, often had mean nitrate concentrations that were significantly different, suggesting the presence of complex factors, including human influence. The logging deck located between Transects C and D may have contributed to high nitrate values in the saprolite of Transect C and in both horizons and the saprolite layer in Transect D. When stabilizing and reclaiming the logging deck, it is possible that grass seed and fertilizer were applied near the 50m position in Transect D, and vertical leaching along with interflow contributed to the high saprolite values in Transect C. However, nitrate variability persisted in Transects A and B, which were unlikely to have been influenced by the logging deck. For example, nitrate values in Transect B were significantly higher than Transect A during the spring. Additionally, despite the steep slope, there appeared to be little movement of nitrate through the hillslope parallel to the stream. This high degree of variability within a relatively

small hillslope area (approximately 0.6ha) suggests that a large number of lysimeter transects is necessary to accurately represent nitrate movement within soils of these steep Appalachian hillslopes.

There was no strong indication of enhanced nitrate removal within the 10-m riparian zone. Nitrate values in the riparian zone in the A horizon were not significantly lower than nitrate values in the adjacent harvested area and are most likely relatively low because of plant uptake within the hillslope. Rapidly growing forests have a higher demand for nitrate than older forests (Mitchell et al. 2003), and this site, in its second growing season, is likely removing most excess nitrate from soil in the harvested area during the growing season. During the spring when most plants are beginning to break dormancy, nitrate values were at their peak and decreased through the summer and fall, indicating a lesser degree of nitrate retention during the dormant season. High concentrations of nitrate in the riparian zone in Transect D during the spring also indicate there may also be limited nitrate removal in the riparian zone during the dormant season. Nonetheless, in the Nantahala National Forest, nitrate concentrations are generally low, often near detection limits in streams (Swank and Vose 1997), so there may be limited potential to produce nitrate. Although riparian buffers can be very efficient in removal of nitrate, especially at sites with excess nitrate from fertilization or harvesting (Lynch and Corbett 1990, Hubbard and Lowrance 1996), a 10-m riparian buffer may be adequate for nitrate removal under conditions of limited nitrate production and leaching in this harvested hillslope.

Nitrate concentrations in the A horizon have been reported to be significantly higher than in the B horizon after disturbance in the Nantahala National Forest (Yeakley et al. 2003), although Waide et al. (1988) found that nitrate concentrations were not significantly different between horizons before or after harvesting. No overall significant difference was found between the horizons at my site, most likely the result of plant uptake and leaching. Relatively high concentrations of nitrate in the saprolite layer and B horizon suggest leaching and groundwater storage may be important nitrate pathways in the southern Appalachian Mountains. Although the majority of previous research does not examine nitrate losses to groundwater, it has been shown that nitrate predominantly moved laterally through the soil and that vertical leaching of nitrate to groundwater was insignificant (Jacobs and Gilliam 1985). However, the well-drained soils of the Nantahala National Forest would be conducive for vertical leaching.

Additionally, once nitrate leaches below the A horizon, there would be little removal by plant uptake or microbial processes.

In recently harvested watersheds, stream nitrate concentrations are often highest during late winter and early spring (Likens and Bormann 1995, Swank and Vose 1997, Lovett et al. 2000, Kaushal and Lewis 2003, Dittman et al. 2007). For my study, stream nitrate concentrations were significantly higher during the summer, a trend that has been noted in reference systems because of dilution effects during the summer low-flows (Swank and Vose 1997). However, nitrate levels in the stream declined in the fall when water levels remained low because of drought; therefore the high summer concentrations were most likely not solely caused by dilution impacts. In the Catskill Mountains, groundwater, which is recharged in the spring during peak soil-water nitrate concentrations, can be the main nitrate source during baseflow (Burns et al. 1998). This groundwater recharge produces a stream nitrate concentration lag of several months to several years, altering nitrate concentration seasonality. My data show that saprolite nitrate concentrations were correlated to stream nitrate concentrations, but this correlation was significant primarily because of the relationship with saprolite concentrations 50-m away from the stream. The saprolite soil solution - stream water relationship is most likely coincidental because of the 50-m distance between the stream concentrations and soil solution concentrations and because groundwater may not be the nitrate source for streams as demonstrated in the Catskills (Lovett et al. 2000). A variety of additional factors could be influencing the summer nitrate stream concentrations, including influences from 1) upstream, 2) the opposite hillslope, and 3) stream channel interactions within the hyporheic zone. Interplay among these factors may help to explain the lack of relationship between stream nitrate concentrations and A horizon and B horizon nitrate concentrations near the stream. However, riparian groundwater and stream nitrate concentrations were strongly correlated indicating mixing between the hyporheic zone and stream.

There was no detectable relationship between laboratory N mineralization potential or nitrification potential and field soil solution nitrate values using monthly, seasonal, or annual means for field solution nitrate. Low pH values have been shown to inhibit nitrification (Robertson 1982), and the relationship between pH and nitrification potential on my site corroborate this finding. However, the lack of relationship between N mineralization potential and nitrification potential and dissolved N in the soil solution may be caused by stump sprouting

and rapid reestablishment of vegetation, resulting in active N uptake within the harvest zone. There were 3,185 to 108,000 stems/ha present during the period of soil solution sampling, which may cause rapid uptake of nitrate. *In situ* N mineralization potential has been shown to positively correlate with overall high nitrate values in soil solution (Dittman et al. 2007), but the laboratory index of N mineralization potential I employed did not corroborate this finding.

2.5.3 Dissolved Organic Carbon

There were few significant seasonal differences in DOC concentrations with only summer values in the A horizon being higher than spring values. Studies have found DOC concentrations to be higher and more variable during the growing season, most likely because of increased organic matter decomposition (Meyer and Tate 1983). However, DOC in my study was similar among summer, fall, and winter. Because of the high variability in DOC concentrations among lysimeters, it can be difficult to determine statistical differences and patterns (Meyer and Tate 1983). Additionally, lack of adequate sample volume for DOC analysis during the fall resulting from drought contributed to the statistical difficulties. Nonetheless, Transect C was significantly greater than the other three transects, possibly because of greater sources of SOM within the transect or relatively shallow bedrock that may have concentrated flow. Concentrations of DOC in the B horizon and saprolite layer were significantly lower and more stable than the A horizon, indicating that DOC has limited leaching down through the profile. DOC concentrations have been shown to increase through the riparian zone (Peterjohn and Correll 1984), and in the Coastal Plain 63% of the DOC leached into streams originated from riparian wetlands, which only represented 6% of the area (Dosskey and Bertsch 1994). In my study there was no evidence that DOC significantly increased in the riparian zone.

One location with high DOC in Transect C (annual \bar{x} = 312mg/L) was removed from analysis, the transect traversed a small alluvial deposit in the first-order mountain stream. Additionally, the soil there was very shallow and bedrock was within 0.5m of the surface. These two factors may have resulted in elevated DOC due to higher amounts of organic matter breakdown and concentrating flow. However, DON was not elevated in this area, indicating that concentrated flow may not have caused the high DOC concentrations. Additionally, despite soil DOC levels as high as 599mg/L, DOC levels in stream samples at this point were not significantly greater (annual \bar{x} = 3.3mg/L) than stream samples at other locations. Dai et al.

(2001) observed that increased levels of DOC in soil did not result in increased DOC in the stream. This may occur because either DOC is not leaching into the stream or is being diluted or transformed in the stream.

Stream DOC concentrations remained relatively stable throughout the year, but fall and winter concentrations were significantly higher than spring and summer concentrations. This may reflect the added input of leaf fall and subsequent release of DOC during fall and winter. Concentrations of DOC in the riparian groundwater were positively correlated with the stream ($r^2 = 0.47$), indicating the likelihood of mixing between the hyporheic zone and the stream. There was no apparent evidence of a linkage between DOC concentrations in the stream and riparian groundwater with DOC concentrations in the soil solution, possibly because DOC concentrations are higher in the soil solution than in the stream as a result of contact with the root zone (Meyer and Tate 1983).

2.5.4 Dissolved Organic Nitrogen

Dissolved organic N was difficult to determine and analyze because of the high detection limit. Using only the data that had DON values above the detection limit is a misrepresentation of DON on the site. As a result, I explored relationships between DOC and detectable values of DON. A variety of studies have shown DOC and DON to be related (Campbell et al. 2000, Kaushal and Lewis 2003, Neff et al. 2003), although some found no relationship (Lovett et al. 2000). Although DOC and DON were related in my study ($r^2 = 0.64$), it was not a linear relationship. The non-linear logarithmic relationship I observed between DOC and DON suggests that the C:N ratio changes as DOC increases. However, using this relationship to predict DON overestimated concentrations in the A horizon (half of the estimated A horizon values are predicted to be greater than the detection limit). Removing the high DOC and DON values to create a linear relationship not only reduced the correlation coefficient ($r^2 = 0.29$), but still overestimated DON values.

Alternatively, I explored using one half of the detection limit, 0.4mg/L, to replace non-detectable values. This method does not over-estimate DON concentrations. However, it masks potential variability on the site. This method was used for my DON analysis because it was the least likely to over-estimate DON values.

Concentrations of DON have been shown in other studies to have significant seasonal variation (Campbell et al. 2000). In situations where seasonal variations occur, DON increases

during late summer and early fall, which is attributed to new litter inputs following leaf senescence and leaf litter breakdown (Currie et al. 1996). However, in my study there was no seasonal variation of DON, potentially because of the limitations associated with DON values below the detection limit.

There were no seasonal statistical differences in DON among the A horizon, B horizon, and saprolite layer, but this difference may have been masked because of the high detection limit and the methodology to predict values below the detection limit. However, the mean annual DON concentration in the A horizon was significantly higher than the mean annual DON concentrations in the B horizon and saprolite layer. After harvesting, increases in organic matter can increase leaching of organic N compounds into the top 10cm of soil, with some DON leaching down to 30cm (Waide et al. 1988). Higher concentrations in the A horizon would be expected because of greater soil organic matter pools, which can also cause high variability in the A horizon. B horizon and saprolite layer concentrations of DON were lower and more consistent because less organic matter is available at these depths.

Dissolved organic N concentrations in the A horizon of Transect C were significantly higher than the other transects. Slightly higher pools of total soil C may have contributed to the increase in DON in this transect (data not shown). Additionally, the riparian zone did not remove excess DON. Riparian buffer removal of DON is variable, with some buffers attenuating sources of DON and others leaking DON, most likely caused by differences in concentrations of labile and recalcitrant forms (Bedard-Haughn et al. 2004). Buffers have been shown to remove up to 60% of DON in surface water as well (Peterjohn and Correll 1984).

With few exceptions, all DON concentrations were below the detection limit in streamwater samples and riparian groundwater. Dissolved organic N can be extremely variable over the seasons in stream water because DON concentrations are highest during storms due to flushing (Kaushal and Lewis 2003, McGlynn and McDonnell 2003). Dissolved organic N was detectable in July in the stream below Transect D (1.89mg/L), well 10 near Transect D (0.83mg/L), and in the B horizon in Transect D 1m from the stream (3.58mg/L). This indicates that the hyporheic zone, stream, and deep soil water had similar DON concentrations and were possibly interacting at that time. In contrast, despite the high DON concentrations at Transect C 1m from the stream (annual \bar{x} = 10.8mg/L), no DON was detectable at the stream sampling point below Transect C. This indicates that DON is either not leaking into the stream or is being

diluted and does not have the same degree of connectivity as observed at the interface of the stream, groundwater, and soil at Transect D.

Dissolved organic N can comprise about 50% or more of the TDN in streamwater (Campbell et al. 2000) and has been shown to comprise 70% of soil solution N, except in agricultural fields where fertilization has been applied (Lowrance et al. 1984b). In all methods used to estimate DON in the soil solution on the site I studied, DON made up a significant amount of the TDN amount, ranging from 35 to 85%, with summer, fall, and winter ratios being typical of those in unpolluted environments (Perakis and Hedin 2002). Although Lovett et al. (2000) showed a negative relationship between DIN and DON, no relationship was observed on my site ($r^2 = 0.034$).

2.6 CONCLUSIONS

Results from this study further our understanding of dissolved C and N on harvested hillslopes in the southern Appalachians. The following conclusions have been formed from the results:

1) Nitrogen mineralization potential in the laboratory from soil samples collected at 0-15cm at one time was not a useful predictor for seasonal *in situ* nitrate soil solution values in the A and B horizons or in the saprolite layer. This lack of correlation may be a function of field soil solution nitrate concentrations being influenced by a variety of factors in addition to N mineralization potential, including plant uptake, microbial immobilization, and denitrification.

2) Excess nitrate leached vertically, and a large percentage of nitrate was at least temporarily present in the B horizon and saprolite. Nitrate that leaches below the A horizon is not likely to be utilized by plants and can be transported to the groundwater and then to the stream. Ammonium, DON, and DOC did not appear to leach vertically because they did not increase in the B horizon or saprolite layer. Ammonium, DON, and DOC are less mobile in soil water than nitrate.

3) The 10-m riparian zone had little impact on nitrate, ammonium, DON, and DOC removal because levels of these solutes entering the riparian area were low. Excess nitrate leached vertically in the profile, and nitrate remaining in the A horizon was likely removed through plant uptake in the harvested area before reaching the riparian zone. There was no difference between ammonium concentrations in the harvested area and riparian zone because of

limited mobility. The riparian zone did not remove excess DON or DOC, as indicated by areas of high DON and DOC within the zone.

4) Nitrate and DOC concentrations were highly variable among transects and among locations within transects reflecting a high degree of site heterogeneity for these solutes. Consequently, a large number of lysimeters should be used to account for this variability in future studies to ensure accuracy in assessing solute distribution and transport.

2.7 ACKNOWLEDGEMENTS

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Appendix

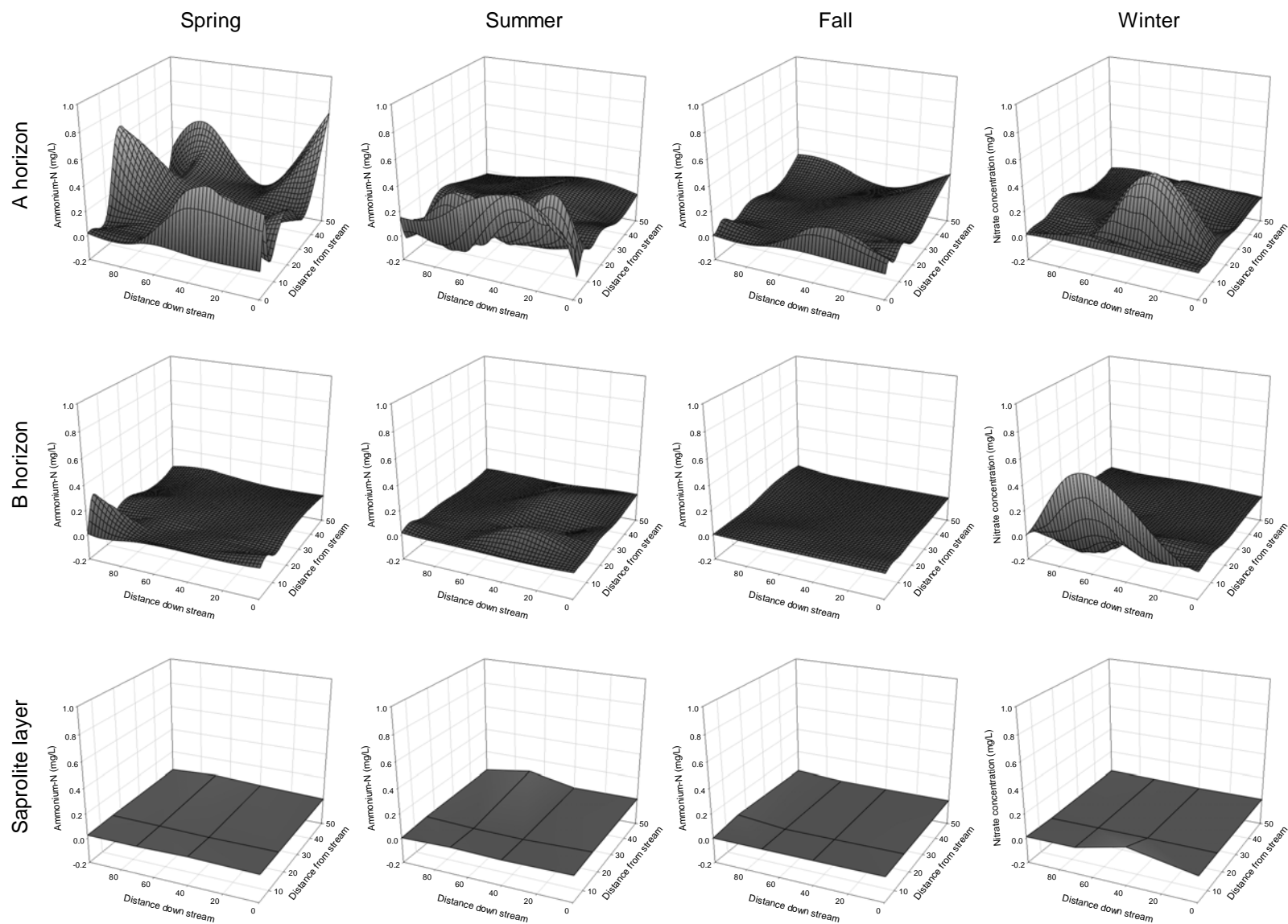


Figure A.1. A 3-D analysis of ammonium by season and horizon for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008.

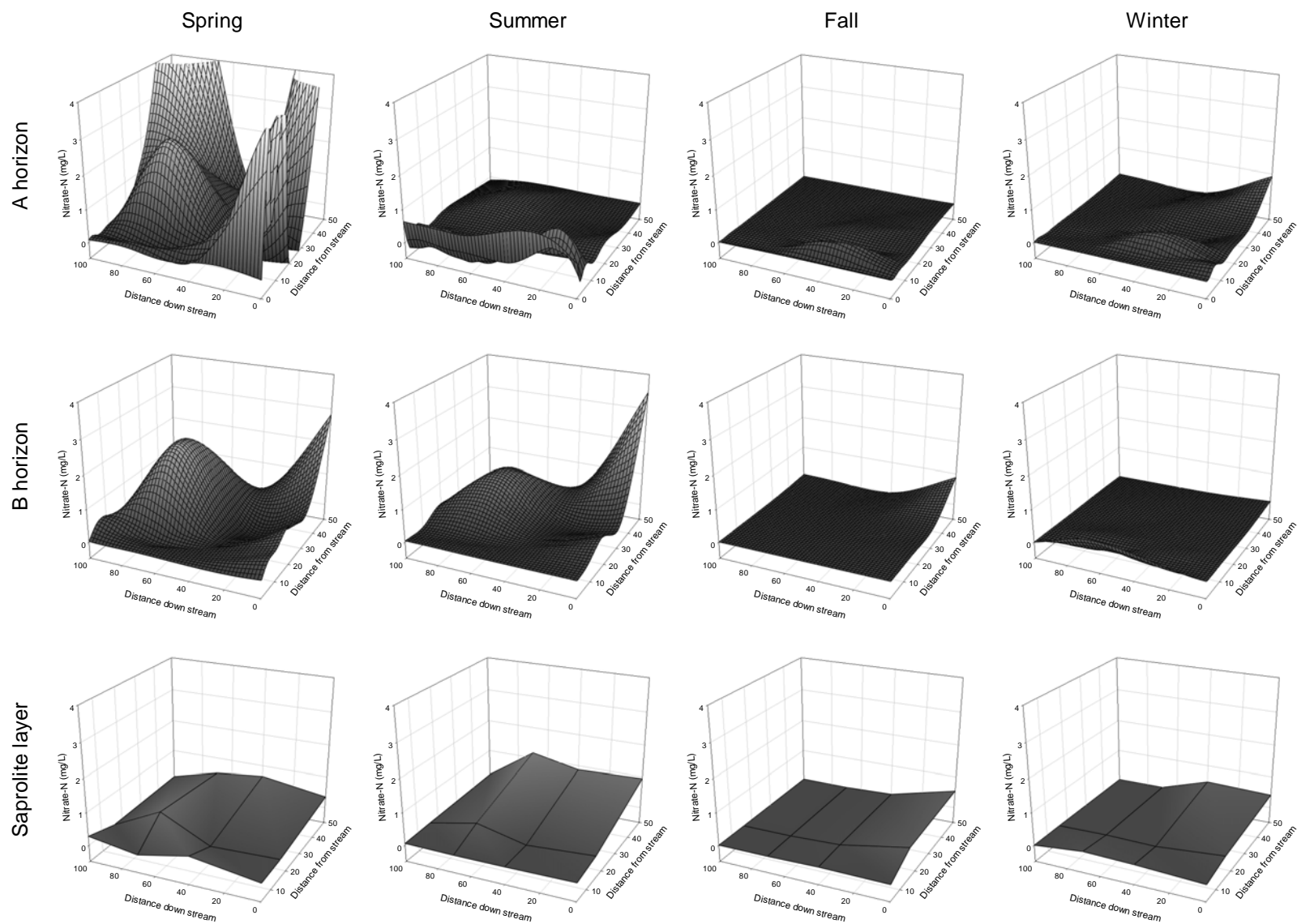


Figure A.2. A 3-D analysis of nitrate by season and horizon for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008.

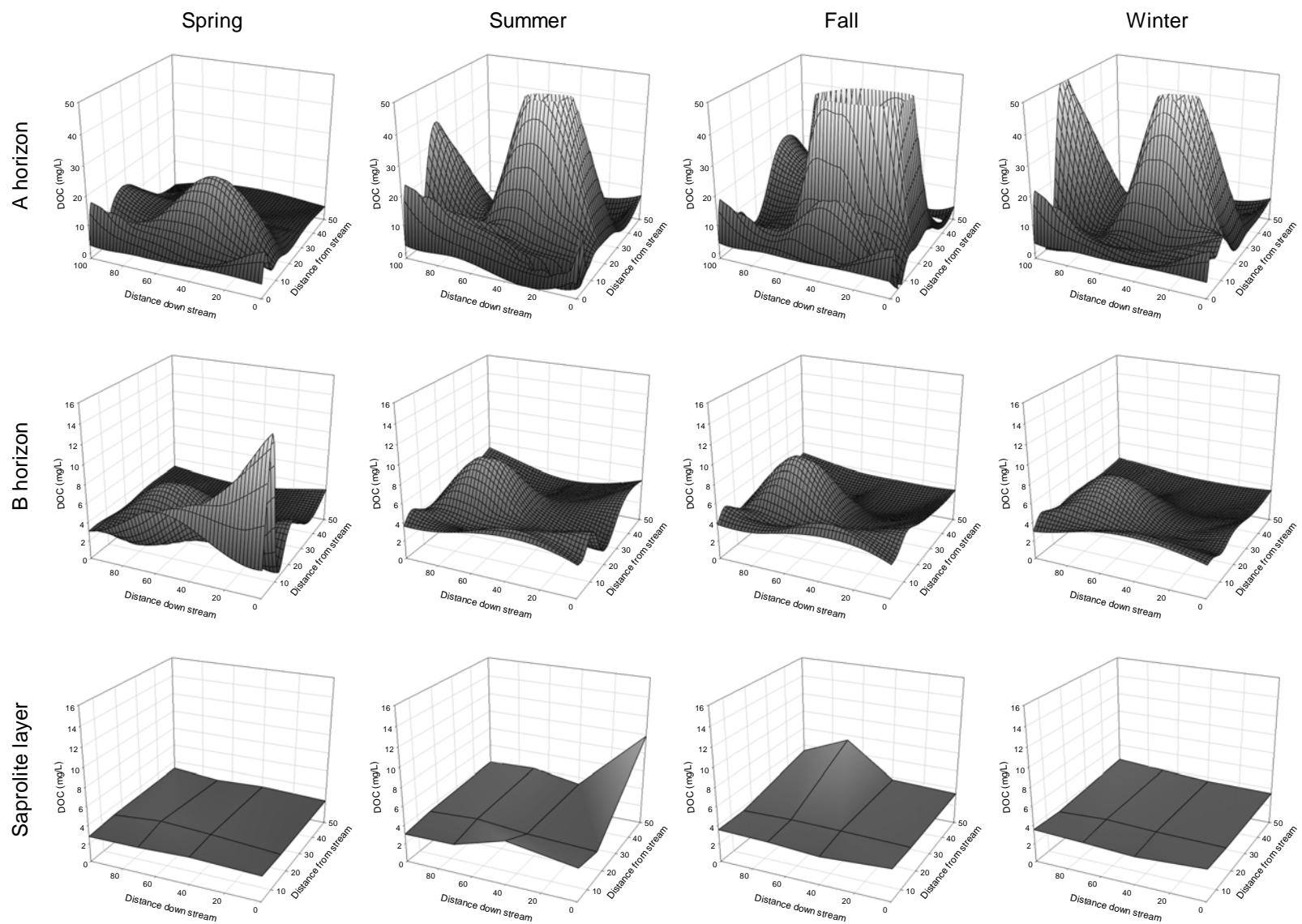


Figure A.3. A 3-D analysis of DOC by season and horizon for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008.

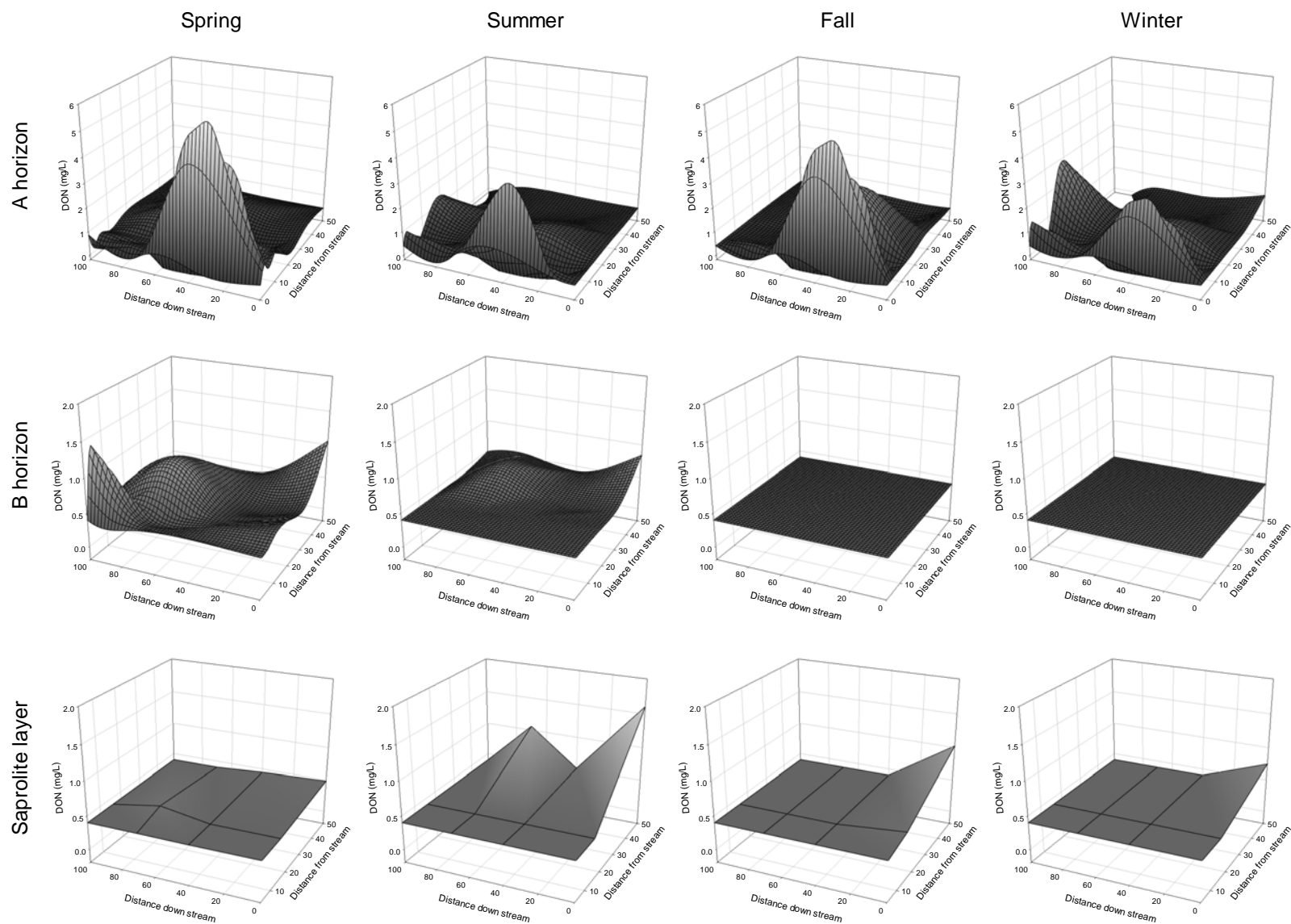


Figure A.4. A 3-D analysis of DON by season and horizon for the Ray Branch site in the Nantahala National Forest, North Carolina for March 2007 through January 2008.

