

**Nutrient Movement in Streamside Management Zones and Piedmont Streams
Following Forest Fertilization**

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Abstract

Many states' Best Management Practices (BMP) programs established Streamside Management Zone (SMZ) widths based on limited or inadequate data with regard to nutrient fluxes from silvicultural activities. Previous studies in forested watersheds have shown slight post-harvest increases of several nutrients in streams. Also, in agricultural settings, increased nitrogen (N) and phosphorous (P) levels have been detected in streams. However, little is known about the effectiveness of recommended forested SMZ widths for controlling nutrient fluxes following fertilizer application. Diammonium phosphate (DAP) and urea fertilizers were applied to subwatersheds of 2 to 3 year-old loblolly pine (*Pinus taeda L.*) plantations upslope from SMZ study areas throughout Buckingham Co., VA. Three replications of four SMZ treatment widths (30.5m, 15.2m, and 7.6m plus a thinned 15.2m SMZ) were studied using surface water collectors, cation/anion exchange membranes, lysimeters, and stream grab-samples. Measurement devices were spaced symmetrically across the SMZ from the uphill SMZ edge to stream edge with grab samples being collected approximately 20m upstream and 20m downstream of the fertilized area. Little nitrogen and phosphorous movement was detected in surface water which was monitored using surface water collectors. Near-surface water flow sampling using ionic exchange membranes resulted in our most complete dataset and showed infrequent lateral ion transport in the litter and upper soil layers even after water passed over an approximately 1m wide, seeded firebreak located between the SMZ dripline and fertilized area. Results from lysimeter samples used to measure subsurface flow were limited due to dry conditions; however, the limited samples indicate that only minute levels of nitrogen and phosphorous are transported

laterally via shallow subsurface and surface flow. Overall, sampling indicated that only minute quantities of nitrogen and phosphorous were ever transported from the fertilized clearcut to the riparian area. Results indicate that even a 7.6m wide SMZ with a seeded firebreak is adequate to protect streams from industrial fertilizer application in a relatively dry year, but wider SMZs may be necessary for other benefits.

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Chapter 1: Introduction

Land Use History

Historically abusive agricultural practices in Virginia have resulted in many forested tracts having shallow O and A soil horizons and, consequently, low levels of soil nitrogen and phosphorous. During the late 1700's and through the 1800's agricultural practices in the Piedmont region caused severe soil erosion and subsequent farm abandonment following the Civil War through the early 1900's (Trimble, 1974). Following land abandonment, fire suppression and land disturbance favored *Pinus spp.* with associates such as *Liquidambar styraciflua* L. and *Quercus nigra* L. (Cowell, 1998). Beginning in the 1950's, many of these less productive sites were converted to pine plantations. More recently, increased pressures on the forested land base due to a growing population and international markets have forced land managers and owners to realize the need for increased productivity. Forest productivity has been shown to increase with supplemental inputs of inorganic nitrogen and phosphorous in the forms of urea (46-0-0) and DAP (18-46-0), and fertilization is a common practice. During the early 2000's approximately 607,000 hectares of forestland were fertilized in the southeastern region on an annual basis (North Carolina State University Forest Nutrition Cooperative (NCSU FNC), 2007).

Background

Public concern over the health of the nation's waters led to the development of the Federal Water Pollution Control Act of 1972 (PL 92-500) and subsequent amendments, which are commonly known as the Clean Water Act (Ice et al., 1997). The Clean Water Act was designed to "set water quality standards for all contaminants in surface waters"

(US EPA, 2007). In order to comply with guidelines established by the Clean Water Act, the state of Virginia has established Best Management Practices (BMP's) for forestry operations (Virginia Department of Forestry (VDOP), 2002). BMP guidelines have important environmental and economical implications because they potentially influence the management of 6.2 million hectares (61 percent of the Virginia land base) of potentially commercial forest land (VDOP, 2002). Virginia's BMP program is considered voluntary except within the Chesapeake Bay Preservation Area, where BMPs are more restrictive and required. Although BMPs are voluntary, the Virginia Silvicultural Water Quality Law (VDOP, 2002) requires that silvicultural activities must not cause water toxicity or significant sedimentation problems greater than the national standard. Therefore, Virginia is considered a quasi-regulatory state due to the combination of voluntary BMPs and the silvicultural water quality law (Aust and Blinn, 2004).

Objectives

Previous studies have shown the ability of forested riparian areas to uptake nutrients and act as nutrient sinks (Lowrance et al., 1984; O'Laughlin and Belt, 1995; Fox et al., 2007). Jacobs and Gilliam (1985) found that Coastal Plain buffer strips of less than 16m were effective for significantly reducing nitrate levels in agricultural drainage water before it reached the stream. However, the typical SMZ width needed to prevent increased N and P levels in upper Piedmont streams in a forested setting is unclear. The primary goal of this study was to determine the effectiveness of various SMZ widths in preventing nitrogen and phosphorous fertilizer from reaching a stream following typical DAP and urea application on a young loblolly pine (*Pinus taeda* L.) stand. This project

was aimed at identifying the appropriate SMZ width for preventing nutrients from entering streams by examining water movement at the soil surface, within the primary rooting zone, and through deeper subsurface flow. Establishing the transportation patterns of nitrogen and phosphorous following fertilization through an SMZ could help forest land managers appropriately designate future harvest boundaries. Specifically, this study examined differences among three SMZ widths (7.6m, 15.2m, 30.5m) and a non-managed and a thinned 15.2m SMZ, currently the most common SMZ width in Virginia.

The study objectives were:

- 1) Compare the effectiveness of streamside management zone width (7.6, 15.2, and 30.5 meter) in preventing nitrogen and phosphorous from reaching a stream following fertilization of a loblolly pine plantation.
- 2) Quantify the amount and patterns of increased nitrogen and phosphorous transported on the soil surface and through the soil subsurface within a streamside management zone.
- 3) Examine the impact of thinning in the 15.2 meter width on the above parameters.
- 4) Assess stream water for nitrogen and phosphorous above and below the point of forest fertilization.

Chapter 2: Literature Review

Streamside Management Zones

Streamside Management Zones (SMZ's) are commonly used BMP's for preventing water quality degradation from forest silviculture operations (Aust and Blinn, 2004). Streamside forests help prevent excess sediment and nutrients from reaching the stream, protect streams from thermal pollution, correct negative aquatic effects of pesticides, and help generate food sources that promote aquatic productivity and diversity (Welsch, 1996). Additional principle functions of riparian areas are to stabilize streambanks, provide a source of spawning gravel, moderate riparian microclimates, and provide wildlife habitat (O'Laughlin and Belt, 1995). Walbridge (1993) noted that forested wetlands provide eight biogeochemical functions (sediment deposition, denitrification, sulfate reduction, phosphorous sorption, nutrient uptake, decomposition of waste organics, sorption of heavy metals, and retention of toxics) that improve water quality and two biogeochemical functions (carbon storage and methane production) that influence global atmospheric changes. During the first year following a harvest in Mississippi, Keim and Schoenholtz (1999) found that streams in logged watersheds without SMZ implementation had approximately three times the sediment concentration as found in non-harvested watersheds and concluded that SMZs are most effective in controlling sedimentation when the forest floor is undisturbed. Adequate buffer width depends on the condition of the buffer (e.g. amount of vegetation and soil disturbance), the relative functional value of the water body (e.g. disturbance regime and plant origin), and the potential impact of adjacent land (e.g. park land versus residencies or farms) (Castelle et al., 1994).

Various widths of SMZ's have been recommended and implemented based on the level of protection desired for a particular type of water body and the percent slope of adjacent lands (VDOF, 2002). However, recommended widths are somewhat arbitrary and established with insufficient scientific basis in regards to effectiveness of various widths in controlling targeted pollutants (Castelle et al., 1994). Additionally, science-based width recommendations were established mostly for perceived adequate sediment control rather than for nutrients. Currently, a 15.2m wide SMZ is the most commonly utilized for a typical upland Piedmont forested stream (VDOF, 2002).

Ability of Streamside Management Zones to Reduce Nutrients

Several researchers, including Jacobs and Gilliam (1985) and Jordan et al. (1993), have found that groundwater nitrate concentrations were reduced significantly by a forested SMZ downslope of cropland. Lowrance et al. (1983) determined that nitrogen inputs to a forested SMZ from an agricultural area via subsurface flow and precipitation were approximately three times higher than in streamflow outputs. Furthermore, they found that 82% of nitrogen entering the SMZ was in nitrate or ammonium form while streamflow outputs of nitrogen were 80% organic. By collecting rainfall, stream samples, surface runoff samples, and well samples Peterjohn and Correll (1984) determined that an approximate 50m forested SMZ below an agricultural watershed removed 0.83 kg/ha/yr of ammonium and 2.7 kg/ha/yr of nitrate from surface runoff waters and an estimated 45 kg/ha/yr of nitrate in subsurface flow. In an examination of a three-zone riparian system, Lowrance et al. (2000) found that riparian forest buffers help improve water quality in agricultural areas even when forest harvesting occurs within the buffer.

Pratt (2008) applied biosolids to a loblolly pine plantation and found a decline in near-surface and deeper subsurface nutrient availability across the SMZ as well as non-statistical patterns suggesting that SMZs reduce nitrogen concentrations in runoff.

Binkley et al. (1999) conducted a review of several other studies of forest fertilization around the world and their impact on streamwater chemistry and found that no strong pattern was apparent between (high or low) nitrate concentrations in streams protected with riparian buffer strips and those not protected. However, forest fertilization best management practices are still recommended to prevent possible situations that could lead to high concentrations of nutrients in streamwater (Fox et al., 2007).

Methods for Sampling Nutrient Movement in SMZs

Lowrance and Sheridan (2005) used Low-Impact Flow Event (LIFE) samplers to collect surface runoff and found increased nutrient loads entering a forested buffer zone. Using surface water samplers is vital in collecting samples from sub-watersheds due to the ability of ephemeral drains to carry potentially high nutrient-enriched surface water following heavy rain events.

Lateral flow is an important path of nutrient movement in surface horizons (Gaskin et al., 1989). Fluxes of SO_4 , Cl, $\text{NO}_3\text{-N}$, K, Ca, Mg, and H are greatest in the A to B horizon and decrease with depth. During dry conditions the greatest lateral flow is higher in the soil profile (Gaskin et al., 1989). Denitrification potential is highest in the top 2cm of surface soil and occurs at higher rates when the soil has higher levels of organic matter and is poorly drained (Ambus and Lowrance, 1991). Cation and anion exchange resin bags have usually been used to quantify nutrient movement in upper soil horizons. However, ionic exchange membranes (Ionics, Inc., Watertown, MA), also

known as IEM's, are being used more frequently due to their many advantages over bags (Elliot, 2006). In contrast to the resin bag form, the membrane form is flat ensuring a constant surface area and better contact with the soil (Huang and Schoenau, 1996). Diffusion problems are reduced because the two-dimensional structure ensures more surface area will be in contact with the soil which undergoes minimal disturbance during installation. Furthermore, the IEM is physically and chemically durable and has a high correlation with soil solution P at low solution concentrations (Cooperband and Logan, 1994).

IEMs were installed horizontally in the A and top of the B soil horizon (1-10cm deep) as well as the litter layer and A soil horizon fringe. The litter layer to A soil horizon interface was studied because a major source and sink of plant nutrients is the litter layer. In regards to nitrogen, the largest proportion of water soluble N and supply rates of organic N can be found in the lowest, most decomposed horizon (O_a or H) of the litter layer. Phosphorous supply rates share the same trend as nitrogen. However, water soluble phosphorous is greater at the upper, less decomposed (O_i or L) horizon (Huang and Schoenau, 1996).

Porous Cup Soil Solution Samplers (PCS) have been commonly used to measure solute transport in sub-surface flow. The range of influence of the suction lysimeter is approximately 0.3 m but varies depending on applied suctions and the specific soil's hydraulic properties. Longer periods of suction result in a large range of influence (Wu et al., 1995). Lysimeters are considered to be a simple and inexpensive way to sample subsurface water for nitrogen and phosphorous, but they have many problems (Cole, 1958, Addiscott, 1990). Unfortunately, PCS performance can be significantly affected by

inherent characteristics of particular samplers or installation differences (Hart and Lowery, 1997). Moreover, cup intake rate, leaching, diffusion, sorption, and screening affect sample concentrations adding variability to the sampling method (Hansen and Harris, 1975). True numeric concentration differences may be skewed because of these inherent problems associated with utilizing lysimeters. However, relative differences in nutrient concentration can give an indication of nutrient transport. Porous cup lysimeters were utilized to pull water samples from several locations between the stream and SMZ dripline where nutrient presence is expected to vary.

Nutrients in streams can be influenced by several natural factors. The surface water/ground water interface is a crucial control point for nutrient fluxes between uplands and streams in that it significantly regulates nutrient transport in both surface runoff and groundwater due to the topographic location of the interface. Also, surface water and ground water are connected when (a) groundwater flows from the uplands into the riparian areas to the active channel and (b) surface water recharges groundwater along the upstream-downstream gradient (Dahm et al., 1998). Wroblicky et al. (1998) found groundwater moving parallel to the stream in high-flow conditions, but during low-flow conditions water moved both toward and away from the stream depending on local variables. In a study regarding nutrient export in stormflow following forest harvest and site-preparation in Texas, Blackburn and Wood (1990) found that larger stormflow events have greater chances of leaching or moving nutrients off site to the stream channel and away from the sub-watershed. Sampling stream water allowed for determination as to whether increased nutrients are penetrating various SMZ widths even if patterns of nutrient movement are unclear.

Plant Nutrient Uptake

Trees require adequate nutrition to perform critical biological processes such as photosynthesis. Most nutrients such as nitrogen (N), phosphorous (P), magnesium (Mg), potassium (K), calcium (Ca), sulfur (S), etc. are transported in water to plant roots via diffusion or mass flow (Brady and Weil, 2000). On many eroded piedmont sites, nutrients are often a limiting factor for tree growth. Bilbrough and Caldwell (1997) found that plants acquire significant gains in biomass from pulses of nitrogen. Acquisition from seasonal, short nutrient pulses is believed to be significant on a yearly basis (Campbell and Grime, 1989; Jonasson and Chapin III, 1991) and responses will depend on the time of the pulse in relation to plant growth stage and environmental conditions (Bilbrough and Caldwell, 1997). Despite the naturally occurring seasonal nutrient flushes, many forest landowners and managers find it economically beneficial to supplement nutrient flushes via fertilization.

Forest Fertilization

Fertilization of pine plantations has increased in the last few decades. In 1990, approximately 80,900 ha (approximately 200,000 acres) of pine plantations were fertilized in the Southeast. This has increased to about 607,000 ha (1.5 million acres) in 2002 (NCSU FNC, 2007). Landowners have been excluding forest harvesting along perennial and intermittent streams in order to follow water quality BMP's for forestry operations. However, these recommendations are based on relatively few scientific studies as to the cost-effectiveness of SMZs in regards to nutrient pollution. Nitrate is the most responsive nutrient to forest harvesting and nitrogen pollution levels exceeded the U.S. drinking water quality standard in some studies (Binkley and Brown, 1993).

Potassium, calcium, sodium, and magnesium have also been found to increase in the stream but to lesser extents (Arthur et al., 1998). For fertilized agricultural fields, nitrogen and phosphorous concentrations in stream water are commonly nine times greater than stream water from forested watersheds. Fertilizers are generally to blame for this increase (Binkley et al., 1999, Fox et al., 2007). As forest landowners increase fertilization rates, frequency, and area, forest fertilization efforts might cause similar water quality issues as found in agricultural fertilization activities. Forest products are generated on a longer rotation than agricultural crops and fertilization operations are less frequent, but there is still the need to determine adequate SMZ widths so that landowners can maximize their land base for revenue without causing water quality issues.

Virginia Water Quality Standards and Criteria

Water Quality Standards (WQS) represent the physical, chemical, or biological characteristics of water for a particular use (i.e. drinking, swimming, fishing, irrigation, etc.) of the designated body of water (Brooks et al., 2003). Narrative and/or numerical criteria define acceptability levels (e.g. 4 mg/l dissolved oxygen) or “free froms” (e.g. free from attributes of sewage) for a particular standard based on aspects such as temperature, dissolved oxygen, pH, nutrient levels, etc. that may be detrimental to humans, animals, plants, or aquatic life (Virginia Department of Environmental Quality (VA DEQ), 2009a). In March 2009 the state of Virginia accepted nitrate levels up to 10 mg/l for public water supply (9 VAC 25-260-140) to achieve the drinking water (and fish consumption) standard. Currently, the model in figure 1 is being developed by Virginia Department of Environmental Quality (VA DEQ) and the Academic Advisory

Committee (AAC) to determine if a water body is able to be utilized as a source for drinking water.

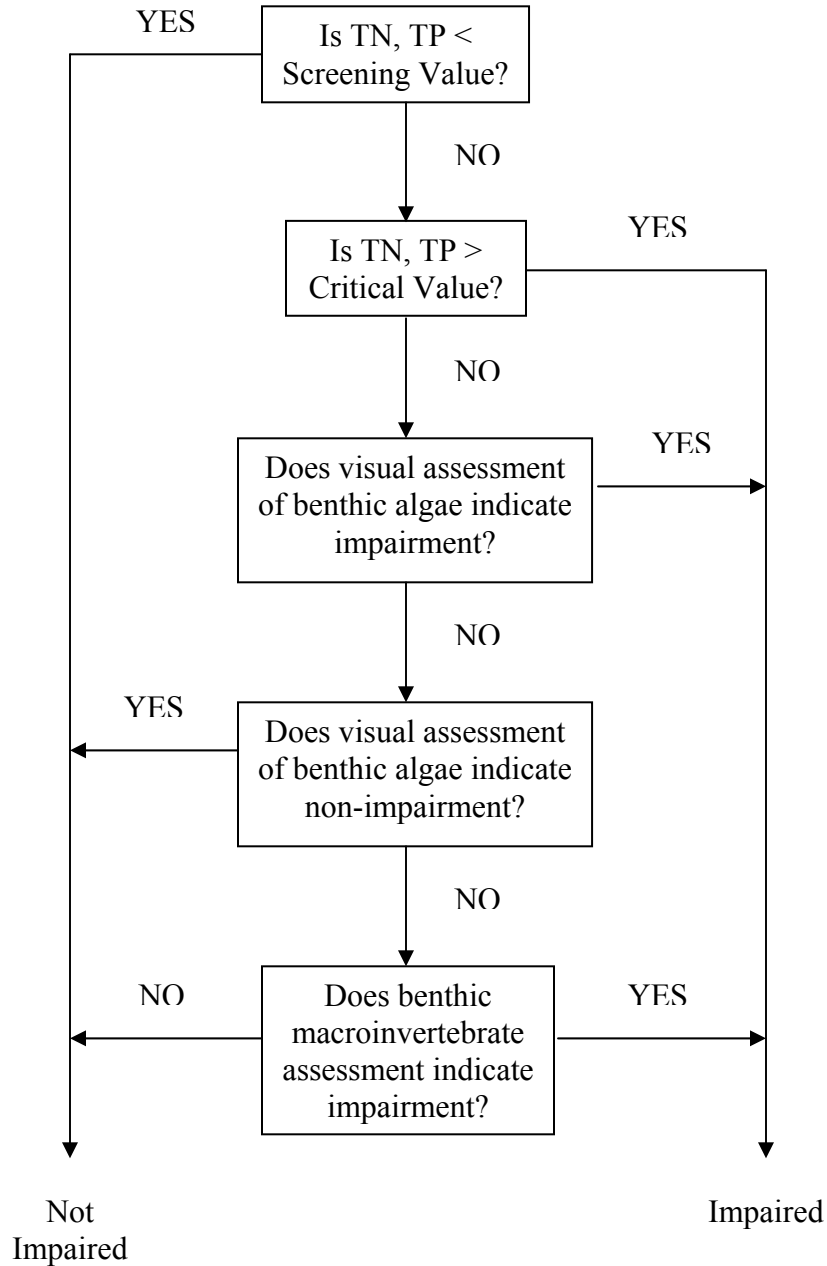


Figure 1. Proposed screening-value approach to nutrient criteria for Virginia’s freshwater wadeable streams, for implementation during pilot program. Figure adapted from “Weight of Evidence Screening Value Approach to Nutrient Criteria Development for Wadeable Streams” (VA DEQ, 2009b). (www.deq.state.va.us/wqs.documents/STRM_SCRN_VAL_WADEABLE.pdf).

Stream impairment for total nitrogen and total phosphorous may exist if levels lie above a certain critical value. However, if nutrient levels fall between a determined screening value and critical value, then algae and macroinvertebrate sampling will be required to determine if the stream is impaired for the drinking water source standard. Drinking water criteria may not be established specifically for ortho-phosphate. Specific acute ammonia freshwater criteria (9 VAC 25-260-155) have only been established for a known pH and the presence/absence of trout. The adoption of total nitrogen and total phosphorous nutrient criteria in the regulatory process for streams and rivers is expected to start in late 2009 (Gregory, 2008).

Hypotheses

Our overall null hypothesis (H_0) is that differences in streamside management zone width and thinning within an SMZ do not affect the movement of applied fertilizer from a planted loblolly pine watershed to the stream. We periodically monitored the surface, near-surface, subsurface, and stream water components for nitrate, ammonium, total inorganic nitrogen (nitrate + ammonium), and ortho-phosphate within each of the different SMZ treatments. We specifically tested each of the following generalized alternative hypotheses:

HA₁: Increased surface, near-surface, subsurface, and stream water nitrate, ammonium, total inorganic nitrogen, and ortho-phosphate levels resulting from fertilization of a loblolly pine plantation will be decreased by increasing SMZ width.

HA₂: Surface, near-surface, subsurface, and stream water nitrate, ammonium, total inorganic nitrogen, and ortho-phosphate levels will increase immediately following fertilization and subsequently decrease.

HA₃: Surface, near-surface, subsurface, and stream water nitrate, ammonium, total inorganic nitrogen, and ortho-phosphate levels will be increased by thinning in an SMZ.

Chapter 3: Methods and Materials

Site Description

Twelve study sites were located in Buckingham County (figure 2) (37°33'00" N Latitude, 78°33'30" W Longitude) in central Virginia (DeLorme, 2005).



Figure 2. Map of Virginia identifying the location of Buckingham County.

This area is commonly referred to as the Upper Piedmont with its rolling terrain and typical elevation ranging from 60m to 460m above mean sea level (Fenneman, 1938). Typical forest management includes establishment of loblolly pine plantations, clearcutting, ground skidding, establishment of fire breaks, chemical weed control, and site preparation with controlled burning. Climate and soils for Buckingham County, VA are described by Wiseman and Seiler (2004). Average annual precipitation for this region is 107cm. Average winter (December to February) temperature is 3.3°C while average growing season (April to September) temperature is approximately 21°C. Virginia piedmont soils are generally highly eroded. Shallow ultisols with argillic horizons overlain with Ap horizons are typical. The Ap horizon is usually low in organic matter and eluvial E horizons are generally minimal or absent. Soil textures are

frequently gravelly loam to gravelly sandy loam over 1:1 clay subsoils (Wiseman and Seiler, 2004). Riparian areas often have higher levels of organic matter, sand, and coarse fragments than the harvested treatment area.

From the late 1700s to late 1800s abusive agricultural practices were common in the area. Much of Buckingham County was abandoned by the farming community as soils were degraded. Land abandonment led to native pine and hardwood forests. Upland areas were dominated by oak species (*Quercus spp.*), red maple (*Acer rubrum* L.), sweet gum (*Liquidambar styraciflua* L.), tulip-poplar (*Liriodendron tulipifera* L.), Virginia pine (*Pinus virginiana* Mill.), and shortleaf pine (*Pinus echinata* Mill). Bottomlands were dominated by red maple, silver maple (*Acer saccharinum* L.), sycamore (*Platanus occidentalis* L.), elm (*Ulmus spp.*), and boxelder (*Acer negundo* L.) (Fleming et al., 2001). Much of these forests were harvested in the mid-1900s and replanted with loblolly pine.

Treatments

All sites were on Mead-Westvaco property and were clearcut harvested between summer 2003 and spring 2004 using standard equipment and systems (ground-based harvesting with rubber tired feller-bunchers and skidder) and then site-prep burned by fall of 2004 (Lakel, 2008). Within each of the twelve study watersheds (1st order intermittent and perennial streams), a smaller contributing sub-watershed (zero order, ephemeral drain) was selected in the clearcut area for the study of fertilizer nutrient movement through various SMZs. These subwatersheds ranged from 0.2 to 1.4 hectares in size. Treatments were arranged in a completely random design with three replications of the following four SMZ treatment widths described by Lakel et al. (2006) (figure 3):

1. 7.6m (25-foot) wide SMZ with no SMZ harvest (7.6m SMZ)
2. 15.2m (50-foot) wide SMZ with no SMZ harvest (15.2m SMZ)
3. 15.2m (50-foot) wide SMZ with 50% SMZ thin (thinned 15.2m SMZ)
4. 30.5m (100-foot) wide SMZ with no SMZ harvest (30.5m SMZ)

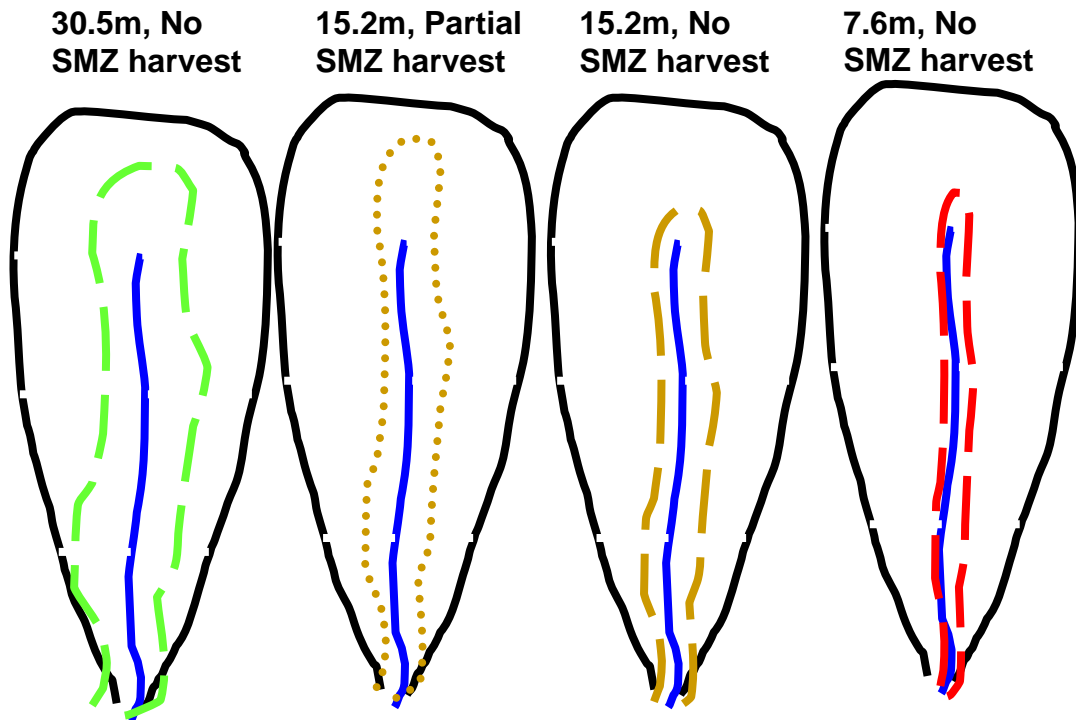


Figure 3. Idealized layout of four watersheds and associated streamside management zone treatments used in the research project located in Buckingham County, Virginia.

In actuality, the 7.6m treatment had some light harvesting within the SMZ. Harvesting consisted of limited single-tree selection between the firebreak and stream. However, no machinery was allowed in the SMZ so soil disturbance did not occur and no chemical weed control or other forest management practice took place within the SMZ.

In July 2007 diammonium phosphate (DAP) and urea fertilizers were applied to the twelve sub-watersheds at common industrial rates of 140.3 and 250.4 Kg/ha (125 and 223 pounds/acre), respectively, by ATV and by cyclone hand spreader. Application yielded 28.1 Kg/ha (25 pounds/acre) elemental phosphorous (P) and 140.3 Kg/ha (125

pounds/acre) elemental nitrogen (N). DAP and urea are the primary fertilizer compounds used for forestry fertilization. It was expected that differences in SMZ width and harvest level would impact the amount of fertilizer nutrient capable of moving from the ephemeral watersheds into the larger study streams regardless of slope, soil, and vegetation differences among SMZ treatments.

In order to adequately determine the effects of streamside management zones on fertilization and water quality we needed to address nutrient movement via surface water, near-surface water, subsurface water, and stream water. We sampled surface water with surface water canisters, near-surface water with ionic exchange membranes (IEM's), subsurface water with lysimeters, and stream water with grab samples. Surface water canisters, IEM's, and lysimeters were utilized between the intermittent stream and SMZ dripline; IEM's and lysimeters were also utilized within the fertilized subwatershed; and grab samples were collected in the stream protected by the SMZ (figure 4).

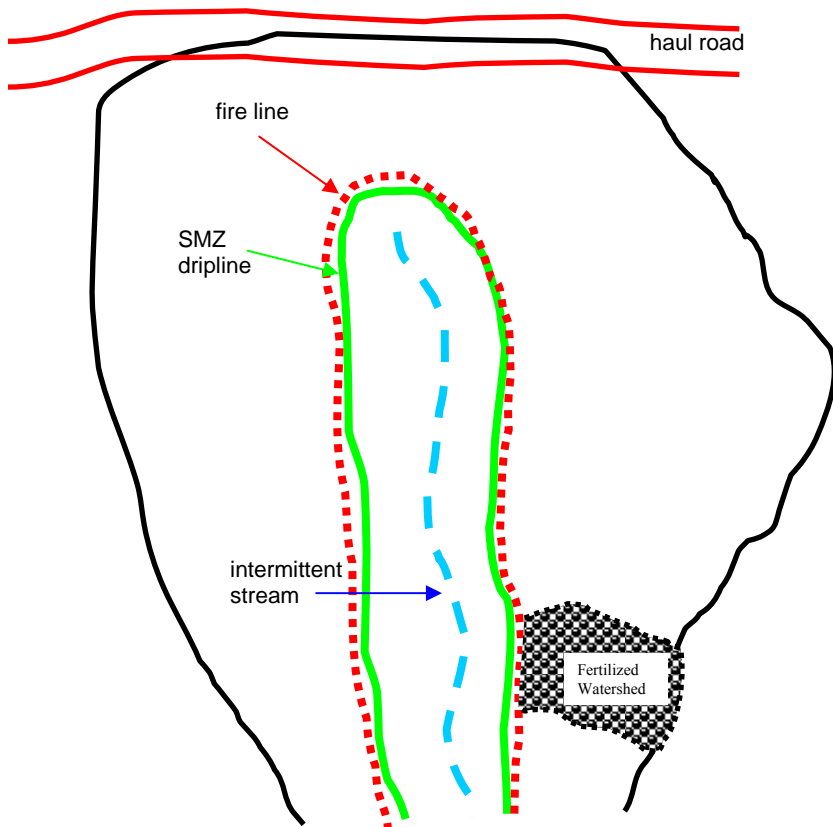


Figure 4. Diagram of typical ephemeral/fertilized watershed location in relation to study SMZ and stream location.

Surface Water Sampling with Canisters: Field Methods

We constructed surface water canisters (Los Alamos National Laboratory, 2008; NYE County Nuclear Waste Repository Project Office, 2008) (figure 5). Materials for one sampler included a 7.62cm diameter PVC end cap, 20cm piece of 7.62cm diameter PVC, a 2.54cm piece of 3.81cm diameter PVC, two 7.62cm to 3.81cm PVC couplings, PVC cement, a hockey ball, and a plastic sink drain strainer. We cemented the end cap to the piece of 20cm PVC. Likewise, we placed cement on the 2.54cm PVC and inserted the 3.81cm diameter ends of both couplings to opposing ends. All components were acid washed in ten percent HCl solution. First, we rinsed both canister ends, the capped end and coupling end, with deionized (DI) water to remove loose contaminants and then

placed them in the acid bath to soak for at least five minutes. Then, we triple rinsed with DI water and set aside to dry. After all the samplers were washed the procedure was repeated for the hockey balls and sink strainers. Once all components were dried the sampler was assembled. A plastic hockey ball was placed in the 20cm piece of PVC with the cap attached on the opposing end. The hockey ball acted as a float to stop water movement in and out of the sampler after filling. Next, one of the two couplings, which are connected by the 3.81cm diameter end, was inserted over the open end of the 20cm piece of PVC (figure 5). Finally, the sink drain strainer was placed in the open end of the sampler to prevent debris from entering during installation and sampling.

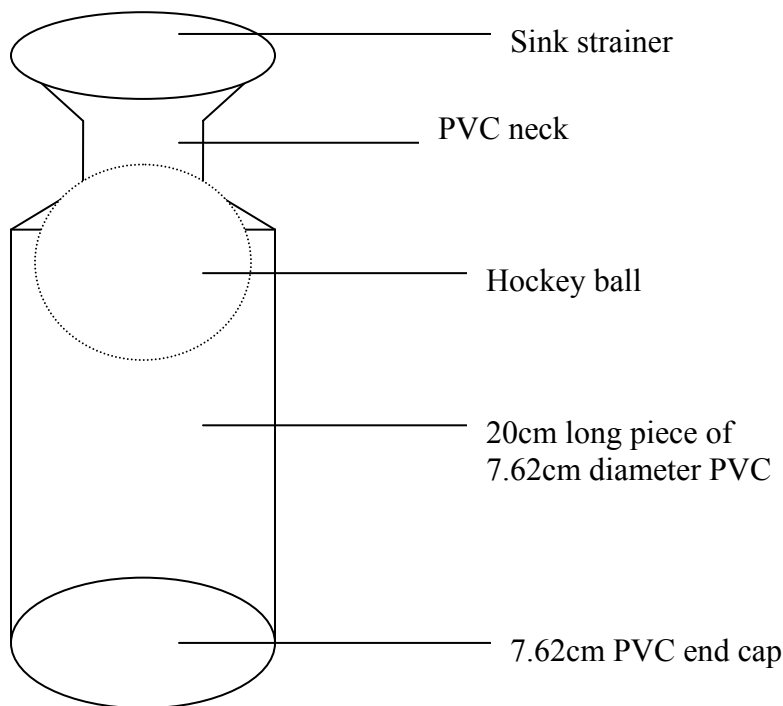


Figure 5. See-through schematic of surface water sampling canister utilized for measuring overland surface runoff.

Two surface water samplers were placed in the riparian area of each study sub-watershed. One was placed near a set of lysimeters near the SMZ dripline. The second

canister was placed with the set of lysimeters near the stream. Furthermore, a control was conducted in a neighboring unfertilized sub-watershed in the same fashion, one sampler at the SMZ dripline and a second close to the stream. Each site contained two samplers in the study sub-watershed and one or two in the control depending on whether topography permitted sampling near the stream for a total of three or four samplers per replication for every SMZ treatment (figure 6).

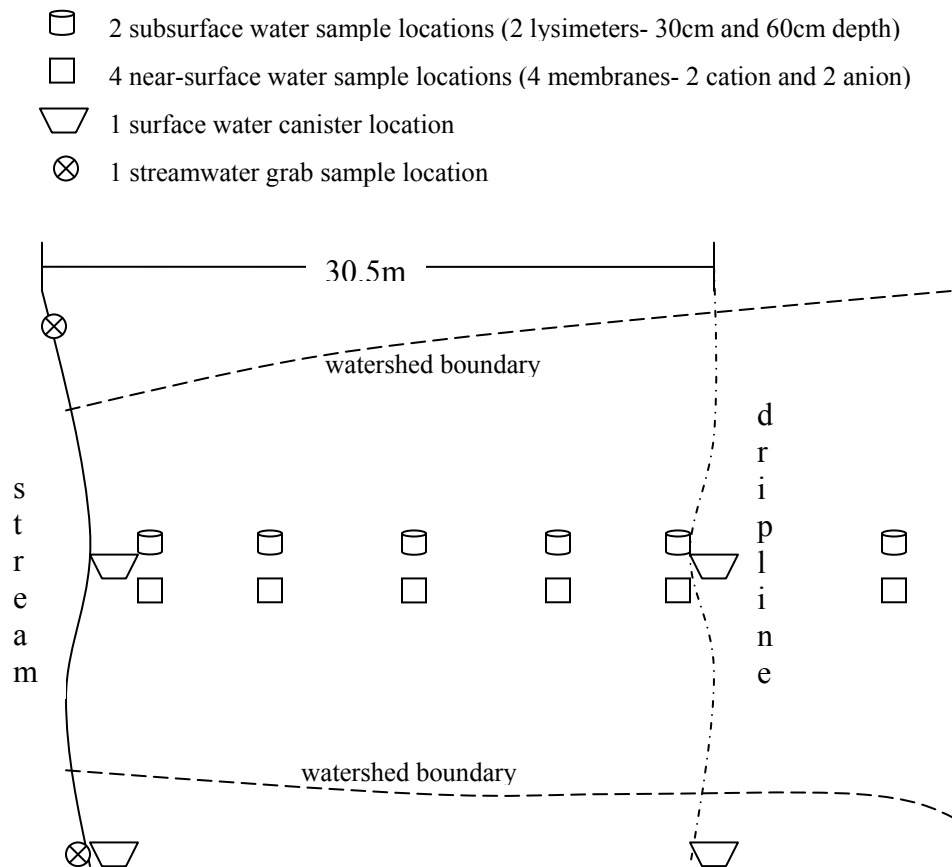


Figure 6. Diagram of typical lysimeter, ionic membrane, surface water sampler, and grab-sample placement/design in a 30.5m SMZ.

Surface water samplers were installed as vertically as possible in the ground with a soil auger and drain tile spade. Small pieces of tarpaulin (tarp) were strung less than one meter above the samplers to prevent direct rainfall and leaf runoff from entering the

canister. Surface water samples were collected and canisters completely emptied every two to three weeks using a long rubber hose, flask, and pump. The amount of water sample within the canister was also recorded. Two sub-samples from each canister were frozen in 20 mL scintillation vials until further analysis could be completed. Some nitrogen degradation in the samples was expected, but results regarding relative changes in concentration were still expected.

Near-surface Water Sampling with Ionics Exchange Membranes (IEM's): Field Methods

Cation and anion transfer membranes (Cooperband and Logan, 1994; Subler et al., 1995) were ordered from Ionics, a segment of GE Water and Process Technologies. These 45.7cm x 101.6cm (18"x 40") sheets were cut into 6.35cm x 6.35cm squares (6.25 sq. inches or 40.32 sq cm) and rinsed in DI water to remove packaging gel. Groups of twenty membranes were placed in plastic Ziploc® containers that were 2/3 full of DI water. Containers were then placed on a shaking machine for five minutes. The contaminated water in the Ziploc® containers was drained and the process repeated with a five percent HCl acid bath. Membranes spent five minutes being shaken in the acid bath, then the acid was drained and the process repeated three times using clean DI water. Finally, the membranes were placed in a carboy that held eight liters of one M NaCl solution to charge. Membranes were charged for no less than 24 hours before being placed in the field.

Membranes (6.35cm x 6.35cm) were installed systematically across each SMZ (figure 6). At each position (clearcut, SMZ dripline, and streamside) membranes were installed in sets of four. One cation and one anion membrane were inserted under the O horizon and one cation and one anion membrane were inserted in the A or top of the B

horizon (1-10cm below the soil surface) by creating a slit in the soil using a gardening trowel. Membranes were placed as flat as possible to minimize the chance for preferential flow. Before the membranes were placed in the field they were rinsed with DI water to remove excess NaCl solution. Due to saturation potential concern, membranes were exchanged every two weeks for the first six weeks following fertilization, every three weeks for the next six weeks, and then approximately every four weeks for the remainder of the study. Time between membrane exchanges was lengthened since movement of fertilizer nutrients across the membrane's surface was expected to decrease with time from fertilization. The number of membranes installed in each SMZ treatment was as follows:

7.6m SMZ Treatment – 12 membranes per replication
(3 positions x 2 depths x 2 membranes types)

15.2m SMZ Treatment – 12 membranes per replication
(3 positions x 2 depths x 2 membranes types)

Thinned 15.2m SMZ Treatment – 20 membranes per replication
(5 positions x 2 depths x 2 membranes types)

30.5m SMZ Treatment – 24 membranes per replication
(6 positions x 2 depths x 2 membranes types)

Subsurface Water Sampling with Lysimeters: Field Methods

Lysimeters (Soil Moisture Equipment Corp., 1999) were constructed to sample subsurface water. One-bar porous cups were glued to a 60cm piece of 5.08cm diameter PVC pipe and the outside seam between the cup and PVC were coated with a thin layer of epoxy to enable the lysimeter to hold pressure. The top of the lysimeter was fitted with a size ten, two-hole stopper. One hole housed a sample 5mm diameter glass tube that extended from the bottom of the lysimeter to about 5cm above the stopper. The

other hole housed a shorter glass tube that was used to insert air and pressurize the lysimeter. The tops of both glass tubes were fitted with a piece of black rubber tubing and connected to one another by inserting opposing ends of a single glass rod. In theory, after pressurizing the lysimeter, the glass rod prevented air from leaking out of the lysimeter.

Each lysimeter was sterilized using a ten percent HCl acid solution. The cup-end of the lysimeter was placed in the acid bath and the lysimeter was charged to fifty centibars of pressure for approximately five minutes. The ten percent HCl solution was then extracted from the lysimeter through the glassware and rubber hosing in order to disinfect the entire apparatus. This procedure was repeated five times for each lysimeter using clean DI water to remove any HCl residue from the lysimeter. Replacement glassware and rubber hosing was cleaned using a squirt bottle of 25% HCl acid solution and triple rinsed from each end with DI water.

Lysimeters were used to pull sub-surface water periodically to determine peak and average nutrient concentrations. Lysimeters were placed in pairs at depths of 30cm and 60cm (or to bedrock where encountered within 60cm) within the riparian area below the test sub-watershed. The number of lysimeters installed in each SMZ treatment was as follows:

7.6m SMZ Treatment - 6 lysimeters per replication
(3 positions x 2 depths)

15.2m SMZ Treatment - 6 lysimeters per replication
(3 positions x 2 depths)

Thinned 15.2m SMZ Treatment – 10 lysimeters per replication
(5 positions x 2 depths)

30.5m SMZ Treatment – 12 lysimeters per replication
(6 positions x 2 depths)

Each SMZ treatment had a pair of lysimeters placed approximately one meter from the main stream and another pair at the SMZ dripline. The thinned 15.2m SMZ had thinned corridors and non-thinned areas within the same SMZ and share the same fertilized area. The 30.5m SMZ had lysimeter pairs placed at symmetrically positioned intermediate points (ideally 7.6m, 15.2m, and 22.9m from the dripline) between the main stream and SMZ dripline (figure 6). All the SMZ treatments included positioning one pair of lysimeters in the fertilized area approximately 15.2 meters (50 feet) from the SMZ dripline. This allowed subsurface water to be sampled before it reached the filtered area. Groundwater samples were collected from lysimeters with an irrometer style vacuum pump into scintillation vials. Samples were originally scheduled to be collected approximately once a month for twelve months following fertilization, but lack of rainfall dictated less frequent sampling. Samples were promptly frozen in 20 mL scintillation vials until laboratory analysis could be conducted.

In-Stream Sampling with Grab Samples: Field Methods

Stream water grab-samples (U.S. Department of Education, 1981; Danielson, 2004) were taken above and below treatment areas to determine whether nutrients applied to the treatment area were reaching the stream and to ensure that our other sampling methods were adequate for monitoring nutrient movement. Stream water grab samples were collected directly from the main stream approximately 20m above the fertilized watershed and 20m below the ephemeral drain outlet (figure 6). A scintillation vial was dipped in the stream where water was moving and samples were collected from the same location each time. The water samples were frozen until lab analysis for nitrate, ammonium, and ortho-phosphate could be performed.

Laboratory Analysis

Water samples collected from surface canisters (surface water), lysimeters (subsurface water), and in-stream (stream water) locations above and below the studied watershed were filtered using Whatman 42 qualitative filter strips and frozen until subsequent processing on an autoanalyzer³ (SEAL, Mequon, WI) for nitrate, ammonium, and ortho-phosphate. After membranes (near-surface water) were removed from the field they were returned to lab and brushed clean of any soil particles or organic material before being individually placed in centrifuge tubes. Twenty-five mL of one M KCl solution were added to each centrifuge tube which was covered with parafilm and capped. The tubes were shaken on each side for thirty minutes before the supernatant was filtered into 20 mL scintillation vials using Whatman Grade Two Qualitative Grade Circles and Sheets. Finally, the vials were placed in a freezer for later analysis. The membranes were then cleaned with DI water to remove any remaining soil or organic matter. The process of one five-minute interval of DI water, one five-minute interval of HCl acid solution, and three five-minute intervals of DI water in Ziploc® containers on the shaker was repeated before the membranes were returned to the one M NaCl solution to be charged. Potassium chloride extractions from the Ionics exchange membranes were analyzed using a TRAACS 2000 auto-analyzer (Bran and Luebbe, Buffalo Grove, IL). All nutrient concentrations provided are true machine values and were not modified based on detection limits of approximately 0.02 or 0.035 mg/l (depending on which machine was used).

Statistical Design

The experiment was arranged as a completely randomized design with three replications of the four SMZ treatments. The SMZ treatments consisted of a 7.6m SMZ, 15.2m SMZ, thinned 15.2m SMZ, and 30.5m wide SMZ. Some data, such as the lysimeter data, interpreted the location distances from the stream within the context as a split block arrangement within a completely randomized design. Periodic measures, such as water samples, were analyzed using the repeated measures technique. Analysis of Variance (ANOVA) testing was utilized on surface water, near-surface water, and stream water testing methods. For stream water samples, nutrient values in the upstream position were subtracted from values in the downstream position and resulting values were analyzed using ANOVA techniques. Unfortunately, sampling dates with baseflow above and below fertilization were so rare in the thinned 15.2m SMZ treatment that this portion of the dataset was deemed too incomplete for analysis. Trends in subsurface water nutrient concentrations were explored with linear regression (Steel and Torrie, 1980; Gomez and Gomez, 1984; British Columbia Ministry of Forestry, 1995). Analysis of variance was not used for the subsurface water samples because of the large number of missing values in this dataset. Regression analysis still allowed us to explore for relationships between nutrient concentrations and SMZ treatments, positions in the SMZ, and sample dates.

These methods and statistical designs were used to accept or reject the null hypothesis that differences in SMZ width do not affect applied fertilizer from entering the stream. The experimental study was aimed at establishing a cause-and-effect relationship

between SMZ width and nutrient movement in surface and sub-surface water flow patterns across the SMZ.

Chapter 4: Results and Discussion

Rainfall

Nutrient movement to streams in forested watersheds is dependent upon water transport of ions downslope. Soil moisture and water movement in forested watersheds are dependent upon multiple factors including watershed size, soil properties, vegetation, stand conditions, management practices, topography, and weather. Our sites consisted of three-year-old loblolly pine stands having Chewacla, Appling, and/or Cecil soils typical of the piedmont, were 0.2-1.4 ha in size, and had slopes from 5-30%. Following fertilization of the study areas in mid-July of 2007, the central region of Virginia experienced a drought that lasted much of the study period. Average mean temperatures were near average while rainfall events during the study period were less frequent than usual (figures 7 and 8). Typical cumulative rainfall for the 15 months monitored is 158.5cm, but our watersheds only averaged 97.2cm of precipitation. Furthermore, rainfall was extremely low in the month immediately after fertilization when higher levels of nutrient movement are expected. Relationships between nutrient fluxes recorded by the various nutrient sampling methods and rainfall will become evident as each method is discussed.

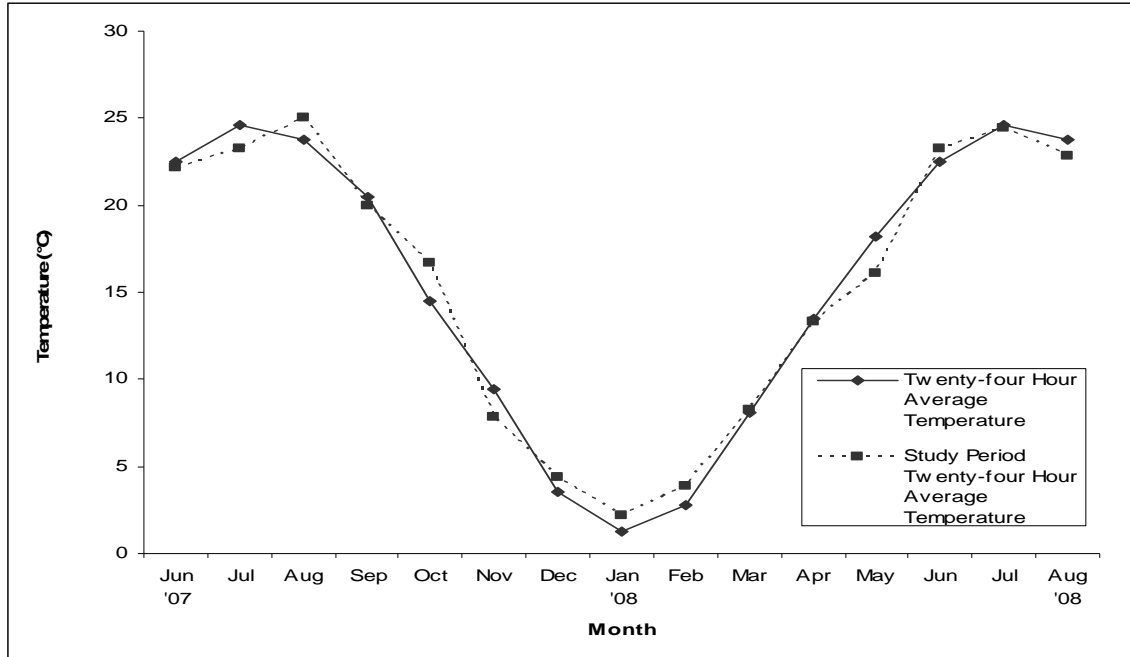


Figure 7. Long-term twenty-four hour average temperature (°C) (recorded from 1961 to 1990) and actual twenty-four hour average temperature during study period for Charlottesville, Virginia. The weather station is approximately 65km from the furthest study site (Weather, 2009; World, 2009). (www.wunderground.com and www.worldclimate.com).

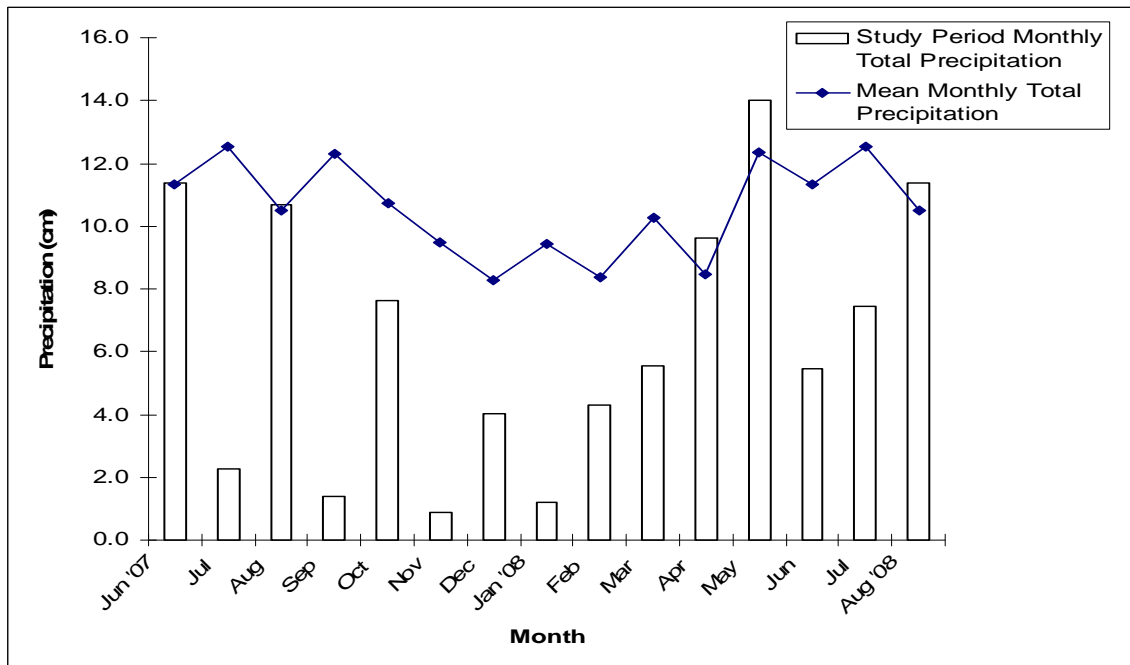


Figure 8. Long-term average monthly total precipitation (cm) (records available from 1973 to 2006) and actual monthly total precipitation during study period for Charlottesville, Virginia. The weather station is approximately 65km from the furthest study site (Weather, 2009). (www.wunderground.com).

SMZ Treatment Effects on Nitrate

Surface Water

Surface water collection via canisters was uneven across sites due to variability in rainfall intensity and duration, surface flow movement, and the sampling position of the canisters. Therefore, the surface canister dataset for any given date may not be complete. In order to have an overall study-long dataset of sufficient sample size, two or three consecutive sampling dates were combined and nutrient levels averaged. The combinations generated a dataset with fewer missing values for five sampling “periods” (table 1).

Table 1. Sampling dates combined to make five sampling periods for surface water analysis.

Period #	Period Name	Sampling Dates
1	Pre-fertilization	6/21/2007, 7/5/2007, 7/23/2007
2	First Month Post-fertilization	8/2/2007, 8/16/2007, 8/30/2007
3	Fall of 2007	9/27/2007, 10/30/2007
4	Winter of 2007	11/18/2007, 12/21/2007
5	Spring of 2008	4/11/2008, 5/7/2008

Results from ANOVA tests were performed on surface water nitrate, ammonium, total inorganic nitrogen, and ortho-phosphate by period for SMZ treatment effects, position effects, and SMZ treatment*position interactions (table 2).

Table 2. Statistical p-values for surface water nitrate, ammonium, total inorganic nitrogen, and ortho-phosphate at five periods (pre-fertilization, first month following fertilization, fall 2007, winter 2007, and spring 2008) for each model effect. Significant p-values at the 0.05 alpha level are highlighted with a darker shade than those only significant at the 0.10 alpha level.

Model Effect	Period	Nutrient			
		Nitrate	Ammonium	Total Inorganic Nitrogen	Ortho-phosphate
Treatment	<i>Pre-Fert</i>	0.961	0.368	0.368	0.368
	<i>Post-Fert (1 month)</i>	0.958	0.888	0.888	0.976
	<i>Fall 2007</i>	0.492	0.090	0.090	0.336
	<i>Winter 2007</i>	0.358	0.749	0.749	0.858
	<i>Spring 2008</i>	0.978	0.102	0.103	0.078
Position	<i>Pre-Fert</i>	0.177	0.337	0.338	0.189
	<i>Post-Fert (1 month)</i>	0.421	0.408	0.408	0.267
	<i>Fall 2007</i>	0.733	0.101	0.100	0.209
	<i>Winter 2007</i>	0.004	0.382	0.384	0.521
	<i>Spring 2008</i>	0.113	0.179	0.171	0.108
Treatment*Position	<i>Pre-Fert</i>	0.126	0.205	0.205	0.166
	<i>Post-Fert (1 month)</i>	0.436	0.350	0.350	0.422
	<i>Fall 2007</i>	0.654	0.131	0.131	0.217
	<i>Winter 2007</i>	0.005	0.672	0.672	0.628
	<i>Spring 2008</i>	0.187	0.118	0.119	0.075

Overall, very few surface water sampling periods had any significant effects. Nitrate levels had a significant sampling position and sampling position*treatment interaction for the winter 2007 sampling period. Ammonium was significant only once for SMZ treatment in the fall 2007 sampling period. Total inorganic nitrogen had a significant treatment and position effect in the fall of 2007. Ortho-phosphate in the spring 2008 sampling period had a significant treatment and position effect.

Surface water nitrate levels immediately following fertilization and during the fall period were not affected by SMZ treatment, position in the SMZ, or SMZ treatment*position interaction. However, nitrate levels in the winter period were significantly affected by SMZ position ($p = 0.004$) and SMZ treatment*position ($p =$

0.005) (table 2). The statistical difference in the winter period for surface water nitrate is mostly due to the elevated levels of nitrate in several of the control positions (figure 9).

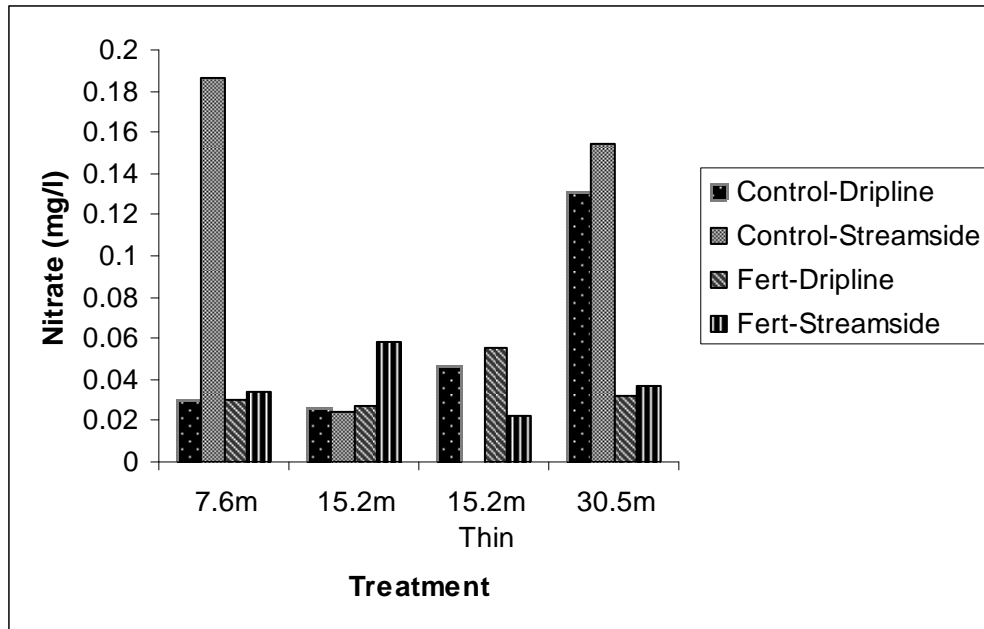


Figure 9. Least-square means surface water nitrate levels (mg/l) as affected by SMZ position and width during the winter period sampling dates (11/18/07 and 12/21/07).

Since the elevations in nitrate levels were in control areas, statistical differences were due to natural variance of nitrate in the ecosystem or activities associated with local road networks rather than fertilizer movement. Furthermore, all average nitrate levels were less than 0.2 mg/l. Nitrate levels only reached 0.9 mg/l or higher in five instances over the entire study period (all on the April 11, 2008 sample date) and were never higher than 4.5 mg/l. Nitrate levels never reached above 0.4 mg/l in the approximately 400 other surface water samples (figure 10).

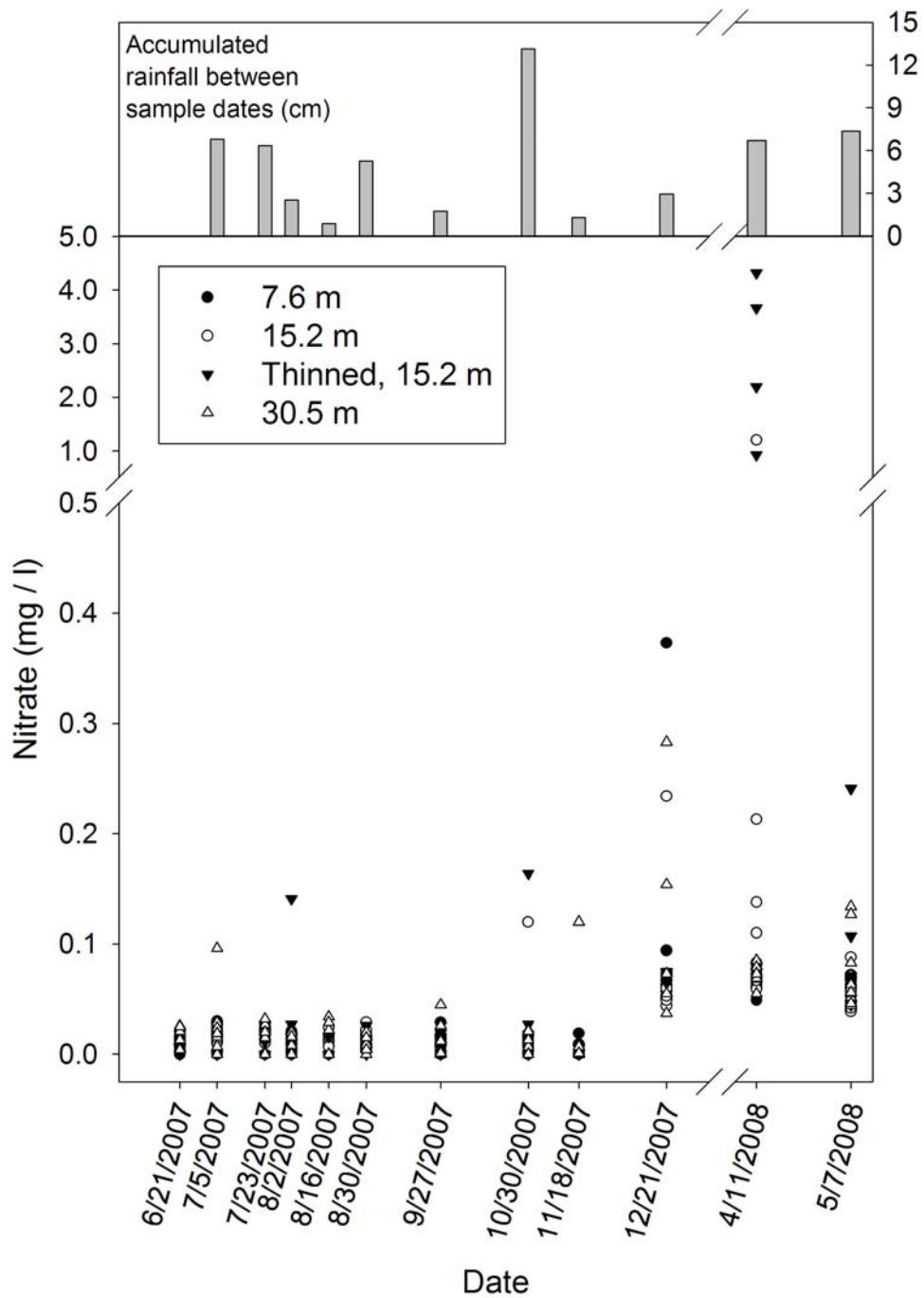


Figure 10. Individual nitrate values (mg/l) for surface water collected at all positions over the entire study period including accumulated rainfall (cm) between each sample date. Samples were not collected from January to March of 2008.

Averaged over the entire study period, nitrate levels showed little change in overland water flow from the SMZ dripline to the stream in either the control or fertilized area. Low average nitrate levels (<0.3 mg/l) for surface water at all canister positions (control-SMZ dripline, control-streamside, fertilized-SMZ dripline, fertilized-streamside) in all SMZ treatments over the entire study period suggest that either nitrate is degrading in the surface canisters from the time the water is trapped to the time it is collected and/or there is extremely low movement of nitrate across the forest floor. Typically, samples should be analyzed as soon as possible and refrigerated for no more than two days to preserve original nitrate levels (Franson, 2005). Otherwise, anaerobic conditions could cause high rates of denitrification (Brady and Weil, 2000). Despite a closing mechanism employed in the surface canisters to seal in the water and keep it cool, nitrate loss to the atmosphere is certainly still possible. Overland flow samples were usually collected from surface canisters within one week of a rainfall event. Possibly, however, water may have been in the canisters up to 20 days.

Near-surface Water

Nutrient transport data via near-surface water flow were analyzed using ANOVA techniques. The position effect was significant for nitrate ($p = <0.001$), ammonium ($p = <0.001$), and total inorganic nitrogen ($p = <0.001$) so the ANOVA was rerun so statistical significance for the other model effects could be determined by position (table 3).

Table 3. Statistical p-values for near-surface water nitrate, ammonium, and total inorganic nitrogen at three positions (clearcut, SMZ dripline, and streamside) for each model effect. Significant p-values at the 0.05 alpha level are highlighted with a darker shade than those only significant at the 0.10 alpha level.

Effect	Nitrate			Ammonium			Total Inorganic Nitrogen		
	Clearcut	SMZ Dripline	Stream-side	Clearcut	SMZ Dripline	Stream-side	Clearcut	SMZ Dripline	Stream-side
Treatment (Trt)	0.008	0.402	0.592	0.292	0.516	0.480	0.013	0.397	0.652
Depth	0.009	0.066	0.368	0.016	0.008	0.951	0.778	0.135	0.374
Depth*Trt	0.179	0.973	0.546	0.150	0.533	0.090	0.619	0.867	0.523
Date	<0.001	0.004	0.012	<0.001	<0.001	<0.001	<0.001	0.004	0.016
Date*Trt	0.004	0.002	0.168	0.002	0.010	0.361	0.047	0.001	0.136
Date*Depth	0.947	1.000	0.172	0.961	0.970	0.034	0.982	0.999	0.139
Date*Trt*Depth	1.000	1.000	0.146	0.998	0.970	0.655	1.000	1.000	0.220

Many statistically significant effects occurred; however the most consistently significant effects were sampling date and a date*SMZ treatment interaction. All clearcut areas were treated with equal amounts of fertilizer, had similar slopes, and underwent similar land management practices. Interestingly, the SMZ treatment effect alone was significant in the clearcut for near-surface water nitrate ($p = 0.008$). Soils for our specific research site locations were not mapped so whether or not soil differences among sites were the reason for significant differences in near-surface water nitrate in the clearcut could not be determined. Nitrate levels for the SMZ treatment effect were not significant at the SMZ dripline or streamside location (table 3). However, Lowrance (1992) found nitrate in shallow groundwater decreased by a factor of seven to nine in the first 10m of a riparian area below a row-crop field and a factor of two in the next 40m and determined there is high denitrification potential in surface soils at the SMZ edge, but denitrification potential is limited by the lack of nitrate which quickly moves deeper in the soil profile.

Subsurface Water

Subsurface water samples collected from lysimeters were also limited by drought conditions during the study period. Subsurface water samples were collected prior to fertilization in May and June, but samples were not available again until late November,

four months after fertilization. Lysimeters pulled so little water that at a single position the two sampling depths, 30cm and 60cm, were often combined into one sample providing a large enough quantity of water to run through the sampling machine. Therefore, we were unable to explore differences of nutrient concentrations by depth. Because of the incomplete sampling, subsurface samples were analyzed for significant relationships using regression techniques. Regression was conducted for each nutrient over distance from the SMZ dripline by each SMZ treatment. Including date in the regression caused the model to fail so it was removed. A week before the first post-fertilization lysimeter sampling on November 25, 2007, nitrate and ammonium fluxes were identified on the IEM's due to a heavy rainfall. However, only 8 of 98 lysimeter sampling locations produced samples on November 25th and only 19 of 98 lysimeter sampling locations produced samples on December 21st. We suspect that heavy precipitation occurring in late October of 2007 did not recharge groundwater to levels where the tension lysimeters were capable of sampling. Many researchers, including Magill et al. (2000), Schreffler and Sharpe (2003), Magill et al. (2004), and Moore (2008) have had difficulties collecting water samples from lysimeters during dry conditions. It is possible that greater amounts of ions would have been transported via subsurface water flow if adequate rainfall had occurred immediately following fertilization.

Using regression, predicted subsurface water nitrate levels significantly decreased with distance from the clearcut for all treatments ($R^2 = 0.22$ and $p = <0.01$ for the 7.6m treatment; $R^2 = 0.21$ and $p = <0.01$ for the 15.2m treatment; $R^2 = 0.22$ and $p = 0.02$ for the thinned 15.2m treatment; $R^2 = 0.20$ and $p = <0.01$ for the 30.5m treatment) (table 4).

Table 4. Predicted subsurface water nitrate levels (mg/l) over the entire study period for each SMZ treatment at sampled distances from the SMZ dripline.

Treatment	Position		
	Clearcut	Dripline	Streamside
	-----mg/l-----		
7.6m	0.82	0.31	0.05
15.2m	2.68	1.27	0.00
15.2m Thin	7.96	3.91	0.00
30.5m	0.50	0.35	0.04

At the streamside position in all treatments subsurface water nitrate has essentially been removed from the SMZ subsurface water with predicted levels being ≤ 0.05 mg/l in every SMZ treatment. Subsurface water samples indicated that there was a greater level of nitrate found in the fertilized clearcut than in the SMZ. Despite various nitrate levels being found in the clearcuts, predicted nitrate levels decreased from the clearcut to the SMZ dripline before becoming almost non-existent at the streamside positions. Similarly, Jordan et al. (1993) found groundwater nitrate concentrations close to 8 mg/l at the edge of an SMZ adjacent to a corn (*Zea mays L.*) field fell to 0.4 mg/l within a forested SMZ. In the 7.6m and 30.5m SMZ treatment of our study, where lysimeters were located in the SMZ at a distance of 7.6m from the dripline, there was little to no nitrate level predicted. In addition, actual average nitrate levels in streamside subsurface water samples were low for all SMZ treatments (<0.4 mg/l) throughout the study period (table 5).

Table 5. Average streamside subsurface water nitrate levels (mg/l) for each SMZ treatment over the entire study period.

Treatment	Nitrate (mg/l)
7.6m	0.119
15.2m	0.287
15.2m Thin	0.377
30.5m	0.099

Stream Water

Drought conditions also caused dry stream channels for about half the study sites throughout the duration of the study. Available stream water samples and ANOVA techniques were used to analyze nutrient transport via stream water flow (table 6). Few effects were significant. Nitrate was significantly affected by SMZ treatment and date and ortho-phosphate was affected by SMZ treatment.

Table 6. Statistical p-values for differences (mg/l downstream - mg/l upstream) of stream water nitrate, ammonium, total inorganic nitrogen, and ortho-phosphate for each model effect. Significant p-values at the 0.05 alpha level are highlighted with a darker shade than those only significant at the 0.10 alpha level.

Effect	Nutrient			
	Nitrate	Ammonium	Total Inorganic Nitrogen	Ortho-phosphate
Treatment	0.039	0.133	0.462	<0.001
Date	0.069	0.468	0.573	0.984
Treatment*Date	0.910	0.840	0.864	0.488

SMZ treatment significantly influenced stream water nitrate values ($p = 0.039$) (table 6).

Although low values are barely above the 0.02 mg/l detection limit, average nitrate increased downstream of the fertilized area and this increase was greater in the 7.6m SMZ treatment than in the 30.5m SMZ treatment (table 7).

Table 7. Average nitrate difference (mg/l downstream- mg/l upstream) in stream samples for each SMZ treatment over the entire study period. Means followed by a different letter differ significantly at the 0.05 alpha level (Tukey's mean separation).

Treatment	Downstream	Upstream	Difference
	-----mg/l-----		
7.6m	0.0428	0.0313	0.0116a
15.2m	0.0462	0.0360	0.0102ab
30.5m	0.0362	0.0336	0.0026b

Downstream and upstream differences are small and average nitrate levels never exceeded 0.05 mg/l (table 7). A water budget was not generated for the fertilized watershed so the actual dilution is unknown.

Nitrate Concentrations over Time

Surface Water

The highest levels of surface water nitrate (1.0-5.0 mg/l) were detected on April 11, 2008 (figure 10). Since these high levels occurred in April, nine months after fertilization, they are probably a result of the spring time nutrient flush rather than fertilizer movement. Furthermore, these increased surface water nitrate levels occurred without a drastic increase in rainfall. Drought conditions in August of 2007 may have restricted the ability to detect typical nitrate levels in surface flow immediately following fertilization.

Near-surface Water

Sample date had a large and highly significant effect on near-surface nitrate levels. This was true in the clearcut, at the SMZ dripline, and at the streamside position (table 3, figure 11).

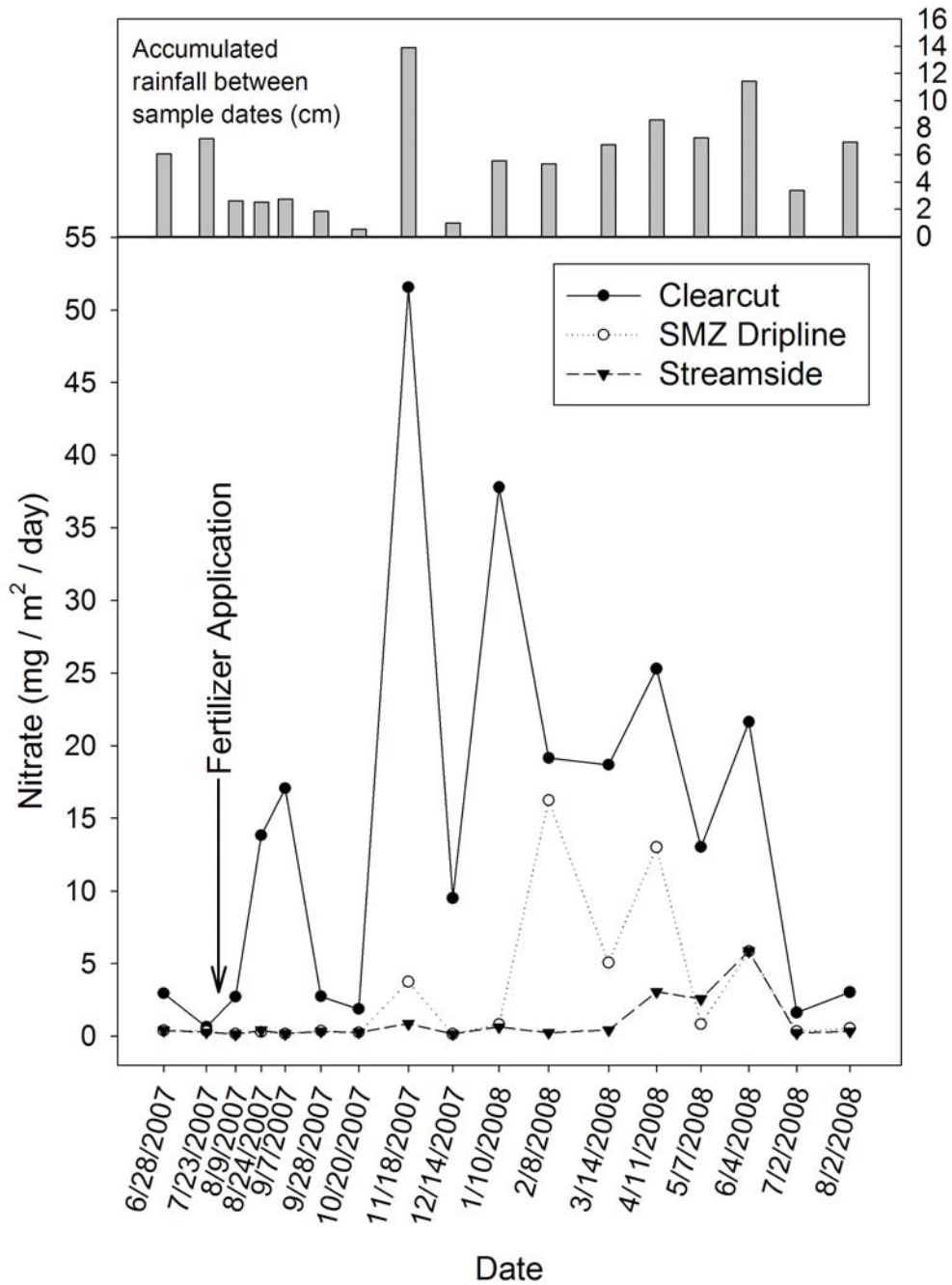


Figure 11. Least-square means for near-surface water nitrate levels ($\text{mg}/\text{m}^2/\text{day}$) as influenced by sampling date and sampling position (clearcut, dripline of SMZ, and streamside) including accumulated rainfall (cm) between each sample date.

Fertilizer was applied on July 23, 2007. Therefore, values up to that date indicate “normal” nutrient levels while values beginning on August 9, 2007 coincide with the first sampling date post-fertilization. Near-surface water nitrate levels spiked slightly following fertilization and greatly in November (mostly in the fertilized clearcut) due to large amounts of rainfall during that sampling period which increased near-surface water flow capable of transporting nitrate.

There was a significant date*SMZ treatment interaction for near-surface water nitrate for the clearcut ($p = 0.004$) and SMZ dripline ($p = 0.002$) (table 3 and 8). Not surprisingly, near-surface water nitrate levels were typically much higher in the clearcut. Levels varied by treatment (despite equal application rates) and date but several dates stand out with very high levels. On November 18, 2007 near-surface nitrate reached as high as $87.1 \text{ mg/m}^2/\text{day}$ in the clearcut of the 15.2m treatment and rates were above $40 \text{ mg/m}^2/\text{day}$ on 7 out of 17 sampling dates. There were only three other dates across the entire study where levels exceeded $40 \text{ mg/m}^2/\text{day}$ in the clearcut. At the SMZ dripline position levels were generally very low in comparison to the clearcut. Levels only exceeded $20 \text{ mg/m}^2/\text{day}$ on two sampling dates and were peculiarly very high ($73.4 \text{ mg/m}^2/\text{day}$) on February 8, 2008 in the 15.2m SMZ treatment. Many of the high levels in either the clearcut at the SMZ dripline followed heavy rainfall, such as on November 18, 2007 (table 8).

Table 8. Least-square means for near-surface water nitrate levels (mg/m²/day) as influenced by the sampling date*SMZ treatment interaction including accumulated rainfall (cm) between each sample date. Letters correspond to a Tukey's mean separation test performed by column at the 0.1 alpha level.

Date	Treatment (Clearcut)				Treatment (SMZ Dripline)				Rainfall
	7.6m	15.2m	15.2m Thin	30.5m	7.6m	15.2m	15.2m Thin	30.5m	
-----mg/m ² /day-----									cm
6/28/2007	3.86b	6.55bcd	1.27b	0.70b	0.44a	0.18b	0.58b	0.28a	6.06
7/23/2007	0.79b	0.88d	0.60b	0.29b	0.41a	0.21b	0.28b	0.48a	7.19
-----Fertilization-----									
8/9/2007	2.85b	2.47d	4.12b	1.38b	0.14a	0.15b	0.20b	0.15a	2.61
8/24/2007	1.67b	45.02abcd	7.90b	0.72b	0.41a	0.23b	0.26b	0.23a	2.52
9/7/2007	0.85b	49.77abcd	10.78b	0.15b	0.18a	0.14b	0.18b	0.15a	2.75
9/28/2007	3.58b	4.37bcd	1.58b	2.00b	0.24a	0.82b	0.27b	0.23a	1.84
10/20/2007	2.21b	1.90d	2.49b	0.87b	0.17a	0.15b	0.28b	0.37a	0.51
11/18/2007	60.99a	87.06a	36.92ab	27.14a	0.12a	13.96ab	0.16b	2.48a	13.89
12/14/2007	8.57b	14.07abcd	10.97b	4.23b	0.15a	0.10b	0.20b	0.09a	0.99
1/10/2008	15.06b	71.78abc	52.40ab	11.92ab	0.55a	0.57b	1.32b	0.54a	5.57
2/8/2008	11.00b	45.97abcd	16.75b	2.86b	1.28a	73.44a	0.39b	0.40a	5.33
3/14/2008	20.09ab	41.02abcd	7.92b	5.70b	5.55b	19.38ab	0.42b	0.43a	6.76
4/11/2008	12.22b	7.52cd	80.79a	0.67b	1.67a	12.79b	24.33a	5.66b	8.58
5/7/2008	12.56b	22.30abcd	6.22b	8.71b	0.22a	1.86b	0.80b	0.43a	7.27
6/4/2008	2.68b	76.04ab	7.33b	0.46b	0.62a	8.71b	10.62ab	0.22a	11.43
7/2/2008	1.73b	1.61d	2.69b	0.45b	0.17a	0.42b	0.34b	0.36a	3.37
8/2/2008	3.00b	2.45d	6.04b	0.62b	0.24a	1.44b	0.24b	0.45a	6.93

Nitrate levels in the clearcut did increase the month following fertilization but not in every SMZ treatment. Least-squared means values shown in table 8 indicate that near-surface water nitrate levels generally increased in the clearcut on November 18, 2007 following a 13.9 cm (5.5 in.) rain event. In our study, the increased amount of nitrate in the springtime in the upper soil and litter layer is often greater than the increases seen immediately following fertilization, especially at the SMZ dripline and near the stream. For example, the least-squared mean nitrate values at the SMZ dripline in the 7.6m SMZ treatment for August 9, August 24, and September 7, 2007 were 0.14, 0.41, and 0.18 mg/m²/day, respectively. However, on March 14, 2008 the least-squared mean nitrate value at the SMZ dripline in the 7.6m SMZ treatment were 5.55 mg/m²/day (table 8).

Sampling depth of near-surface water nitrate was found to have significantly different values in the clearcut ($p = 0.009$) and the SMZ dripline ($p = 0.066$) positions (table 3). The average nitrate level in the clearcut over the duration of the study was 11.8 mg/m²/day in the litter layer and 17.1 mg/m²/day in the A to B soil horizons. At the SMZ dripline average nitrate levels were 2.4 and 3.3 mg/m²/day for the litter layer and A to B soil horizons, respectively. Therefore, overall average near-surface nitrate levels were higher in the A to B soil horizons than in the litter layer.

Subsurface Water

Few subsurface water samples were collected at 30cm and 60cm depths in the clearcut due to lack of soil moisture, but subsurface water collection was more successful at the SMZ dripline and within the SMZ. Nitrate concentrations found in subsurface samples were observed over time (figure 12). Samples collected in the fertilized clearcut were not evenly distributed among SMZ treatments and were removed so that a few samples with elevated nutrient levels would not bias the comparison of treatments over time. For instance, on November 25, 2007 one cutover sample had 9.5 mg/l of nitrate and on February 16, 2008 another cutover sample had 21.8 mg/l of nitrate. Samples with this high of concentration certainly would have raised the average concentrations for each treatment by each date. By removing the clearcut samples in the 15.2m treatment on November 25, 2007 and February 16, 2008 the average nitrate concentration drops from 3.0 and 2.7 mg/l to 0.1 and 1.0 mg/l, respectively. After samples collected in the clearcut were removed, the largest peak in subsurface water nitrate existed in late winter/early spring (February 16, 2008) where it averaged 4.5 mg/l in the thinned 15.2m treatment.

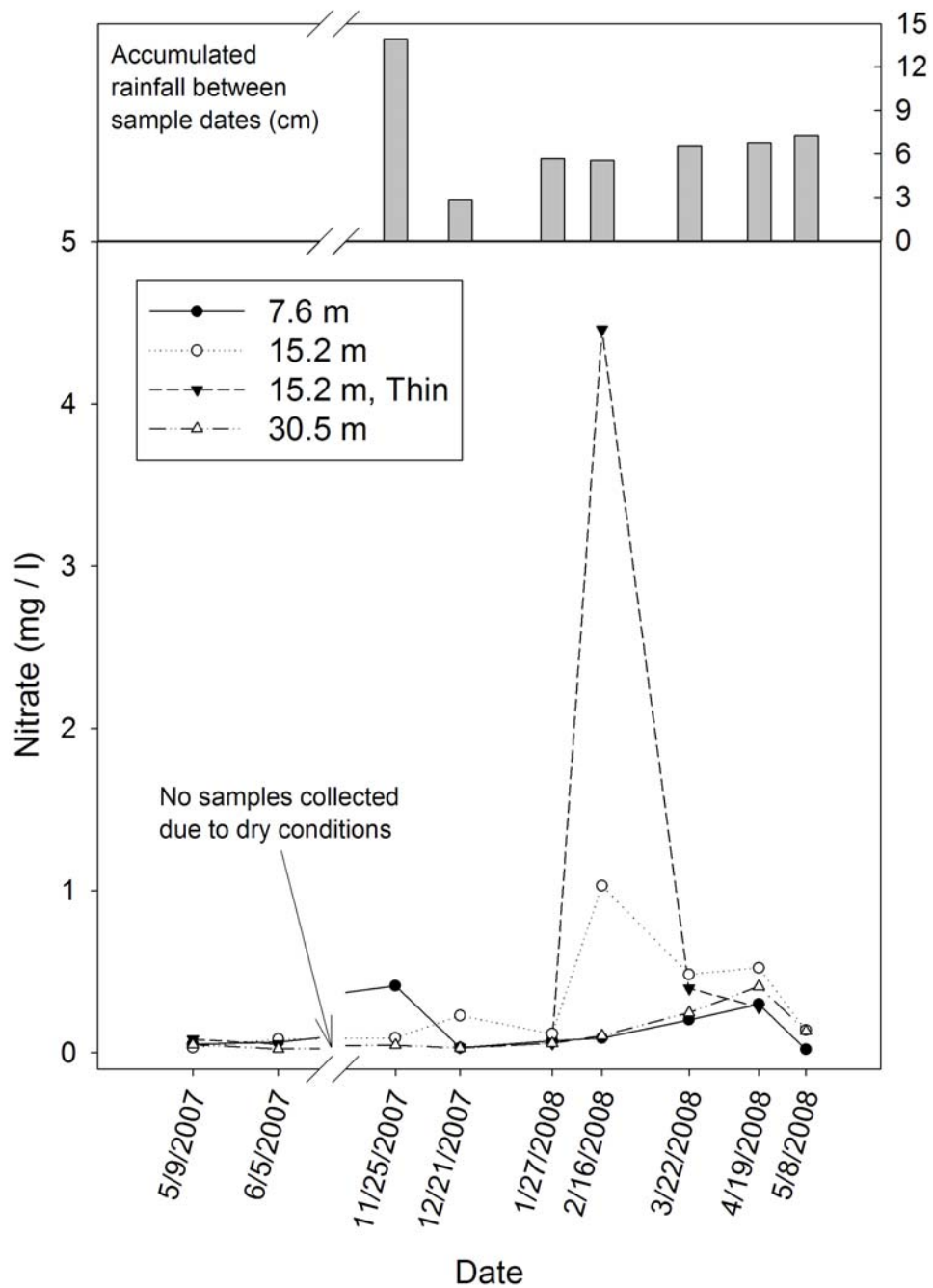


Figure 12. Average subsurface water nitrate levels (mg/l) at all SMZ locations over the sampling dates for each SMZ treatment including accumulated rainfall (cm) between each sample date. Samples collected in clearcut are not included.

Stream Water

Date had a significant effect on stream water nitrate differences ($p = 0.069$) (table

6). There were no apparent unusual spikes in stream water nitrate levels at the downstream position during the study period (figure 13).

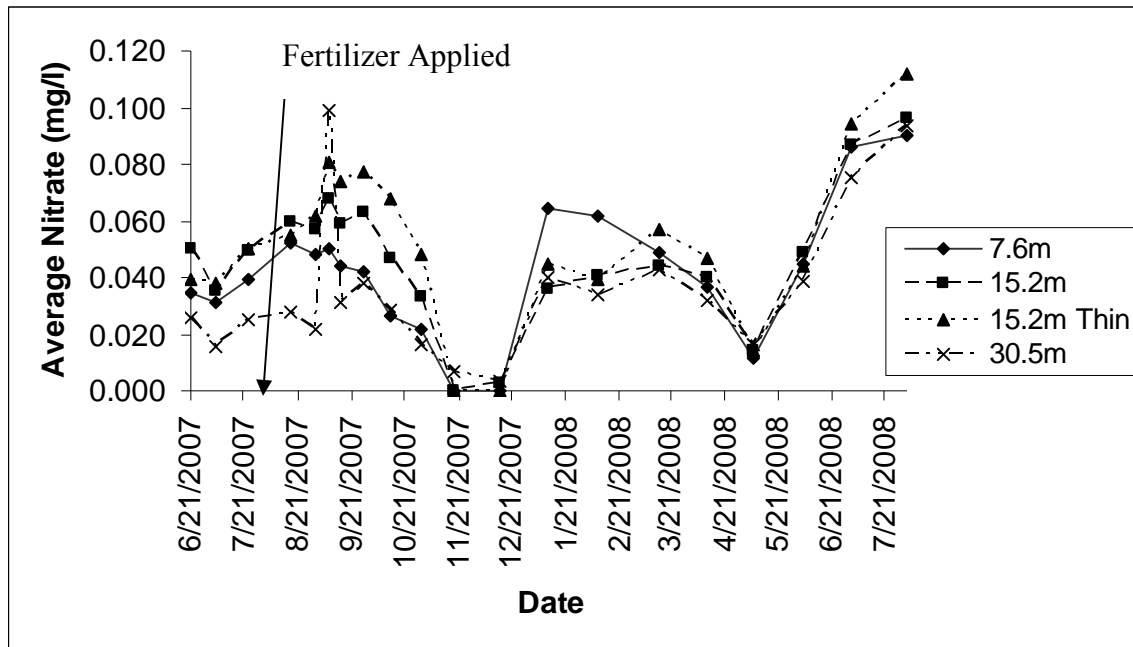


Figure 13. Average downstream nitrate levels (mg/l) in stream water samples for each SMZ treatment over the entire study.

Average stream water nitrate levels did not exceed 0.1 mg/l and did not spike following fertilization on July 23, 2007. Increases in average nitrate levels are very small and do not appear to be higher in streams with narrower SMZ widths. Furthermore, nitrate increased at greater levels almost a year after fertilization than they did immediately following fertilization. Even though a SMZ treatment effect was significant ($p = 0.039$) when upstream and downstream levels were compared, it appears that nitrate levels in stream water are actually dictated almost exclusively by sampling date.

Thinning Effects on Nitrate

Near-surface Water

In the thinned 15.2m treatment we sampled near-surface water nitrate both in a harvested corridor and in a non-thinned portion of this treatment; however, no statistical difference occurred between these sampling locations. For further analysis these two sub-sampling locations were averaged and this average used as the thinned 15.2m experimental unit. A general assumption is that narrower SMZs and thinned SMZs would be less adequate in regards to keeping fertilizer from the stream. If this were the case, nitrogen levels would be highest in the 7.6m and thinned 15.2m SMZ treatment and lower in the non-thinned treatment and lower still in the 30.5m SMZ treatment. However, the highest streamside nitrate levels occurred in the non-thinned 15.2m SMZ treatment due to three outlier points on the same study site. These high levels (36.9, 59.7, and 123.5 mg/m²/day began at the April 2008 sampling date, approximately nine months after fertilization. Therefore, we believe that something abnormal took place (such as an animal dying in the study area) on this location in late March or early April that caused temporary elevated near-surface water nitrate levels at this one location.

Subsurface Water

Average streamside subsurface water nutrient levels were extremely low (<0.4 mg/l) in both the thinned and non-thinned 15.2m SMZ treatment (table 5). Our results indicate that thinning a 15.2m SMZ is adequate for preventing fertilizer induced nitrate fluxes from entering a stream.

SMZ Treatment Effects on Ammonium

Surface Water

Fall surface water ammonium was significantly influenced by SMZ treatment ($p = 0.090$) and position in the SMZ ($p = 0.101$) (table 2 and figure 14). The 30.5m SMZ treatment had significantly higher ammonium than the 7.6m and non-thinned 15.2m SMZ and was greatest overall (figure 14).

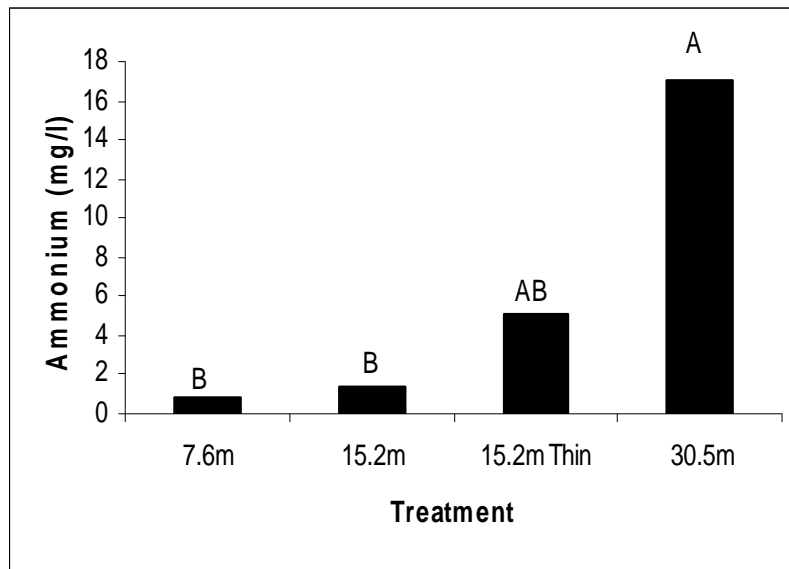


Figure 14. Least-squared means surface water ammonium levels (mg/l) for each SMZ treatment during the fall sampling period (September 27, 2007 and October 30, 2007). Letters correspond to a Tukey's mean separation test performed at the 0.10 alpha level.

The 30.5m SMZ treatment had five data points (out of seventeen) that were abnormally high (>19 mg/l). When these five numbers were removed, the least-squared means falls from 17.0 to 3.6 mg/l but is still significantly different from the other SMZ treatments at the 0.1 alpha level. Similarly, the thinned 15.2m SMZ treatment had two data points (out of eighteen) that were abnormally high (>19 mg/l). When these two numbers were removed the least-squared means dropped from 5.0 mg/l to 2.6 mg/l.

Near-surface Water

When an ANOVA was conducted testing the model effects by position, SMZ treatment did not significantly influence near-surface water ammonium levels. Besides date, the only model effects that were significant at the streamside positions were the depth* SMZ treatment interaction ($p = 0.090$) and the depth*date interaction ($p = 0.034$). Ammonium in the near-surface water was significantly different by sampling depth in the clearcut ($p = 0.016$) and the SMZ dripline ($p = 0.008$) positions (table 3). In the clearcut ammonium levels over the duration of the study averaged $49.9 \text{ mg/m}^2/\text{day}$ in the litter layer and $35.2 \text{ mg/m}^2/\text{day}$ in the A to B soil horizons. Similarly, at the SMZ dripline average ammonium over the duration of the study averaged 2.8 and $2.1 \text{ mg/m}^2/\text{day}$ for the litter layer and A to B soil horizons, respectively. Therefore, overall average near-surface water ammonium levels were higher in the litter layer than in the A to B soil horizons. These findings are opposite to the results for nitrate. One theory regarding these findings is that nitrate, an anion, is more able to leach downward in the soil profile while ammonium, a cation, is less mobile.

Subsurface Water

The pattern of ammonium concentration with distance from the clearcut was explored using regression (figure 15).

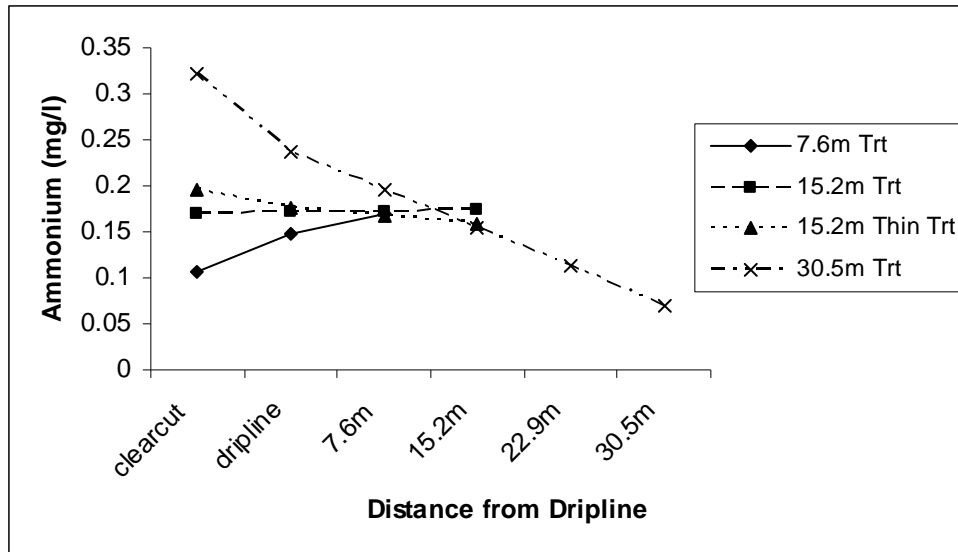


Figure 15. Predicted subsurface water ammonium levels (mg/l) over the entire study period for each SMZ treatment at sampled distances from the SMZ dripline.

A significant pattern was only found for the 30.5m SMZ treatment ($R^2 = 0.02$ and $p = 0.31$ for the 7.6m treatment, $R^2 = <0.01$ and $p = 0.96$ for the 15.2m treatment, $R^2 = 0.01$ and $p = 0.67$ for the thinned 15.2m treatment, and $R^2 = 0.20$ and $p = <0.01$ for the 30.5m treatment). Furthermore, predicted concentrations from the regression were less than 0.35 mg/l regardless of position (figure 15). Average ammonium levels in streamside subsurface water samples across the entire study period were low for all SMZ treatments (<0.2 mg/l) (table 9).

Table 9. Average streamside subsurface water ammonium levels (mg/l) for each SMZ treatment over the entire study period.

Treatment	Ammonium (mg/l)
7.6m	0.171
15.2m	0.198
15.2m Thin	0.140
30.5m	0.060

Ammonium Concentrations over Time

Surface Water

Ammonium levels detected in the surface water sampling canisters were difficult to interpret due to high levels of non-fertilizer nutrient variation in overland water flow. Furthermore, we suspect possible surface water contamination. Though earthworm presence was not recorded we believe that the very high nutrient values found in the 30.5m SMZ treatment may have been caused by earthworm (*Lumbricus terrestris*) activity in the watersheds. At several points early in the study we recall pulling dead earthworms from the canisters with the sample water. The presence of decaying earthworms or other insects coupled with the small quantities of water collected from streamside canisters 30.5m from the SMZ dripline may have biased the data with samples extremely high in nutrient concentration. The high numbers were traced back to two SMZ's dominated by hardwoods. Johnston and Crossley (2002) found that earthworms were abundant in hardwood forests but rare in southern pine forests.

Even when abnormally high data points were removed during the fall season, statistical differences between the 30.5m SMZ treatment and the other SMZ treatments existed. Furthermore, high levels of ammonium were randomly detected in the streamside surface flow canisters throughout the study period (including prior to fertilization), not only immediately after fertilization or heavy rainfall. We suspect that some level of ammonium contamination is present in replications one and two in the 30.5m SMZ treatment since most of the individually high samples came from these two subwatersheds. In addition to the surface canisters trapping earthworms and insects, it is possible that old log decks located at the top of these watersheds may be slowly leaking

nutrients through the clearcut and SMZ. Other researchers, such as Moore (2008) who found increased nitrate values in lysimeter samples, have been suspicious of nutrient inputs from uphill logging decks. Wynn et al. (2000) suspected higher concentrations of nitrate and total nitrogen may have been the result of agricultural activities in the upper part of their study watersheds. However, suspected contamination from log decks was not apparent when sampling near-surface water. Contamination from log decks was also not noticed in the subsurface water data, but few samples were collected from either of the watersheds.

The other unique attribute of the two 30.5m SMZ treatments with high levels of ammonium in surface water was their slope. Replication one had an approximate 30% slope in the SMZ and 15% in the clearcut while replication two had an approximate 30% slope in the SMZ and 8% in the clearcut. The slopes in the fertilized area of these two subwatersheds were typical of the other ten studied subwatersheds. However, these two subwatersheds had the highest SMZ slopes below any two fertilized areas with the next two closest being 21% and 15%. Rivenbark and Jackson (2004) found that steep slopes along with larger contributing areas and greater amounts of bare ground increased the chance for water breakthroughs to occur from the adjacent silvicultural site through the SMZ to the stream channel. SMZ width recommendations based on slope do not differ (and may not even directly exist) widely across the United States because of variable field study results (Lee et al., 2004). However, there is a universal agreement that increased slope (along with soil texture and reduced ground cover) results in increased water velocity and, therefore, requires a wider SMZ to protect streams (VDOF, 2002). Perhaps the two subwatersheds in our study with 30% slopes had overland water flow

velocity great enough to carry a burst of nutrients 30.5m with initial water flow and deposit them in the canisters with minimal water. An increase in water did not mean an increase in nutrients because the “overland water pathway” to the canister may have been wiped clean of nutrients with the initial movement of water. These two subwatersheds averaged approximately 275mL and 775mL of water at the streamside and SMZ dripline, respectively, when rainfall was great enough for surface water flow collection.

Streamside canisters held at least 25mL of water 61% of the times sampled while SMZ dripline canisters held at least 25mL of water 88% of the times sampled. However, the streamside canisters contained more than 250mL of water on only 13% of the collection dates while SMZ dripline canisters contained more than 250mL of water on 70% of the collection dates. The implication is that canisters at the SMZ dripline may have held similar total amounts of nutrients as canisters 30.5m away from the SMZ dripline but were more diluted since more water was typically able to reach them more often.

Near-surface Water

The date of sampling was significant for near-surface water ammonium at the clearcut ($p = <0.001$), SMZ dripline ($p = <0.001$), and streamside positions ($p = <0.001$) (table 3). Near-surface water ammonium levels spiked following fertilization on July 23, 2007 (figure 16) although nitrate levels lagged behind ammonium levels (figure 11). Pratt (2008) noticed a similar lag of nitrate availability in comparison to ammonium following application of biosolids to a loblolly pine plantation in the Virginia piedmont. Ammonium levels again spiked in November (mostly in the fertilized clearcut) due to large amounts of rainfall during that sampling period which increased near-surface water flow capable of transporting ammonium.

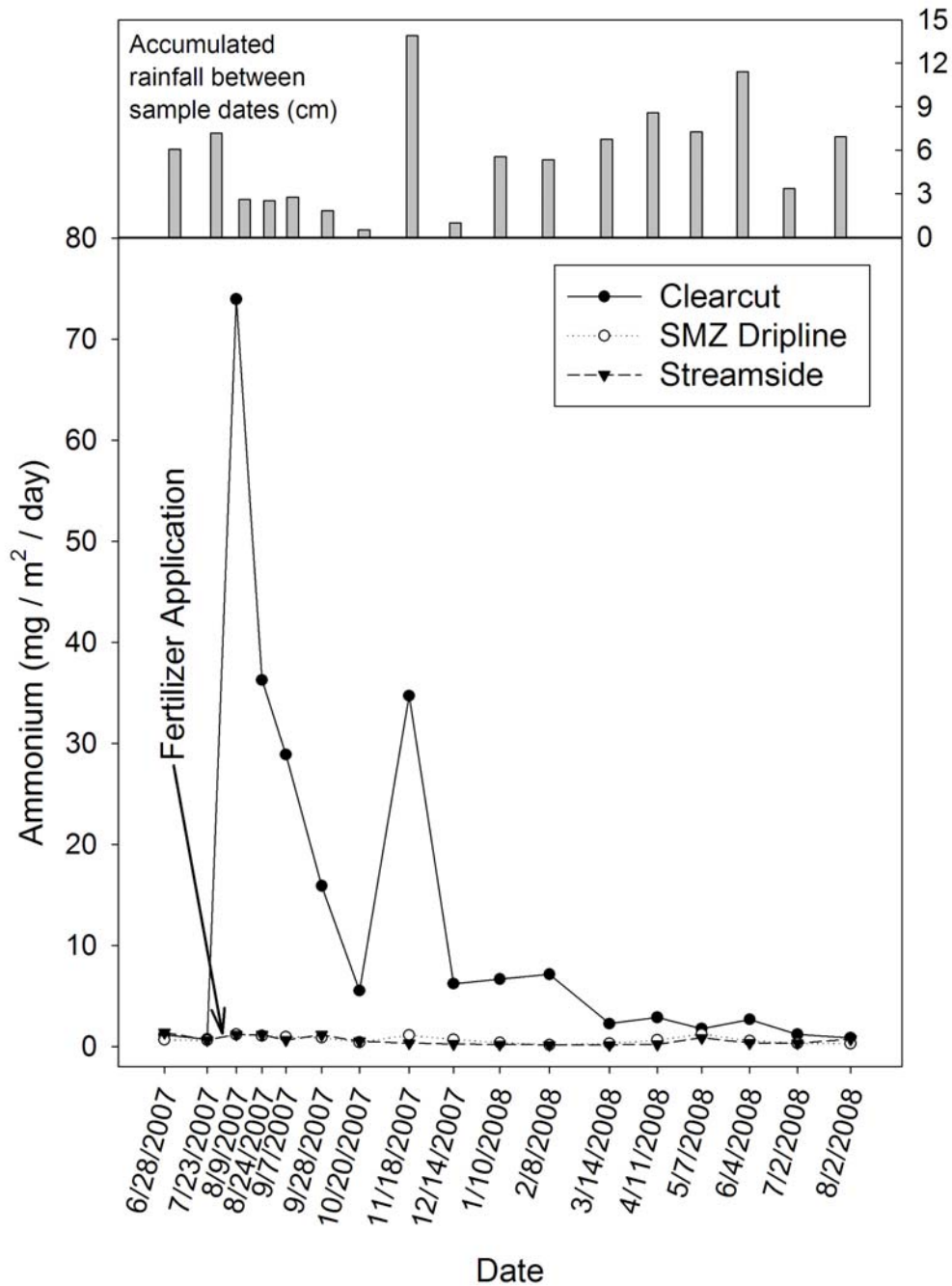


Figure 16. Least-square means for near-surface water ammonium levels ($\text{mg}/\text{m}^2/\text{day}$) as influenced by sampling date and sampling position (clearcut, dripline of SMZ, and streamside) including accumulated rainfall (cm) between each sample date.

There was a significant date*SMZ treatment interaction for near-surface water ammonium at the clearcut ($p = 0.002$) and SMZ dripline ($p = 0.010$) positions (table 3). Ammonium availability in our fertilized clearcuts showed an immediate response to DAP and urea application with significantly increased levels in the clearcut on August 9, 2007 when levels were as high as 114.5 mg/m²/day in the clearcuts of the 15.2m SMZ treatment (table 10). Ammonium levels at the SMZ dripline never exceeded 2.5 mg/m²/day on any sampling date and did not show a significant increase following fertilization.

Table 10. Least-square means for near-surface water ammonium levels (mg/m²/day) as influenced by the sampling date*SMZ treatment interaction including accumulated rainfall (cm) between each sample date. Letters correspond to a Tukey's mean separation test performed by column at the 0.1 alpha level.

Date	Treatment (Clearcut)				Treatment (SMZ Dripline)				Rainfall
	7.6m	15.2m	15.2m Thin	30.5m	7.6m	15.2m	15.2m Thin	30.5m	
	-----mg/m ² /day-----								cm
6/28/2007	0.81c	1.24c	2.20c	0.27b	0.41a	0.53a	0.75b	0.87ab	6.06
7/23/2007	1.04c	0.70c	0.69c	0.53b	0.66a	0.44a	0.53b	0.85ab	7.19
	-----Fertilization-----								
8/9/2007	83.85a	114.48a	88.61a	12.19ab	1.29a	0.84a	0.82b	2.07ab	2.61
8/24/2007	17.41bc	68.04ab	13.57bc	39.77a	0.76a	1.02a	1.37ab	0.97ab	2.52
9/7/2007	18.36bc	25.29bc	42.12b	29.78ab	1.07a	1.10a	0.33b	1.75ab	2.75
9/28/2007	21.82bc	21.55bc	18.58bc	0.27b	0.48a	1.26a	0.70b	1.35ab	1.84
10/20/2007	9.94c	2.99c	7.31c	1.82b	0.29a	0.23a	0.66b	0.39ab	0.51
11/18/2007	55.95ab	25.07bc	42.34b	15.50ab	0.23a	2.33a	0.15b	2.29a	13.89
12/14/2007	8.34c	10.67bc	6.15c	0.45b	1.27a	0.97a	0.53b	0.11b	0.99
1/10/2008	7.12c	9.36bc	5.87c	4.18b	0.16a	0.40a	0.68b	0.11b	5.57
2/8/2008	6.32c	13.19bc	6.54c	2.56b	0.10a	0.39a	0.14b	0.06b	5.33
3/14/2008	0.49c	3.89c	2.09c	1.98b	0.18a	0.63a	0.28b	0.14b	6.76
4/11/2008	5.75c	5.74bc	0.55c	0.42b	0.66a	0.23a	1.02ab	0.27ab	8.58
5/7/2008	0.83c	4.25c	1.42c	0.60b	0.31a	0.66a	2.37a	0.71ab	7.27
6/4/2008	0.80c	7.82bc	0.86c	1.24b	0.25a	0.23a	1.12ab	0.33ab	11.43
7/2/2008	1.52c	0.92c	1.46c	0.87b	0.35a	0.39a	0.36b	0.08b	3.37
8/2/2008	1.06c	0.86c	1.12c	0.39b	0.19a	0.25a	0.17b	0.63ab	6.93

Subsurface Water

As discussed previously, few subsurface water samples were collected at 30cm and 60cm depths in the clearcut due to lack of soil moisture, but subsurface water collection was more successful at the SMZ dripline and within the SMZ. Samples collected in the fertilized clearcut were not evenly distributed among SMZ treatments and were removed so that a few samples with elevated nutrient levels would not bias the comparison of SMZ treatments over time. Average subsurface ammonium concentrations were all below 0.5 mg/l with the exception of November 25, 2009 where concentrations from the 7.6m SMZ averaged 1.18 mg/l (figure 17)

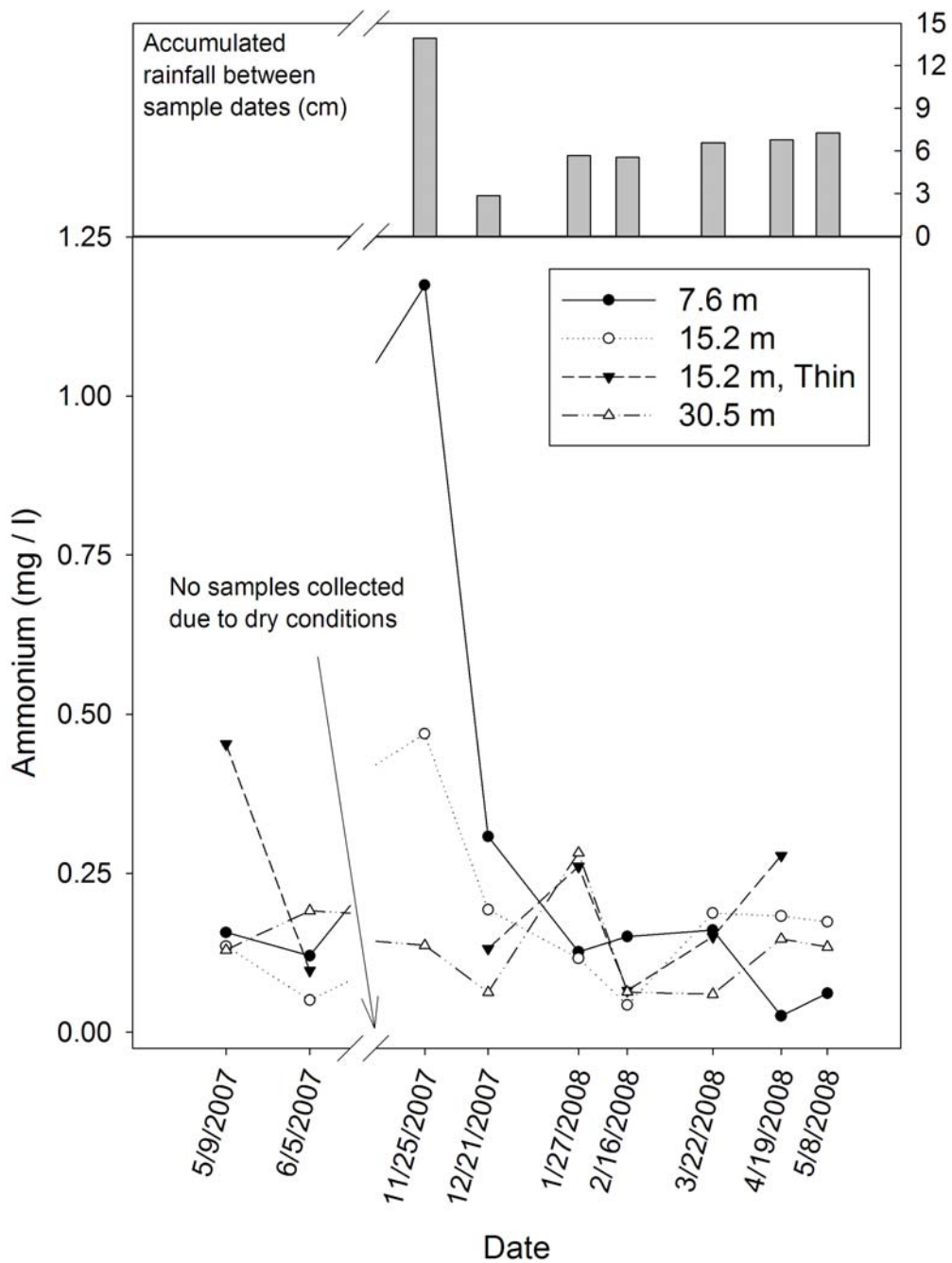


Figure 17. Average subsurface water ammonium levels (mg/l) at all SMZ locations over the sampling dates for each SMZ treatment including accumulated rainfall (cm) between each sample date. Samples collected in clearcut are not included.

Results from near-surface water sampling showed that increased levels of ammonium were certainly present after fertilization in the clearcuts (figure 16). The fact that average ammonium was low (≤ 1.2 mg/l) in riparian subsurface water samples (figure 17) suggests that either (a) ammonium is not readily transported via subsurface flow, (b) ammonium underwent nitrification to nitrate which leached vertically, and/or (c) the few subsurface water samples collected were acquired too long after fertilization had occurred and excess ammonium was long gone from the riparian area. Cations such as ammonium are held tightly by soil particles (Brady and Weil, 2000) so low levels of transport in subsurface flow during a drought year is not surprising. There are many processes affecting ammonium in soils (Vitousek and Melillo, 1979) and nitrification occurs at varying rates based on temperature and soil conditions (Gray and Taylor, 1935; Boswell, 1955; Weber and Gainey, 1962; and Havill et al., 1977). Taylor et al. (1982) found that nitrate production was reduced in summer months and attributed the decline to an exhausted ammonium supply that was utilized by increased populations of soil microbes. Ammonium inputs from fertilizer may have been fixed to clay materials, underwent nitrification, volatilized, or were utilized by plants, but ammonium was not found in subsurface water flow in the SMZ below the fertilized area five months after fertilization.

Thinning Effects on Ammonium

Surface Water

High average surface water ammonium levels in the thinned 15.2m SMZ treatment resulted from 13% of the samples being greater than 10 mg/l. More specifically, immediately after fertilization one streamside sample was 324 mg/l and after a heavy rainfall another streamside sample reached 133 mg/l. These two high

concentrations occurred on the same study site which has a well-defined ephemeral channel that starts in the fertilized area and continues into the SMZ. These high outlier values suggest that ammonium can reach streams protected by a thinned 15.2m SMZ if a long, channeled pathway is available to collect and transport overland water flow from the fertilized area to the stream.

Near-surface Water

Similar to nitrate, there was no statistically significant difference in ammonium levels between the thinned corridors and non-thinned areas of the 15.2m thinned SMZ. On the same research sites Wadl (2008) determined that a thinned 15m buffer did not adversely affect carbon dynamics and stream biota. Kreuzweiser and Capell (2001) suggested that riparian buffer zones may be unnecessary to protect streams from sedimentation in hardwood forests that have 50% of their basal area selectively harvested.

Subsurface Water

Predicted subsurface water ammonium levels from regression analysis were less than 0.2 mg/l for both a thinned and non-thinned 15.2m forested SMZ treatment (figure 15). Lowrance et al. (2000) concluded that timber harvesting in the riparian area has little effect on groundwater nutrient movement toward streams as no significant differences of ammonium levels existed and only slight increases of nitrate at the stream were found. Lowrance et al. (1983) found a dramatic 13-fold increase of stream transported ammonium when a pasture riparian zone was utilized instead of a forest.

SMZ Treatment Effects on Total Inorganic Nitrogen

Surface Water

Total inorganic nitrogen values are the addition of nitrate and ammonium concentrations. The purpose of analyzing total inorganic nitrogen was to discover any possible significant differences among model effects that were not discovered from analyzing nitrate or ammonium individually. Fall surface water total inorganic nitrogen values were significantly influenced by SMZ treatment effect ($p = 0.090$) and SMZ position effect ($p = 0.100$) (table 2). This significant difference was due to abnormally high ammonium levels which were previously discussed.

Near-surface Water

The SMZ treatment effect was significant in the clearcut for near-surface water total inorganic nitrogen ($p = 0.013$). As with nitrate and ammonium, a date*SMZ treatment interaction was significant in the clearcut ($p = 0.047$) and at the SMZ dripline ($p = 0.001$) positions for near-surface water total inorganic nitrogen (table 3).

Results from the ANOVA also indicate there was significant position effect on total inorganic nitrogen. There was an obvious decrease in near-surface total inorganic nitrogen levels throughout the study period between the clearcut and SMZ dripline (table 11). The least-squared means value for total inorganic nitrogen was $27.4 \text{ mg/m}^2/\text{day}$ but significantly lower at $3.8 \text{ mg/m}^2/\text{day}$ at the SMZ dripline. However, there was no significant difference between total inorganic nitrogen levels at the SMZ dripline ($3.8 \text{ mg/m}^2/\text{day}$) and streamside ($1.7 \text{ mg/m}^2/\text{day}$) positions (table 11).

Table 11. Least-squared means for near-surface water nitrogen levels (mg/m²/day) for each position over the entire study period. Letters correspond to a Tukey's mean separation test performed by row at the 0.10 alpha level.

Nutrient	Position p-value	Position		
		Clearcut	SMZ Dripline	Streamside
		-----mg/m ² /day-----		
Nitrate	<0.0001	14.41a	3.06b	1.09b
Ammonium	<0.0001	13.03a	0.76b	0.60b
Total Inorganic Nitrogen	<0.0001	27.44a	3.82b	1.69b

Only baseline total inorganic nitrogen levels seemed to exist at intermediate locations throughout the SMZ. The 30.5m SMZ treatment contained near-surface water sampling points spread symmetrically throughout the SMZ. There was not a consistent decrease in nitrogen levels as greater distance from the SMZ dripline to the stream was achieved (figure 18).

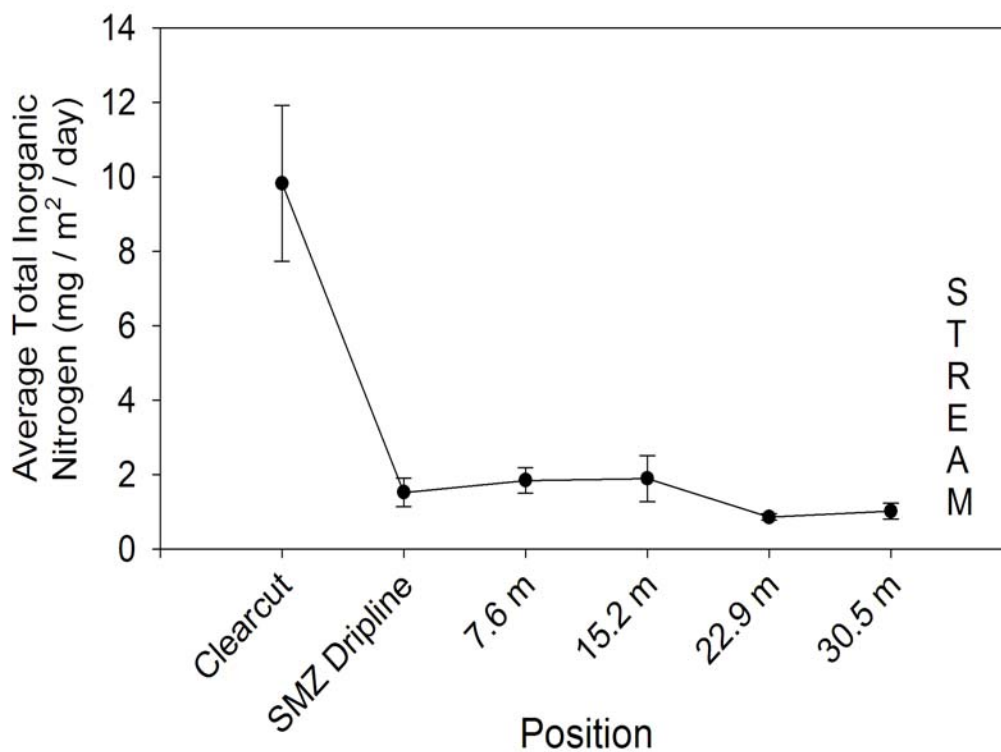


Figure 18. Average near-surface water total inorganic nitrogen levels (mg/m²/day) across the 30.5m SMZ treatment from the dripline to the streamside. The standard error (standard deviation ÷ √sample size) is displayed for the mean at each position.

Data from intermediate points in the 30.5m SMZ treatment did not suggest that nitrogen levels were higher in upslope areas of the SMZ in comparison to downslope areas near the stream. Pratt (2008) found limited lateral nutrient movement in a riparian area following a biosolid application to a loblolly pine stand. In our study, as distance from the SMZ dripline was achieved, we expected continuously decreasing nitrogen values, but they were non-existent. Instead, low, sporadic nutrient levels at the intermediate sampling points indicated that minimal amounts of nitrogen were entering or being mineralized in the SMZ and being transported via water in the litter layer and upper soil layers. Overall, there seems to be no reason to believe that significant nutrient movement was occurring from the dripline through the SMZ in either the litter layer or the A to B soil horizons during dry conditions.

Subsurface Water

Average total inorganic nitrogen levels in streamside subsurface water samples were low and never exceeded 0.6 mg/l for all SMZ treatments (table 12).

Table 12. Average streamside subsurface water total inorganic nitrogen levels (mg/l) for each SMZ treatment over the entire study period.

Treatment	Total Inorganic Nitrogen
	(mg/l)
7.6m	0.289
15.2m	0.484
15.2m Thin	0.517
30.5m	0.159

Nitrogen levels in overland, near-surface, and subsurface samples did not provide enough evidence to suggest that varying SMZ treatments or fertilization would have negatively impacted water quality. Furthermore, differences between downstream and upstream levels of total inorganic nitrogen were not significant at the 0.10 alpha level for any

model effect (table 6) and average concentrations downstream of the fertilized area never exceeded 0.25 mg/l.

Total Inorganic Nitrogen Concentrations over Time

Near-surface Water

There was no significant difference in total inorganic nitrogen between the litter layer and upper soil layer. Near-surface water total inorganic nitrogen was significantly influenced by sampling date in the clearcut ($p = <0.001$), SMZ dripline ($p = 0.004$), and streamside ($p = 0.016$) positions (table 3, figure 19).

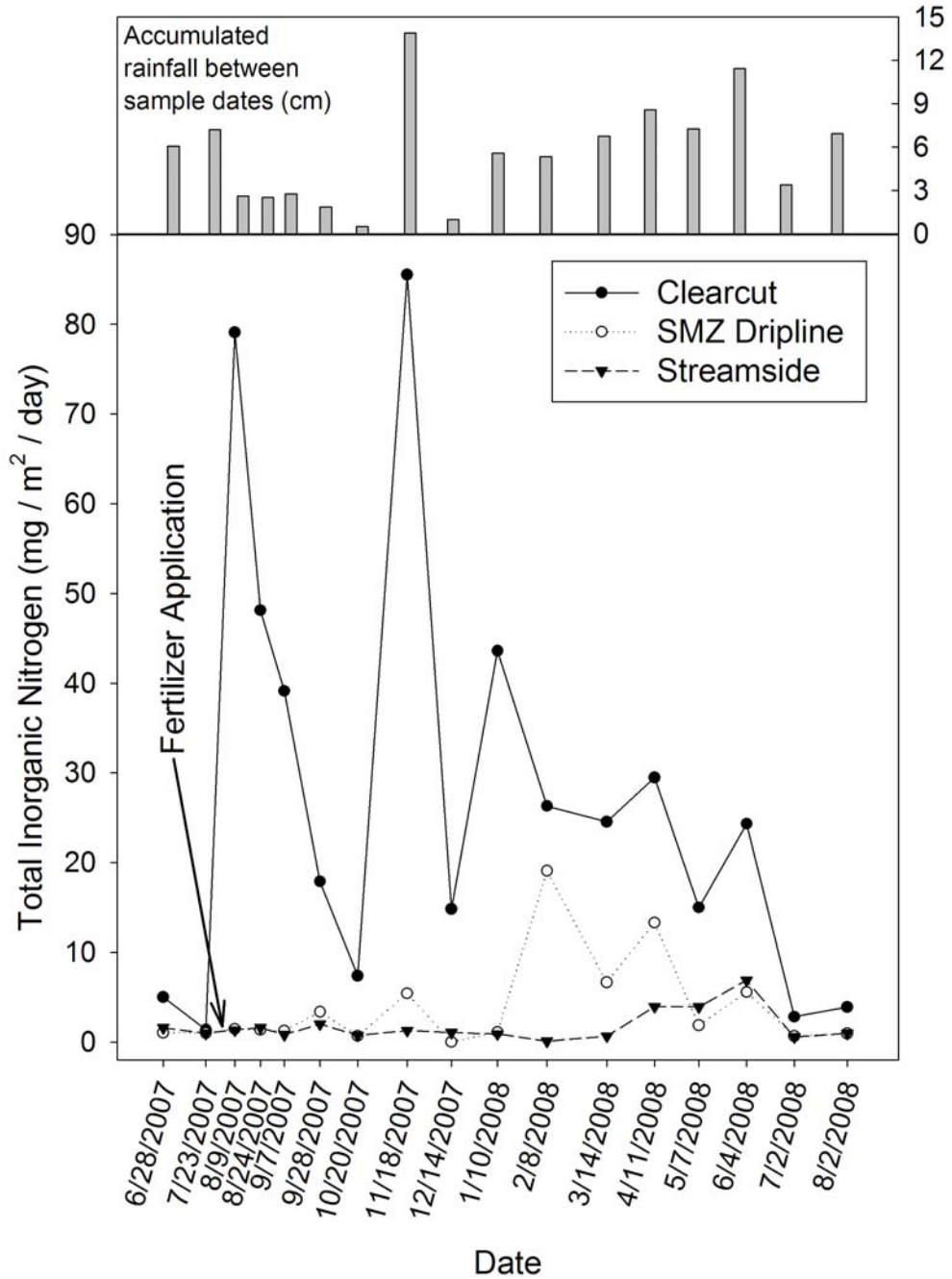


Figure 19. Least-square means for near-surface water total inorganic nitrogen levels (mg/m²/day) as influenced by sampling date and sampling position (clearcut, dripline of SMZ, and streamside) including accumulated rainfall (cm) between each sample date.

Near-surface water total inorganic nitrogen levels spiked immediately following fertilization on July 23, 2007. In November, total inorganic nitrogen levels also spiked to 85.5 mg/m²/day in the clearcut and rose slightly to 5.4 mg/m²/day at the SMZ dripline due to large amounts of rainfall during that sampling period which increased near-surface water flow capable of transporting nitrogen. Total inorganic nitrogen levels at the SMZ dripline and streamside were also slightly elevated during the spring of 2008 (figure 19).

There was a significant date*SMZ treatment interaction (alpha 0.1) for near-surface total inorganic nitrogen at the clearcut and SMZ dripline positions (table 13).

Table 13. Least-square means for near-surface total inorganic nitrogen levels (mg/m²/day) as influenced by the sampling date*SMZ treatment interaction including accumulated rainfall (cm) between each sample date. Letters correspond to a Tukey's mean separation test performed by column at the 0.1 alpha level.

Date	Treatment (Clearcut)				Treatment (SMZ Dripline)				Rainfall
	7.6m	15.2m	15.2m Thin	30.5m	7.6m	15.2m	15.2m Thin	30.5m	
	-----mg/m ² /day-----								cm
6/28/2007	4.67c	7.81ab	3.47d	4.07c	0.85a	0.71b	1.46b	1.15a	6.06
7/23/2007	1.83c	1.58b	1.28d	0.82c	1.07a	0.65b	0.94b	1.33a	7.19
	-----Fertilization-----								
8/9/2007	93.13ab	116.95a	92.73a	13.58abc	1.43a	0.99b	1.15b	2.21a	2.61
8/24/2007	17.45bc	113.06a	21.47bcd	40.49ab	1.17a	1.25b	1.76b	1.20a	2.52
9/7/2007	19.21bc	75.06ab	46.74abcd	15.50abc	1.24a	1.24b	0.64b	1.91a	2.75
9/28/2007	19.82bc	29.46ab	20.17bcd	2.12c	1.05a	9.03ab	1.29b	2.06a	1.84
10/20/2007	12.15bc	4.90b	9.80cd	2.69c	0.46a	0.38b	1.07b	0.77a	0.51
11/18/2007	116.94a	103.27ab	79.26abc	42.64a	0.17a	16.28ab	0.44b	4.77a	13.89
12/14/2007	16.91bc	19.80ab	17.12bcd	5.47c	1.42a	0.00b	0.86b	0.21a	0.99
1/10/2008	22.18bc	81.14ab	54.95abcd	16.10abc	0.71a	0.97b	2.12b	0.65a	5.57
2/8/2008	17.32bc	59.16ab	23.29abcd	5.42c	1.37a	73.83a	0.65b	0.46a	5.33
3/14/2008	36.83bc	44.90ab	8.69bcd	7.69bc	5.72a	19.43ab	0.83b	0.57a	6.76
4/11/2008	22.17bc	13.27ab	81.34ab	1.09c	2.33a	19.44ab	25.49a	5.94a	8.58
5/7/2008	13.38bc	26.56ab	10.69bcd	9.31bc	0.53a	2.52b	3.30b	1.14a	7.27
6/4/2008	3.48c	83.87ab	8.20d	1.71c	0.87a	8.94b	11.88ab	0.55a	11.43
7/2/2008	3.26c	2.54b	4.15d	1.32c	0.52a	0.80b	0.83b	0.44a	3.37
8/2/2008	4.06c	3.31b	7.16d	1.01c	0.43a	1.69b	0.54b	1.07a	6.93

The least-squared means values (table 13) indicated that nitrogen levels generally increased in the clearcut following fertilization and on November 18, 2007 when 13.9 cm (5.5 in.) of rain fell just prior to sampling. Total inorganic nitrogen levels in the clearcut

remained elevated in the spring, mostly due to increased nitrate (figure 11 and table 8), and then returned close to pre-fertilization levels in late spring and early summer of 2008. The relatively low levels of total inorganic nitrogen at the SMZ dripline, particularly after fertilization, indicate that inorganic nitrogen from fertilization was not transported from the clearcut to the SMZ dripline in the upper soil or litter layers. Concentrations at the SMZ dripline only exceeded 10 mg/m²/day on six occasions.

Many studies have shown evidence of heavy nitrogen movement in riparian forests below fertilized areas resulting from groundwater flow (Jackson et al., 1973; Lowrance et al., 1983; Peterjohn and Correll, 1984). However, increased levels of nitrogen during the spring of 2008 are probably accredited to spring-time nutrient flushes rather than increased movement of fertilizer nitrogen. Increased spring nitrogen concentrations in our study were found at least six months after fertilization and were typically not as high as increases immediately following fertilization. Increased total inorganic nitrogen concentrations were also found in conjunction with warmer temperatures and increased rainfall that were believed to stimulate microbial activity. Furthermore, despite no significant decrease in rainfall, nitrogen concentrations began to drop around the time of expected heavy plant uptake (table 13). Ewel (1978) states an essential characteristic of riparian ecosystems is laterally flowing water that fluctuates one or more times during the growing season. Increased nutrient availability in upper soil layers and the litter layer during the spring is well documented (Gupta and Rorison, 1975, Burke, 1989).

Subsurface Water

Subsurface water samples collected in the fertilized clearcut were not evenly distributed among SMZ treatments and concentrations within the clearcut are not reflective of the efficacy of the SMZ width. Therefore, clearcut samples were removed when comparing total inorganic nitrogen concentrations over time so that a few samples with elevated nutrient levels would not bias the comparison of SMZ treatments over time (figure 20).

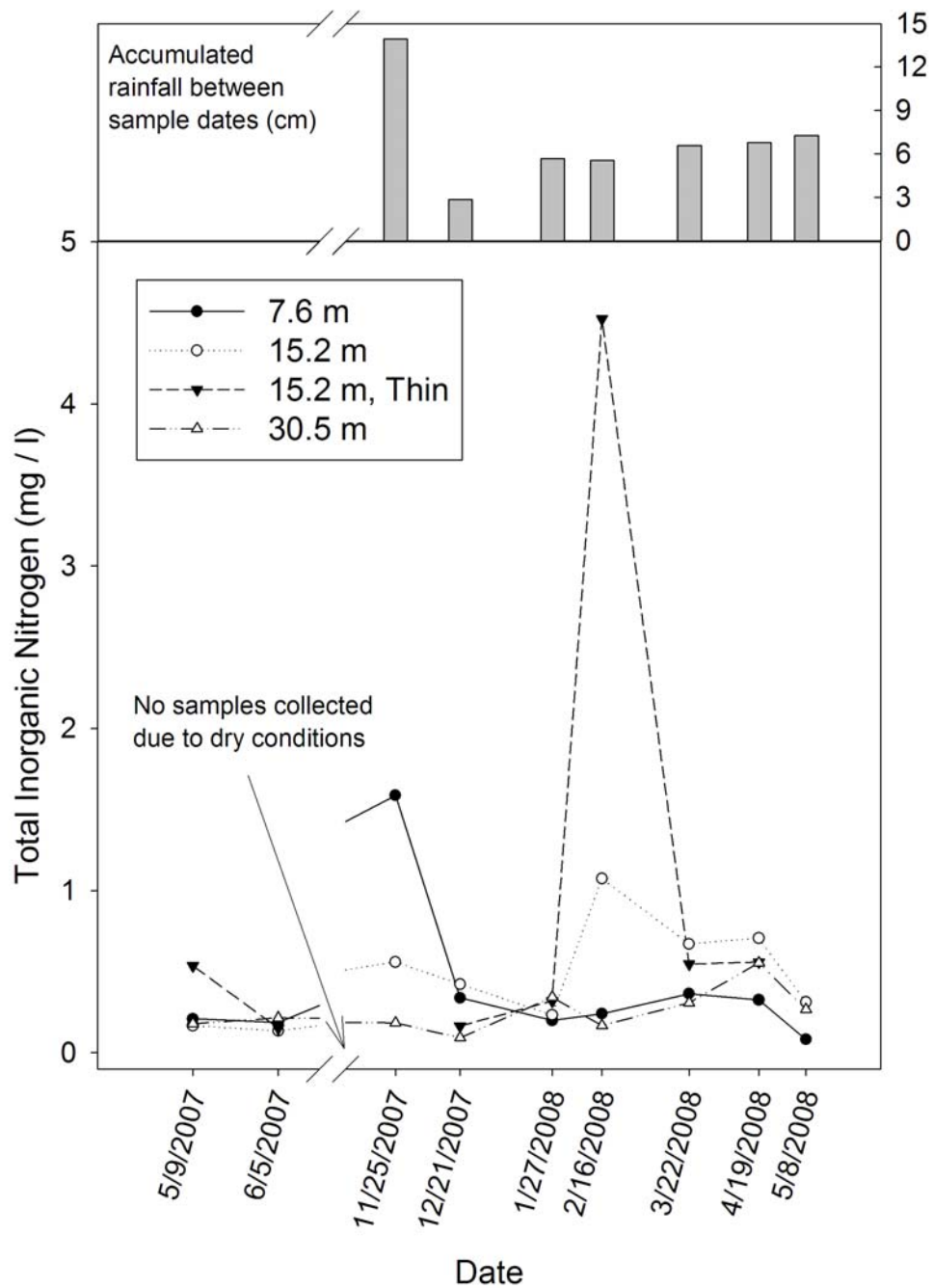


Figure 20. Average subsurface water total inorganic nitrogen levels (mg/l) at all SMZ locations over the sampling dates for each SMZ treatment including accumulated rainfall (cm) between each sample date. Samples collected in clearcut are not included.

Average total inorganic nitrogen never exceeded 5 mg/l at any date. The first subsurface water nutrient spike occurred on November 25, 2007, a month following the heavy rainfall discussed earlier where 13.92cm (5.48in) of rain fell in a 29 day period prior to sampling. The flux in total inorganic nitrogen at this point was primarily due to ammonium (figure 17). Nitrogen concentrations in subsurface water flow did not reach above an average of 2 mg/l at any given SMZ treatment at this time. Most of the flux in total inorganic nitrogen shown on February 16, 2008 was due to increased levels of nitrate (figure 12).

We believe that an increase in total inorganic nitrogen during late February and early March was actually due to a spring-time flux of nutrients rather than a flush from fertilizer application that occurred approximately seven months earlier. Taylor et al. (1982) found that late winter and early spring months demonstrated maximal levels of available nitrogen that progressively declined in to the summer months. Most of the subsurface water samples were collected at least five months after fertilization so it is likely that average sample levels represent normal nutrient levels for winter and spring periods and were not affected by fertilization.

Thinning Effects on Total Inorganic Nitrogen

Near-surface Water

As with nitrate and ammonium, there were no statistically significant differences in total inorganic nitrogen between the harvested corridors and non-thinned areas of the thinned 15.2m SMZ treatment. As a result, data were combined in one average and used to conduct a full analysis of all SMZ treatments. The thinned 15.2m treatment showed increases over time similar to the other treatments. Concentrations of total inorganic

nitrogen were elevated in the clearcut following fertilization and heavy rainfall in November and elevated at the SMZ dripline in the spring due to the non-fertilizer nutrient flux previously described (table 13). When an ANOVA was run by position on near-surface total inorganic nitrogen, the thinned 15.2m treatment was not significantly different than any other treatment (table 3).

Subsurface Water

Subsurface water total inorganic nitrogen concentrations averaged near 5 mg/l in the thinned 15.2m SMZ treatment on February 16, 2008. Increased concentrations on February 16, 2008 (approx. 1 mg/l) existed in the non-thinned 15.2m SMZ treatment as well (figure 20).

SMZ Treatment Effects on Ortho-phosphate

Surface Water

Spring surface water ortho-phosphate levels were significantly influenced by SMZ treatment ($p = 0.078$) and a SMZ treatment*position interaction ($p = 0.075$) (table 2). Overall, average surface water ortho-phosphate levels were very low (<2 mg/l) at all positions and SMZ treatments (table 14).

Table 14. Average surface water ortho-phosphate levels (mg/l) for each SMZ treatment by position over the entire study period. Shading indicates averages that were at or below the 0.02 mg/l detection limit.

Average Ortho-phosphate Treatment	Position			
	Control-Dripline	Control-Streamside	Fert-Dripline	Fert-Streamside
	-----mg/l-----			
7.6m	0.020	0.545	0.020	0.070
15.2m	0.099	0.095	0.032	0.020
15.2m Thin	0.094	0.187	0.055	1.121
30.5m	0.020	0.020	0.315	1.511
Overall Average	0.057	0.210	0.106	0.629

Near-surface Water

In order to determine if the expense and time of running thousands of samples for near-surface water ortho-phosphate was justifiable, a small subset was analyzed at pre-fertilization and worst-case scenario post-fertilization dates. There was no indication from near-surface water ortho-phosphate samples that suggest ortho-phosphate moved from the clearcut to the SMZ dripline or streamside in the 7.6m SMZ treatment. The entire anion membrane set was not analyzed because ortho-phosphate showed little or no sign of being transported in litter or shallow subsurface water flow. Approximately 85% of available phosphorous is bonded to small soil particles (Welsch, 1996) which were unable to pass through the ionic exchange membranes (IEM's). We found no significant ortho-phosphate movement from the upland fertilized which is not surprising since Lowrance et al. (1983) found that phosphorous in precipitation caused a greater phosphorous input to a riparian area than water movement from an upland agricultural area.

Subsurface Water

Similar to near-surface levels, ortho-phosphate was basically non-detectable in subsurface water samples collected in the fertilized clearcut or the SMZ when averaged over the entire study period. The average concentration for each treatment at all sampled distances from the SMZ dripline were below the 0.02 mg/l detection limit. Average stream water ortho-phosphate levels were also below the 0.02 mg/l detection limit in samples collected above and below the fertilized area.

Ortho-phosphate Concentrations over Time

Surface Water

Typical surface water ortho-phosphate levels at any particular date, SMZ treatment, and position were low (<1.0 mg/l 95.5% of the time). In period five (spring 2008), SMZ treatment effect ($p = 0.078$) and SMZ treatment*position interaction ($p = 0.075$) were significant (table 2). This was probably due to unexplainably high average ortho-phosphate levels (>3.5 mg/l) at the fertilized streamside location in the 30.5m SMZ treatment. Two replications in the 30.5m SMZ treatment, that also had high levels of ammonium in surface water samples, had abnormally high surface water concentrations of ortho-phosphate which biased the ANOVA causing SMZ treatment effect and the SMZ treatment*position interaction to be significant.

Phosphorous is a limited nutrient in many streams and lakes and can cause eutrophication in water bodies experiencing heavy influxes (Brooks et al., 2003). Past literature suggests phosphorous bonds tightly to soil particles and is mostly immobile unless attached to suspended sediment. For instance, Cullen (1983) found that the majority of phosphorous in aquatic ecosystems is transported in the particulate form during storm events. Peterjohn and Correll (1984) found that 94% of phosphorous entering a riparian forest adjacent to cropland came from surface runoff and phosphorous retention by the riparian forest was 80%.

Near-surface Water

Near-surface water ortho-phosphate levels at the streamside location in the 7.6m SMZ treatment were minimal to non-existent immediately following fertilization and after a heavy rainfall (table 15).

Table 15. Average near-surface water values of the 7.6m SMZ treatment for ortho-phosphate levels (mg/m²/day) at each position (clearcut, SMZ dripline, and streamside) for a date prior to fertilization (7/23/2007), two dates immediately following fertilization (8/16/2007 and 8/24/2007), and a date after heavy rainfall (11/18/2007). Shading indicates averages that were at or below the 0.035 mg/l detection limit.

Ortho-phosphate Position	Sample Date			
	7/23/2007	8/16/2007	8/24/2007	11/18/2007
	-----mg/m ² /day-----			
Clearcut	0.035	30.40	8.34	9.22
SMZ Dripline	0.05	0.04	0.25	0.035
Streamside	0.035	0.13	0.04	0.035

Immediately following fertilization, average clearcut ortho-phosphate concentrations reached as high as 30.40 mg/m²/day. However, very little near-surface ortho-phosphate reached the SMZ dripline as concentrations were ≤0.25 mg/m²/day following fertilization and a heavy rainfall in November. On average, near-surface water ortho-phosphate levels at the streamside were ≤0.13 mg/m²/day. Subsurface water ortho-phosphate concentrations were basically unaffected by time as average concentrations only reached above the 0.02 mg/l detection limit once (0.03 mg/l on November 25, 2007 in the 7.6m treatment).

Chapter 5: Conclusions

We accepted (failed to reject) our null hypothesis that differences in streamside management zone width and thinning did not affect the movement of applied fertilizer from a planted loblolly pine watershed to the stream. With only a few exceptions, results indicated that 7.6m wide SMZs with 1m wide, seeded firebreaks are sufficient to prevent nitrate, ammonium, and ortho-phosphate movement to the stream. However, results were obtained during dry conditions and could be different for wetter years. Typical cumulative rainfall for the 15 months monitored is 158.5cm, but our watersheds only averaged 97.2cm of precipitation. Furthermore, rainfall was extremely low in the month immediately after fertilization when higher levels of nutrient movement are expected. Our results suggest that even our two minimal treatments, the 7.6m SMZ and the thinned 15.2m SMZ between the stream and firebreak, are adequate to protect streams from inorganic nutrient fluxes, at least during relatively dry conditions following fertilization.

Overall, nutrients did not move laterally from the clearcut to either SMZ dripline or streamside positions. Near-surface water nitrogen levels were statistically higher in the clearcut than at the SMZ dripline and streamside positions and these two SMZ positions were statistically similar when compared across the entire study period. Nitrate in surface water were also low and only reached levels greater than 1 mg/l in five of approximately 400 samples, and levels never reached 5 mg/l. Regressions conducted on subsurface samples indicated little to no presence of nitrate within 7.6m of the SMZ dripline and downstream nitrate levels in the streams averaged <0.05 mg/l for all treatments. Stream levels for ammonium averaged <0.20 mg/l and were below the 0.02 mg/l detection level for ortho-phosphate in every treatment.

Sample date was highly significant in near-surface water sampling. Levels of nitrate and ammonium significantly increased immediately after fertilization and after a heavy rainfall approximately 4 months after fertilization. Nitrogen levels also increased significantly, but less dramatically, in the spring likely due to natural nutrient fluxes from increased microbial activity. Furthermore, the highest nitrate levels in surface water were collected during the spring. Typical subsurface concentrations of nitrogen were low on every sample date in every treatment and SMZ position. Concentrations in stream water samples were variable across time but did not have sudden increases after fertilization or heavy rainfall in any treatment. Ortho-phosphate concentrations in surface water were <1 mg/l in 95.5% of the samples and no treatment had an average sub-surface water ortho-phosphate level >0.035 mg/l on any date. Near-surface water ortho-phosphate increased to concentrations greater than 8 mg/m²/day in the clearcut during the first month after fertilization and after a heavy rainfall in November, but concentrations were <0.3 mg/m²/day at the SMZ dripline and streamside on those same dates.

The thinned treatment was originally designed to be a split treatment where harvested corridors and undisturbed portions of SMZ would be compared side-by-side. No statistical difference was found between the two areas so the data were combined into a single thinned 15.2m treatment. Average subsurface levels were <0.4 mg/l and <0.2 mg/l for nitrate and ammonium, respectively, for both the thinned and non-thinned 15.2m SMZ treatments. Elevated levels of ammonium were noticed in surface water samples in the thinned 15.2m treatment; however this was due to a few unusually high values. For example, one streamside surface water sample was unusually high (approximately 324 mg/l) following fertilization while another was high (approximately 133 mg/l) following

a heavy rain in November. Thirteen percent of samples in this treatment were above 10 mg/l of ammonium suggesting there may be a slight effect due to thinning.

Overall, SMZ width had minimal effect on the amount of nutrient that reached the stream. SMZ treatment ability to control nutrients from reaching the stream is ranked in table 16. Rank was established using average streamside nutrient concentrations over the duration of the study for each nutrient at each location of water flow monitored. The exception is stream water for which the rank was based on the average difference between upstream and downstream measurements over the duration of the study. The rank in table 16 is sufficient at showing non-statistical patterns only.

Table 16. Non-statistical ranking of SMZ treatment’s ability to control nutrient concentrations at various locations of water monitoring where (1) means most effective and (4) means least effective. Ortho-phosphate was not included because most readings were below the 0.02 mg/l detection limit.

Nutrient	Location	7.6m SMZ	Thinned 15.2m SMZ	15.2m SMZ	30.5m SMZ
		-----Rank-----			
Nitrate	Surface	1	4	3	2
	Near-surface	3	4	2	1
	Subsurface	2	4	3	1
	Stream	3	N/A	2	1
Average Nitrate Rank		2.25	4	2.5	1.25
Ammonium	Surface	2	3	1	4
	Near-surface	2	3	1	4
	Subsurface	3	2	4	1
	Stream	2	N/A	1	3
Average Ammonium Rank		2.25	2.67	1.75	3
Total Inorganic Nitrogen	Surface	2	3	1	4
	Near-surface	3	4	2	1
	Subsurface	2	4	3	1
	Stream	2	N/A	1	3
Average Total Inorganic nitrogen Rank		2.25	3.67	1.75	2.25
Overall Average Rank		2.25	3.44	2.00	2.17
Overall Median		2	4	2	1.5

Based on the non-statistical overall rankings, the 7.6m, 15.2m, and 30.5m SMZs were similarly effective at controlling nutrient fluxes in or near the stream. The thinned 15.2m SMZ appears less effective than the non-thinned SMZ treatments. However, actual concentrations in the thinned 15.2m SMZ treatment were only slightly higher than the non-thinned SMZ treatments and, more importantly, were not at concentrations that violated Virginia water quality criteria for drinking water.

We never found nitrate levels greater than 10 mg/l in any sampling method. Therefore, according to criteria established by the Virginia Department of Environmental Quality, industrial fertilizer application in young loblolly pine stands in the Virginia piedmont does not impair streams as a source for drinking water in regards to nitrate levels if at least a 7.6m SMZ is utilized between the firebreak and stream. Despite the lack of ammonium and phosphorous criteria for drinking water sources in Virginia, our results indicate that a 7.6m SMZ is wide enough to protect surface water quality from forest fertilization since ammonium and phosphorous tended to be mostly immobile. However, more research is needed to see if similar results would exist with more abundant rainfall. The data reflect SMZ effectiveness as used during typical forest operations and do not reflect efficacy in either agricultural or urban settings.

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