

ABSTRACT

DUARTE, NATASHA. Nitrogen form and availability measured with ion exchange resin in a Loblolly pine stand on the Coastal Plain of North Carolina. (Under the direction of Robert Mikkelsen.)

Understanding how management affects long-term site productivity will help sustain forest productivity. In 1991, the USDA Forest Service installed the Long-Term Soil Productivity study in the Croatan National Forest in Craven County, NC. The study objectives were to compare indices of plant-available inorganic N from ion-exchange resin (IER) in bead and membrane form and aerobic incubations in a 8-week study, and to analyze the effects of harvest intensity and site preparation on N availability and tree growth ten years after planting. Site treatments included three levels of organic matter removal and two levels of compaction arranged in a strip-plot design replicated in three blocks. Block 1 consisted primarily of Goldsboro soil, while Blocks 2 and 3 consisted of Lynchburg. The two-month study showed no correlation of the N availability among the three techniques. The short duration of the study and the low soil fertility at the site may have contributed to the lack of correlation, indicating that the two forms of IER may not be equally effective at low nutrient concentrations. Through the 2001 growing season, IER membranes were used to measure soil NO_3 and NH_4 biweekly. Non-linear analysis indicate that total inorganic N recovered from the IER membranes was significantly influenced by interactions between block, organic matter removal treatment and compaction level ($p=0.005$). Total basal area of loblolly pines was significantly impacted by block ($p=0.015$) and organic matter removal treatment ($p=0.032$). At year ten, treatment effects can still be seen on both soil processes and tree productivity.

NITROGEN FORM AND AVAILABILITY MEASURED WITH ION EXCHANGE
RESIN IN A LOBLOLLY PINE STAND ON THE COASTAL PLAIN OF
NORTH CAROLINA

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1. Introduction:

Long-term site productivity is influenced by both biotic (species and genotype) and abiotic factors (soil productivity, slope, and precipitation) (Morris and Miller, 1994), and can be defined as maintaining or increasing biomass productivity on a given site over time. Physical, chemical, and climatic factors interacting within a biological framework characterize a site's productive potential (Powers et al., 1990; Fox, 2000). The most dynamic factor influencing plant growth potential is soil productivity (Powers et al., 1990), which includes the ability of a soil to provide support, water, and nutrients to trees and plants. This productivity, in part, is maintained through the activity of a large range of soil biota that contribute to the development of soil structure, decomposition of organic matter, and nutrient mineralization and transformation.

Long-term site productivity has been the focus of numerous studies (e.g. Coleman et al., 1982; Ballard and Gessel, 1983; Dyck and Mees, 1989; Gessel et al., 1990; Powers, 1990; Dyck et al., 1994; Cole, 1995; Fox, 2000). In general, this literature reports that management-induced losses in site organic matter and degradation of soil physical properties, including bulk density and porosity, will most often negatively impact long-term soil productivity and therefore, long-term site productivity. Forest harvesting and site preparation remove nutrients and disrupt aspects of the nutrient cycling processes, as well as affecting soil physical properties.

An important question raised by forest soil scientists is whether soils can sustain the long-term needs of forest stands under intensive site preparation practices, shortened rotations,

and/or higher utilization standards (Stone, 1987; Powers et al., 1990). Sustaining forest long-term site productivity requires an understanding of the processes that affect the ability of a soil to supply necessary nutrients and water and of the regulation of competition for resources (Kimmins, 1994).

During harvest on many intensively managed plantations, heavy equipment such as feller-bunchers, skidders and forwarders are used. Multiple passes of this equipment often leads to compaction and/or rutting of the soil throughout the site. The compaction caused by these activities leads to increases in bulk density and soil strength and significantly alters pore size distribution which impacts soil water holding capacity, soil aeration, microbial activity, nutrient availability, and root penetration (DeWitt and Terry, 1983; Gent et al., 1984; Miwa et al., 1998; Lenhard, 1986; Powers et al., 1990; Walkinshaw, 1998; Zhou et al., 1998; Carter et al., 1999; Fox, 2000). Differences in soil texture, soil moisture content during harvest and site preparation, as well as type of equipment and number of passes, regulates the severity of the soil damage (Burger et al., 1985, Aust et al., 1995, Fox, 2000). Soil damage during logging can decrease long-term site productivity, especially on fine-textured soils (Fox, 2000).

Effects of forest floor disturbance and mineral soil compaction on subsequent tree growth may not be evident for some time. On poor or fine-textured soils, compaction and the loss of forest floor organic matter may cause a decline in growth and yield of succeeding generations of trees (Jorgensen, et al., 1980; Fox, 2000). The rate of decline depends

greatly on the nutrient status of the mineral soil reserve and the mineralization release rate of these nutrients (Jorgensen et al., 1980).

The proportion of soluble nutrients in the soil is low; typically only 1 to 2% of the total quantity is available for plant uptake (Brady and Weil, 1999). Soils differ greatly in their ability to supply nutrients necessary to sustain forest productivity. The buffering capacity of a soil reflects the concentration of plant-available nutrients in the soil solution while the supply of nutrients at any given time is influenced by the net balance of nutrients that are being added and removed from the soil system. Nutrients become available for plant uptake through processes such as mineralization, N₂ fixation, weathering, atmospheric deposition, and fertilization. Nutrients become unavailable for plant uptake through immobilization by soil microorganisms and through chemical and mineralogical reactions including precipitation and adsorption reactions and ionic fixation within the lattice network in clay minerals.

Nitrogen (N) is an essential plant nutrient and plays a role in determining the uptake of other essential nutrients, such as potassium and phosphorous. Nitrogen is often a growth-limiting factor in many forest ecosystems and, because N availability is relatively sensitive to environmental changes, it is often targeted as a key indicator of site disturbance (Keeney, 1980; Munson et al., 1993). Bound mostly within soil organic matter, N must first be released through microbial decomposition or mineralization, an enzymatic processes through which complex proteins and associated compounds are simplified and hydrolyzed to NH₄. Under oxidizing conditions, NH₄ is microbially

transformed into NO_3 when the soil environment is favorable (temperature, pH, moisture, etc.) Annual net N mineralization has been shown to be an important limiting factor in non-fertilized forest production (Nadelhoffer and Aber, 1984).

Effects of tree harvesting and site preparation (e.g. windrowing) on soil organic matter and carbon-nitrogen (C:N) interactions may be the most important factors for long-term site productivity (Johnson, 1994; Burger and Pritchett, 1984). Soil organic matter (SOM) has a significant influence on site productivity as it affects physical (bulk density, water holding and nutrient storage capacity), biological (microbial populations), and chemical (cation exchange capacity) properties of the soil. Removal of this nutrient-rich layer results in increased evaporation from the soil, enhanced thermal conductivity, and reduced heat capacity. The degree of biomass removal, ranging from stem-only harvest, whole-tree harvest, and whole-tree harvest plus forest floor removal has a direct impact on quantity, quality, and the C:N ratio of residues left to decompose on site. Johnson (1994) provides a good historical perspective for concerns over the impacts of harvesting on soil conditions and forest productivity. Nitrogen deficiency of the subsequent planting may result from either a large amount of woody residue left on the site, resulting in N complexation, or complete removal of all organic material, resulting in the loss of a readily-mineralizable N pool (Burger and Pritchett, 1984). Nitrogen availability is a function of substrate quantity and quality, and environmental conditions, all of which can be impacted by harvesting practices and site preparation. Mineralization of N from SOM is the basis of long-term N availability to unfertilized forest trees.

Increased mineralization and nitrification rates after clear cutting are well documented, varying with climate, soil conditions, and amount of disturbance (Burger and Pritchett, 1984; Vitousek and Matson, 1985; Fox et al., 1986; Vitousek et al., 1992). Increased nitrification can promote losses of N from the soil system due to the high mobility of NO_3 and a production exceeding that which young trees require. Leaching losses of NO_3 will also promote cation losses from the soil (Munson et al., 1993).

There are numerous laboratory methods for predicting N mineralization or developing indices of soil N availability (e.g. anaerobic and aerobic incubations, total N, and extractable N (Hart et al., 1994)). Chemical extraction procedures, though used successfully in most agricultural settings, do not work well in forest soils and have limited use in ecological studies (Keeney, 1980; Carlyle and Malcolm, 1985). Nutrient availability in forest ecosystems depends on the interaction between soil, vegetation, and environmental processes, dynamic factors that are often not accounted for in laboratory procedures. This is especially true for N analysis, as N is one of the most dynamic soil nutrients and chemical extraction provides only 'snap shots' of potential availability. Nitrogen mineralization is greatly affected by soil microenvironment (soil temperature, soil moisture, aeration), and the accuracy of these indices for providing realistic estimates of plant available N has been challenged because these factors are altered in the laboratory. Though a wide variety of methods have been used to assess forest soil N availability, none is widely accepted (Binkley, 1984). For example, tension lysimeters do not express a flux, since the sampled volume is uncertain, and zero tension lysimeters,

while permitting flux calculations, require the collection of large volumes of leachate and may require some degree of sample isolation (Carlyle and Malcolm, 1985).

The use of ion exchange resins (IER) is gaining in popularity as an alternative method for determining plant available N *in-situ* and under controlled laboratory conditions. Ion exchange involves the redistribution of ions from solution to the resin via exchange for counter-ions on the exchange resin. This redistribution occurs through diffusion. There are many types and forms of IER, each with its own specific properties that affect its function. Most synthetic ion exchange resins are solid organic polymers with an electrostatic charge, neutralized with a low affinity counter-ion (Skogley and Dobermann, 1996). Skogley and Dobermann (1996) describe the production of most IER as styrene polymerized with itself to produce long chains, which are then reacted with divinylbenzene to produce cross-linkages. This process accounts for much of the variation in internal porosity (and therefore exchange capacity) that has been seen between batches of resin, as varying degrees of cross-linkage can be obtained. Macroporous IER are the most common resins used in soil studies and, due to their spherical external shape, are referred to as IER beads. Macro- and micropores are both present in the IER beads, the internal surface areas potentially exceeding $10^5 \text{ m}^2 \text{ kg}^{-1}$. Ion exchange resin in membrane form are becoming a popular form of IER used in soil studies. The chemical structures of the ion exchange membranes (IEM) are very similar to those of the IER beads. The membranes, often made of hydrocarbon or fluorocarbon polymers, are extruded into sheets and combined with reinforcing material to provide dimensional stability and mechanical strength (Skogley and Dobermann, 1996).

Ion accumulation on IER appears to be sensitive to on-site micro-environmental conditions that regulate mineralization processes. Interpretation of N accumulation on IER can, however, be problematic. High concentrations of N on IER could result from high net mineralization rates, high ion mobility, or high water flow. Despite the difficulty in separating these factors, the IER technique is useful as all of these factors also affect the delivery of ions to tree roots. Full ion recovery from IER is not expected, but the values are used as a relative index of plant-available nutrients. The verification of percent recovery becomes less important where IER data are used in comparative studies among sites rather than for studies requiring absolute recovery for quantification of ion fluxes (Binkley, 1983 and 1984; Hart and Binkley, 1984; Binkley and Hart, 1985; Binkley et al., 1986).

Documentation of the process of ion-exchange began approximately 150 years ago and synthetic ion exchangers are almost 70 years old (Dorfner, 1991; Skogley and Dobermann, 1996). Ion exchange resin extractions have been used to assess plant nutrient availability for only about five decades (Pratt, 1951; Amer et al., 1955; Arnold, 1958), although more than 300 journal articles have been written during this time (Qian and Schoenau, 1997). Pratt (1951) was the first to use cation exchange resin beads for the extraction of available K from soil. The majority of the work, however, has involved the use of anion exchange resin beads to estimate plant available P (e.g. Amer et al., 1955; Bowman et al., 1978, Sibbesen, 1983; Yang and Jacobson, 1990). The majority of this early work reported improved estimates in the relationship of plant K, S, and P

contents and predicted soil nutrient availability using IER extraction compared to conventional soil testing techniques. Conventional methods of testing soil nutrient status are inherently static and do not account for the kinetics of nutrient release and transport, and may mobilize nutrients other than those that are truly plant available (Qian and Schoenau, 1997). Several articles chronicle early work with IER and P and K estimates (Qian et al., 1992; Schnabel et al., 1993; Schoenau et al., 1994; Skogley and Dobermann, 1996; Huang and Schoenau, 1996).

Ion exchange resin has been used in many diverse applications, such as to measure nutrient supply rate in soil (Qian and Schoenau, 1997), potential nutrient supply rates in soil through long-term burial (Sikora and Yakovchenko, 1996), field microsite assessment of soil nutrient supply rates in forest ecosystems (Persson and Wiren, 1995), mapping nutrient availability patterns in the root zone using large sheets of membrane (Savic et al., 1986), soil mapping for precision farming, monitoring river water composition, measuring sodicity hazard in soil, measuring micronutrients and metal toxicity in soils, and assessing organic compounds in soil (the last five studies detailed by Qian and Schoenau, 1997).

Initial studies with IER used a technique whereby loose resin beads were mixed with soil samples in the lab and then recovered for chemical analysis. However, separation of soil and the beads prior to analysis was difficult. To overcome this obstacle, resin beads were enclosed in nylon or polyester mesh bags prior to adding them to the soil (Sibbesen, 1977). In the 1980s, several studies were conducted using both anion and cation

exchange resins together for simultaneous extraction of plant-available nutrient ions (e.g. Binkley and Matson, 1983; Binkley, 1984; Hart and Binkley, 1984; Carlyle and Malcolm, 1985; Binkley et al., 1986; DiStefano, 1986; Gibson, 1986; Hart et al., 1986; Krause and Ramlal, 1987; Lundell, 1989).

Gibson (1986) used IER bags to study short-term temporal and spatial heterogeneity of ion supply in grazed and ungrazed grassland soils. He reported that NH_4 was positively related to micro-topography and strongly affected by the soil moisture, while IER-extractable NO_3 more closely reflected soil NO_3 concentrations. Gibson noted that the concentration of IER-extractable nutrients, in general, were little affected by diffusion, but rather collected from whatever soil solution passed by the bag. While this might reflect short-term ion supply in a soil, he concluded that the long-term potential availability was not necessarily reflected.

Binkley and Matson (1983) were the first to use resin bags *in-situ* to measure N availability in forest soils. They compared their IER bag technique to six other methods for predicting soil N availability: total N, initial extractable inorganic N, anaerobic incubation, aerobic incubation, boiling water extraction, and extraction following autoclaving. In a one-year controlled greenhouse experiment with well-mixed soils, the IER technique correlated well with all of the traditional indices of N availability, but in three forest stands, IER yielded estimates of N-availability estimates different from the controlled experiment. Binkley and Matson concluded that resin bags are sensitive to on-site conditions not discerned by more widely accepted lab techniques. There is still no

agreement on a method that provides an absolute prediction of forest soil N availability, making it difficult to say which technique is the most accurate under a particular set of site conditions. Predictions from the *in-situ* IER technique may better reflect the effect of forest floor morphology, temperature, and moisture fluctuations on N mineralization and ion transport that are purposely not incorporated into laboratory or greenhouse studies.

As early as 1984, Binkley (1984) considered the potential effects of soil ion concentration, water content, and plant-microbial competition for N on the regulation of the adsorption of NO_3 and NH_4 by IER. He reported that NO_3 adsorption was dependent on soil NO_3 content while NH_4 values were highly affected by the soil moisture. Due to high mobility in soil, the first addition of water beyond field capacity transported the bulk of the NO_3 to the resin bags. The IER-adsorption of NH_4 , however, increased incrementally with each addition of water to the system, even with NH_4 additions. No NO_3 or NH_4 appeared to accumulate on the IER bags when the pots were kept at field capacity. The greater mobility of NO_3 may tend to over-estimate soil NO_3 compared with NH_4 . Increasing microbial competition for nutrients by adding cellulose greatly reduced the total N accumulation on resins. The availability of N to tree roots is a function of mineralization, immobilization, and transport processes. The sensitivity of IER to ion transport and mobility may be useful for assessing N availability to tree roots, which are also affected by these factors.

Across 12 sites in North Carolina, Hart & Binkley (1985) found that IER-extractable NO_3 represented 20-95% of the total inorganic N recovered, even though all sites showed net

NO₃ immobilization during aerobic lab incubations. The higher IER-adsorption rates of NO₃ may limit the NO₃ from participating in immobilization, though Binkley's 1984 study showed that soil microorganisms can be effective competitors for soluble N. Hart and Binkley concluded that on-site variation in temperature and moisture conditions (and the corresponding effects on microbial processes), combined with the much greater mobility of NO₃ in the soil, tended to overestimate soil NO₃.

Another study conducted by Binkley et al. (1986) compared the results of the two *in-situ* methods of buried soil bags and IER bags, at eight sites in Wisconsin. Though the climate and soil types are very different in Wisconsin and North Carolina, their findings were consistent in both studies. In 1980-1981, N mineralization was assessed by the buried bag technique. Unsieved soil cores in polyethylene bags were incubated for one-month time periods through the growing season and at longer intervals during the winter. In April, 1983, IER bags were buried at the same sites and were left in place through November. The 1983 IER data correlated well with the 1980-1981 buried-bag soil incubation results ($r^2=.62$). The primary differences found were in the form of inorganic N recovered. The buried-bag results indicated that NO₃ was the primary form of inorganic soil N due to rapid NH₄ oxidation. Analysis of the IER bags indicated that both forms of inorganic N were present in all sites. The combined IER-N correlated well with above ground net primary production ($r^2=.72$), litter fall N ($r^2=.77$), and fine root biomass ($r^2=.91$). On nutrient poor sites however, low mineralization rates and low NH₄ mobility may cause overemphasis of small amounts of NO₃ relative to NH₄.

Carlyle and Malcolm (1985) noted some issues with the use of *in-situ* IER bags to estimate nutrient availability, including the selection of the best form of bag material, continuity of contact with the soil, microbial growth on the resin bag or the resin itself, and resin durability. Considerable soil drying of the site took place between collections during their 200-day study, which adversely affected the resin beads. Resin does not function when dry since exchange occurs only in an aqueous environment and they also observed that the IER beads often cracked on re-wetting. Under these dry conditions, the IER beads accumulated a small amount of NO₃, an order of magnitude lower than NH₄. Though this may be a common situation for coniferous forests, it differs from the results obtained in other studies. Carlyle and Malcolm concluded that although the IER bags method may not be suitable where drying phases may occur, short-term changes might be reflected in the IER values often missed by other methods.

Several other researchers have used IER bags in confined and unconfined coring techniques where resin bags were placed at the bottom of *in-situ* cores to measure N leaching. The use of IER bags simplified traditional techniques and proved accurate at estimating NO₃ leaching rates when used *in-situ* and under controlled laboratory settings (Hubner et al., 1991; Schnabel et al., 1993; Wyland and Jackson, 1993; Kjønnaas (1999)). Kjønnaas (1999) used unconfined cores to compare dissolved inorganic nitrogen accumulated in resins with dissolved inorganic nitrogen fluxes in throughfall and in soil water and found significant correlations for both ($r^2=.92$, $p<.0001$ and $r^2=.34$, $p<.01$, respectively). Kjønnaas concluded that IER bags, though unable to adsorb all incoming

dissolved inorganic N, provided valuable data on small-scale differences in NO₃ leaching.

The potential disadvantages of using IER beads in bags includes the trapping of fine roots and soil particles in the bags, root intrusion, tearing and/or unsealing of bag edges, and disintegration of bag material or resin. The results from IER, though shown to give appropriate estimates of plant-available nutrients, have also been reported to be strongly influenced by the resin/soil/solution ratios (Zou, 1992), shaking time (Qian et al., 1992), type and ionic saturation of the resins (Skogley et al., 1990), temperature (Yang et al., 1991) and the method used to recover the adsorbed ions from the resin (Somasiri and Edwards, 1992).

Skogley et al. (1990) developed a method called the phytoavailability test (PST) where IER is encapsulated in a rigid coating or shell. The capsule, covered with a saturated soil paste for 2-3 days, acts as an infinite sink, measuring ion adsorption as a function of time. The rate of ion release from different soil surfaces and their subsequent diffusion through the bulk soil determine the cumulative nutrient adsorption by the capsule.

Other developments with the use of IER include their use to extract pesticides from soil or to characterize organic matter using carbonaceous resin (Dobermann et al., 1994).

Vaidyanathan and Nye (1996) used paper sheets impregnated with IER to measure diffusion rates in soils *in-situ*, and Abrahms and Jarrell (1992) developed a bioavailability index for phosphorous based on this method. Savic et al. (cited in Dobermann et al.,

1994) placed large sheets of ion exchange membrane (IEM) onto soil monoliths to map nutrient patterns in the root zone, partly in combination with the application of an electric voltage.

The extraction of soil nutrients using IEM was first introduced by Saunders (1964). Saunders used anion exchange membranes to extract soil P and showed that its ability to predict soil P concentrations was as good as the resins in bead form. Much work has been conducted in the lab since that time, all reporting high correlations between estimates of nutrient availability using IER and plant uptake. This high correlation has led many of the researchers to recommend standard use of IER in soil testing labs, due to the ability to test for all plant nutrient ions with one easy, relatively quick test (Skogley et al., 1990, 1996; Schoenau and Huang, 1991; Qian et al., 1992; Schoenau et al., 1994).

Qian et al. (1992) concluded that IEM provided a better index of macronutrient availability than conventional chemical-based extractants because the resin membrane continuously removes ions from soil solution, preventing equilibrium, similar to the action of plant roots. If the membrane exchange capacity becomes saturated, however, the IER membrane becomes more dynamic, potentially exchanging ions back into the soil solution during pulses of other soluble ions or for those with greater affinity for the exchange sites (higher valence ions). Schoenau et al. (1994) tested 130 soil types from across Western Canada comparing IEM with conventional soil laboratory extractions. Using a 15 minute extraction, they found estimates of nutrient availability using IEM and chemical extraction were significantly correlated, with IEM capable of providing a

simultaneous index of relative P, K, N, and S availability. These researchers believe that IEM offers many advantages over conventional soil tests, especially in assessment of nutrient availability, because the membranes closely simulate the action of plant roots in nutrient absorption, acting independently of soil type.

Huang and Schoenau (1997) moved IEM techniques from the laboratory into the forest with a study considering plant nutrient availability, fine roots, and small depth increments in the forest floor (Oa, Oe, and Oi horizons). They compared *in-situ* IEM techniques with the laboratory water extraction procedure for predicting nutrient availability and found that both methods could be considered to provide an estimate of the potentially available soil nutrients. The litter layer acts as a major source and sink for plant nutrients, nutrient supply rates varying greatly between the Oa, Oe, and Oi horizons.

Huang and Schoenau concluded that IEM methodology is especially appropriate for these thin surface layers of a forest floor.

The advantages of IER in membrane form include a flat structure that ensures constant surface-area and better contact with the soil, minimal soil disturbance, overall increased sensitivity and convenience compared with conventional soil sampling and extraction techniques. Micro-scale variability can easily be considered when using IEM to assess forest nutrient status both horizontally and vertically.

Skogley and Dobermann (1996) have suggested that there is still too much inconsistency with how IER is being used by researchers, in both bead and membrane form. Their

article thoroughly details resin types and properties and suggests a classification scheme to assist in uniformity amongst studies. They contend that though a lack of knowledge and experience has led to apparent confusion concerning appropriate use of resins in many studies, resins still have great potential for soil nutrient evaluation if used correctly.

Several important resin properties, including bead size, resin chemistry, exchange capacity, initial saturation of counter ions of the resin, and soil moisture content, greatly affect the kinetics of nutrient adsorption in this system and can thereby influence IER and IEM performance (Skogley and Dobermann, 1996; Qian and Schoenau, 1997; Kjølne, 1999). The ion exchange system will ideally integrate both chemical and biological transformations in soil as well as diffusion limitations into the measurement of nutrient availability.

Qian and Schoenau (1997) summarized the use of IEM and also outlined basic chemical and physical properties and made recommendations for their use. The IEM have a high degree of chemical stability under diverse conditions, such as in acid and alkali solutions, organic solvents and in the presence of strong reducing and some oxidizing agents. This stability ensures that the resin matrix remains chemically unchanged by ionic interactions that take place at the functional groups, and the resin exchange sites can be easily regenerated. When left in soil for extended periods (more than a few weeks), the membranes often darken due to organic matter (fulvic and humic acids) accumulated in its lattice structure. Studies have concluded that this discoloration causes minimal

interference in extracting inorganic ions with membranes (Cooperband and Logan, 1994; Qian and Schoenau, 1997).

The ion exchange capacity of IEM is generally lower per weight than that of the bead form because membranes are made by enmeshing resin permanently in the polytetrafluoroethylene (PTFE) backbone. This lower exchange capacity must be taken into account when deciding how long to leave the membrane buried in the soil. When the original exchange capacity becomes saturated, IEM changes from an ion sink to a more dynamic exchanger, releasing soil ions for other ions in solution due to pulses of ions or ions with higher valences. Resins have an inherent selectivity or affinity for different ions; H and OH are typically used as the counter-ions as they have the lowest ionic affinities. The affinities vary with counter-ion type however and, for this reason, manufacturers provide lists of affinities for the various resins they produce. It's important to acknowledge that the ion exchange capacity can vary from batch to batch, regardless of the resin form or counter-ion used (Skogley and Dobermann, 1996; Qian and Schoenau, 1997; Kjønnaas, 1999).

Ion adsorption conditions are the most important factors affecting how IEM works, soil moisture ranking as most important parameter for *in-situ* placement, reflecting a relationship with diffusive flux. No significant temperature effects have been reported for ion exchange between 10 to 30° C for N, P, K, and S removal. An effect was observed between 4 to 10C° for N and S, and may reflect the effect of increasing viscosity of water at low temperatures (Qian and Schoenau, 1997). These moisture and

temperature effects on IEM efficiency are important, and not necessarily limitations, since these factors also effect plant uptake of nutrients.

While IER technology provides an interesting and dynamic alternative to traditional extraction techniques, there are still many inconsistencies in how IER is used, and some caution needs to be used when comparing IER results from different studies (Skogley and Dobermann, 1996; Qian and Schoenau, 1997). The greatest differences are in resin type or form, duration of burial (which may reflect soil processes differently, especially for very short burials), removal of soil particles from the IER prior to extraction, different concentrations and/or volume of elution solutions, regeneration of the ion exchange sites, and lastly, unit expression of results. Those who have provided reviews of the technology and use of IER (e.g. Dobermann et al., 1994; Skogley and Dobermann, 1996; Qian and Schoenau, 1997) have brought these potential discrepancies forward with a call for more standardization. More studies are needed to compare the different resin types under different conditions, in controlled settings as well as in the field.

The objectives of the studies presented here were (1) to analyze the effects of harvest intensity and site preparation on nitrogen availability and tree growth during year ten (2001) of the USDA Forest Service Long-Term Soil Productivity (LTSP) study in North Carolina; (2) to carry out an eight-week methodology study with *in-situ* IER bags and IEM and laboratory aerobic incubations to compare soluble N indices (summer 2001); and (3) to compare recovery rates from IER bags and IEM in solutions of known

concentrations of NH_4 and NO_3 and with repeated elutions (data included in appendix C; analysis forthcoming).

Background for the USDA Forest Service Long-Term Soil Productivity program:

Powers et al. (1989) provides an in depth review of long-term and retrospective studies and concludes that, where there have been documented declines in site productivity, organic matter loss and decreases in soil macroporosity have consistently been results of site management. At the 7th North American Forest Soils Conference, Powers et al. proposed a Long-Term Soil Productivity (LTSP) program to evaluate the fundamental relationships between soil type, long-term productivity, and forest management practices

A standardized experimental design was developed by the USDA Forest Service and, in coordination with National Forest System, was put in place across the United States and in Canada on a gradient of site and climatic conditions. The treatments, focusing on organic matter removal and soil compaction, depict the extremes of these factors, so that all current management practices would fall within the bounds of the experiment. The null hypotheses being tested by the LTSP program are (1) that pulse changes in SOM and/or soil porosity do not have sustained impacts on a site's productive potential; (2) that any treatment impacts will occur across climate and soil variations; (3) that any impacts documented can be ameliorated; and (4) that plant diversity has no impact on a site's productive potential (Powers, 1999).

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2. Nitrogen differentiation by laboratory aerobic incubations compared with *in-situ* ion exchange resin beads and membranes

INTRODUCTION:

The proportion of soluble nutrients in the soil is low, typically only 1 to 2% of the total quantity is available for plant uptake (Brady and Weil, 1999). Soils differ greatly in their ability to supply nutrients necessary to sustain forest productivity. The buffering capacity of a soil affects the concentration of plant-available nutrients in the soil solution, while the supply of nutrients at any given time is influenced by the net balance of nutrients that are being added and removed from the soil system. Nutrients become available for plant-uptake through processes such as mineralization, N₂ fixation, weathering, atmospheric deposition, and fertilization. Nutrients become unavailable for plant uptake through immobilization by soil microorganisms and through chemical and mineralogical reactions including precipitation and adsorption reactions and ionic fixation within the lattice network in clay minerals.

Nitrogen (N) is an essential plant nutrient which plays a role in determining the uptake of other essential nutrients, such as potassium (K) and phosphorous (P). Nitrogen is often a limiting factor in many forest ecosystems and, because N availability is relatively sensitive to environmental changes, it is often targeted as a key process or indicator of site disturbance (Keeney, 1980; Munson et al., 1993). Bound mostly within soil organic matter, N must first be released through microbial decomposition or mineralization, an enzymatic process through which complex proteins and associated compounds are simplified and hydrolyzed to NH₄. In oxidizing conditions, NH₄ is microbially transformed into NO₃ if the soil environment is favorable (temperature, pH, moisture,

etc.). Annual net N mineralization has been shown to be an important limiting factor for growth in non-fertilized forest production (Nadelhoffer and Aber, 1984).

There are numerous laboratory methods for predicting N mineralization or developing indices of soil N availability, including anaerobic and aerobic incubations, total N, and extractable N analysis (Hart et al., 1994). Nitrogen mineralization is greatly affected by soil microenvironment (soil temperature, soil moisture, aeration) and the accuracy of these tests for providing realistic estimates of plant available N has been challenged because these factors are altered in the laboratory.

The use of ion exchange resins (IER) is gaining in popularity as an alternative method for determining plant-available N *in-situ* and under controlled laboratory conditions. Ion exchange involves the redistribution of ions from solution to the resin via exchange for counter-ions on the exchange resin. This redistribution occurs through diffusion. There are many types and forms of IER, each with their own specific properties that affect their function. Most synthetic ion exchange resins are solid organic polymers with an electrostatic charge, neutralized with a low affinity counter-ion. Skogley and Dobermann (1996) describe the production of most IER as styrene polymerized with itself to produce long chains, which are then reacted with divinylbenzene to produce cross-linkages.

Uncontrolled reactions during this process account for much of the variation in internal porosity (and therefore exchange capacity) that has been seen between batches of resin, as varying degrees of cross-linkage can be obtained. Macroporous IER are the most common resins used in soil studies and, due to their spherical external shape, are referred

to as IER beads. Macro- and micropores are both present in the IER beads with the internal surface areas potentially exceeding $10^5 \text{ m}^2 \text{ kg}^{-1}$. Ion exchange resin in membrane form are becoming a popular form of IER used in soil studies. The chemical structures of the ion exchange membranes (IEM) are very similar to those of the IER beads. The membranes, often made of hydrocarbon or fluorocarbon polymers, are extruded into sheets and combined with reinforcing material to provide dimensional stability and mechanical strength (Skogley and Dobermann, 1996).

The quantity of ions adsorbed on a resin is affected by the rate of soil nutrient mineralization, ion mobility, chemical precipitation, and competition for the soluble nutrients. The high mobility of NO_3 , for example, often leads to higher NO_3 than NH_4 collection in IER and IEM. The quantity of NH_4 recovered from the IER surfaces is very dependent on the volume of water passing through the soil and over the IER. Collection of NO_3 does not appear to be affected in this way (Fisher and Binkley, 2000).

Consequently, IER may differently estimate the availability of inorganic N forms in soil solution.

Many studies have considered the potential of IER as a laboratory testing procedure (Sibbesen, 1977; Schoenau and Huang, 1991; Qian et al., 1992; Skogley, 1992; Somasiri and Edwards, 1992; McLaughlin et al., 1993; Dobermann et al., 1994; Schoenau et al., 1994; van Raji, 1994), as well as how IER compares to other *in-situ* techniques for estimating N mineralization (Binkley and Matson, 1983; Binkley et al., 1986; Lundell, 1989; Hubner et al., 1991; Cooperband and Logan, 1994; Huang and Schoenau, 1996).

The objective of this study was to compare IER in membrane form with IER beads, *in-situ*, to determine if plant-available N indices measured by the two IER forms can be correlated. Correlation between IER in membrane form with IER beads will allow comparison among studies using these different forms.

METHODOLOGY:

Study description:

In 1991 the Southern Forest Research Station cleared a 60-year old natural pine-hardwood stand and established treatment plots on the Croatan National Forest in Craven County, in the Lower Coastal Plain region of North Carolina. Prior to harvest, three 4-hectare blocks were designated. Nine 0.4-hectare plots were established in each block where three levels of organic matter removal and three levels of compaction were combined in a 3 x 3 factorial design. Soil compaction levels ranged from no compaction, to moderate and severe compaction. Organic matter removal treatments included stem-only (only useable stems were removed from the plots), whole-tree (all stems, branches and foliage were removed), and whole-tree plus forest floor (all stems, branches, foliage, and forest floor material organic material were removed).

On the non-compacted plots, tree boles were removed by cranes and the different levels of organic removal were done by hand. On plots receiving moderate compaction, tree boles were removed with skidders and any additional organic removal was done by hand. The forest floor was removed with a bulldozer equipped with a shear blade on the severe compaction treatment plots. Biomass and N removals associated with the organic matter

removal were 37,000, 168,000, and 218,000 kg biomass ha⁻¹, and 46, 146, and 500 kg N ha⁻¹, on the stem-only, whole-tree, and whole-tree plus forest floor treatments, respectively (USFS SRS RWU-4154, unpublished data).

The mineral soil was compacted with a vibrating drum roller, without vibration for moderate compaction and with full vibration for severe compaction. To create better conditions for severe compaction on the stem-only and whole-tree plots, branches, foliage, and other forest floor material were removed prior to compaction and then redistributed by hand. Post-treatment, the average soil bulk density in the surface 15 cm was 1.28 and 1.48 g cm⁻³, for the non-compacted and severely compacted plots, respectively (USFS SRS RWU-4154, unpublished data). There was no statistically significant difference in soil bulk density between the moderately and severely compacted plots.

After the treatments were in place, each 0.4-hectare plot was split into two 0.2-heactare plots for vegetation control treatments (no control and complete control). Complete vegetation control is obtained by repeated applications of Accord herbicide and manual removal of understory growth with a handsaw as necessary. More details regarding the treatments and project design were reported by Powers et al. (1990).

The effects of harvest intensity and site preparation on nitrogen availability and tree growth were assessed for eight weeks (in June and July 2001) of the tenth growing season using traditional IER beads enclosed in nylon bags and the alternative IER

membranes. In this study, only the no compaction and severe compaction treatments, across all three levels of organic matter removal, in the vegetation-controlled plots, were included (Figure 2.1). Four sampling locations per plot were randomly selected by tree number and ordination, and placed 1 meter away from the tree.

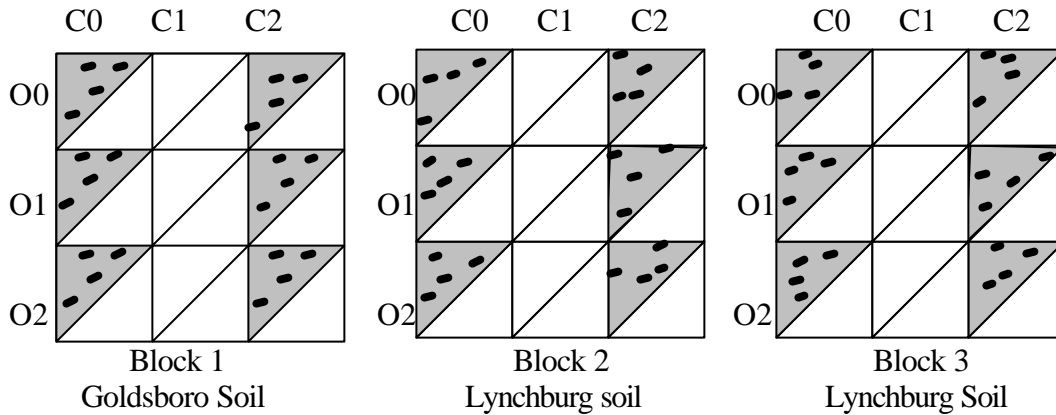


Figure 2.1: Year 10 inorganic N measurements at the Forest Service NC LTSP site in the Croatan National Forest, Craven County, NC. The shaded area indicates the plots receiving complete vegetation control; black dots represent the 4 random sample locations within each plot. C0, C1, and C2 indicate compaction levels of none, moderate, and severe, respectively; O0, O1, and O2 indicate organic matter removal levels stem-only, whole-tree, and whole-tree plus forest floor, respectively.

Site description:

The Croatan LTSP site was blocked to account for soil drainage characteristics. Block 1 consists primarily of moderately well drained Goldsboro soil (fine-loamy, siliceous, thermic aquic Paleudults) while Blocks 2 and 3 consist of somewhat poorly drained Lynchburg soil (fine-loamy, siliceous, thermic Aeric Paleaquults). Block 3 is more poorly drained than Block 2.

Depths of O and A horizons were measured in December 2001, by augering holes at each sampling location. The average depth of the O horizon at the sample sites varied among the 3 blocks, with the shallowest depth in the drier Goldsboro soil in block 1 and increasing with wetness to the more poorly drained Lynchburg soil in Block 3 (Table 2.1). Depths of O horizon also varied within each block, in reverse order of organic matter removal treatments. Two of the eight sampling locations of the whole tree removal treatment in block 3 were located in depressions, and had deeper than expected O horizons. The texture of A horizons of each treatment plot, in all three blocks, was estimated by the hand-feel method as sandy-loam. The average depths of the A horizon in Blocks 1, 2, and 3 are 23, 16, and 19 cm, respectively; within each block there was large variation in depth to gray soil, indicating differences in seasonal high water tables.

Average pH in the surface 0 to 5 cm also varied among the three blocks (Table 2.1). The Goldsboro soil in Block 1 ranged from a pH of 3.6 to 5.2, and averaged 4.2; the Lynchburg soil in Blocks 2 and 3, ranged from pH values of 3.5 to 4.5 and 3.2 to 4.4 with averages of 3.9 and 3.8, respectively.

Table 2.1. Average depths of O and A horizons, depth to gray soil, and average pH by block.

Block	Ave. depth of O Horizon (cm)	Ave. depth of A Horizon (cm)	Depth to Gray (cm)			Ave. pH (0-5 cm)
			Min.	Max.	Ave.	
1	1	23	5	38+	24	4.2
2	2	16	4	25+	13	3.9
3	2	19	4	30+	19	3.8

Only the A horizon was characterized, therefore '+' indicates the deepest measured A horizon without gleying.

Volumetric soil moisture was measured on each sample date with a MoisturePoint TDR (Environmental Sciences, G.S. Gabel Corporation, Canada) automatically calibrated for a sandy-loam texture. The TDR probes were 20 cm in length, and represented average water content over the 20-cm depth. This data was used to help explain the variability in recovered inorganic N from the PRS™ probes and IER bags.

An on-site weather station measured precipitation and temperature during the two-month period of June and July. Total rainfall was 12 cm and the average air and soil temperatures were 24.6°C and 21.9°C, respectively. Precipitation, and soil and air temperature data for June and July 2001 are summarized in Table 2.2.

Table 2.2: Mean temperature, precipitation, and volumetric soil moisture data for June and July 2001 Croatan LTSP site.

Month	Mean temp (°C)		Total precipitation (cm)	Soil moisture (cm ³ /cm ³)
	Air	soil at 10 cm		
June*	24.7	21.3	0.2	24.4
July	24.4	22.5	11.8	23.5

*Some temperature and precipitation data missing for June

Plant root simulator probes:

Plant root simulator probes (PRS™), available from WesternAg Innovations¹ (Saskatoon, Saskatchewan, Canada), were used to measure plant-available N in the soil solution.

PRS™ probes are pretreated anion and cation exchange membranes encased in a plastic

¹Use of trade names does not constitute an endorsement by either North Carolina State University or the USDA Forest Service.

probe form (Figure 2.3). The PRSTM probes are 15 cm long and approximately 3 cm wide, each membrane is approximately 5 cm long and has a total surface area of 17.5 cm². These probes have a maximum ion capacity of 590 μg NO₃ and 2740 μg NH₄ 10⁻¹ cm⁻² anion and cation resin, respectively (WesternAg Innovations Inc., 2001).

At each sampling location, roots were severed with a shovel to a depth of 25 cm in a 25-cm diameter circle to ensure measurement of net N mineralization, as opposed to nutrient surpluses after root uptake. In this way, roots were appropriately hindered while maintaining soil water exchange throughout the sampled area. Roots were re-severed on a monthly basis.

Thin vertical slits were made for 0 to 5-cm and 5 to 10-cm sampling depths, which enabled evaluation of the interface between the Oa and A horizons and the 5 to 10-cm portion of the A horizon. Plant Root Simulator (PRSTM) probes containing anion and cation resin membranes were inserted to each depth (Figure 2.2), and the soil then gently repacked at the surface to ensure contact between the resin membrane and the soil. Each PRSTM probe was collected and replaced with a recharged probe every two weeks.

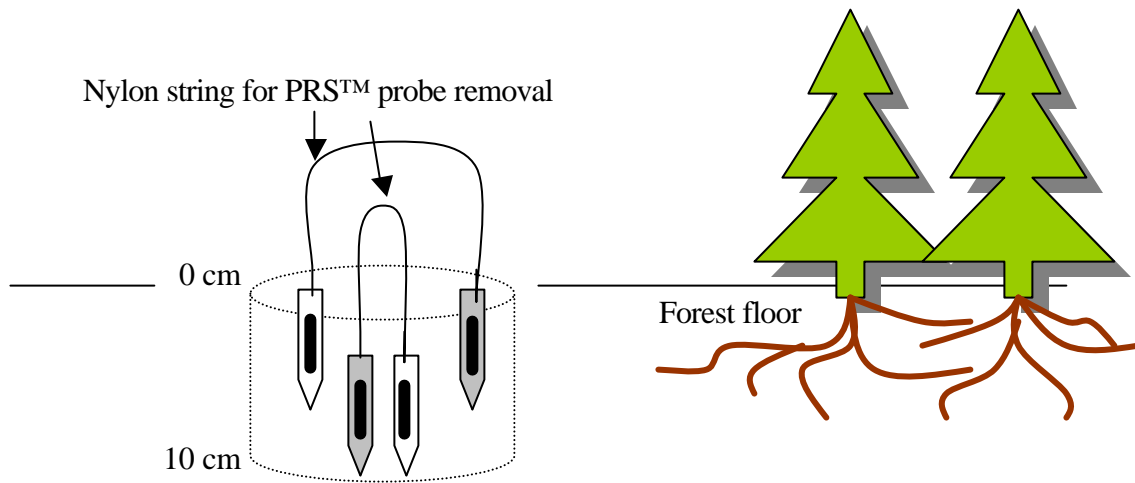


Figure 2.2: Placement of PRS™ probes is depicted within the 25-cm cylinder where roots were severed. The white probes represent the anion exchange membranes and shaded probes represent the cation exchange membranes. (Note that trees are not depicted to scale)

Resin bags:

Resin bags were constructed out of nylon mesh and included two sections, one with 10 g Sybron IONAC ASB-1POH anion resin beads, and the other with 10 g Sybron IONAC C-251 H⁺ cation resin beads (Sybron Chemicals Inc., Birmingham, NJ). The dimension of each resin bead section was approximately 4 x 4 cm, and a band of heat-applied glue separated the sections and sealed all ends (Figure 2.3).

A bulb planter, with an approximate diameter of 10 cm, was used to remove cores of soil to 5- and 10-cm depths. Resin bags were placed 25 to 30 cm away from the PRS™ probes, at each depth (Figure 2.4) and at each of the four sampling locations, before the soil was carefully replaced. By removing a soil core, roots were effectively severed

similarly for resin bags and PRSTM probes. Unlike the probes, the resin bags were left in place for the entire eight weeks.

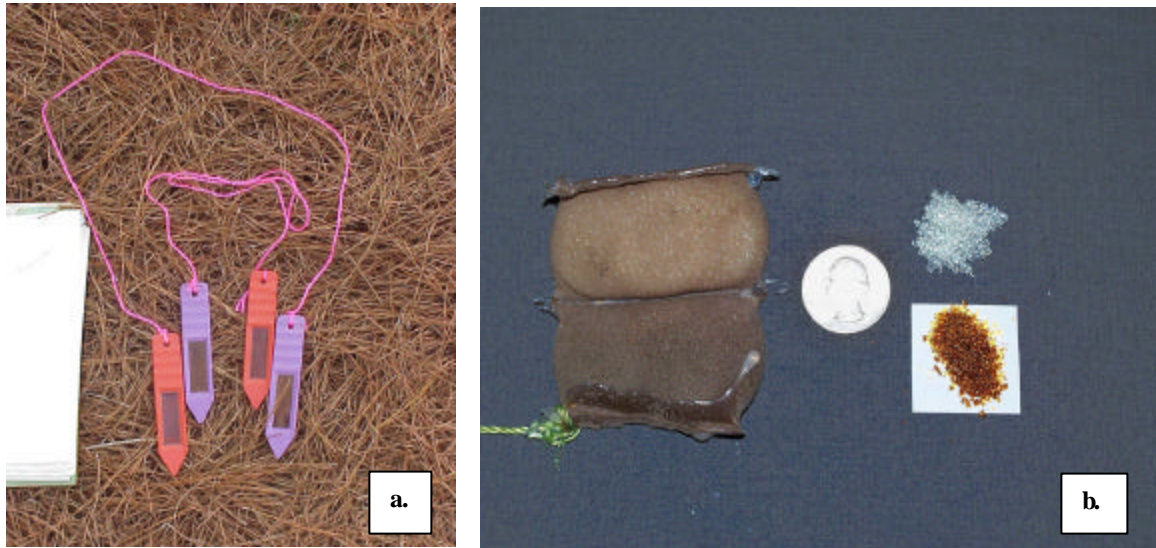


Figure 2.3: (a.) PRSTM probes from WesternAg Innovations. Red probes contain anion exchange membranes; purple probes contain cation exchange membranes. A full size clipboard provides scale. (b) Resin bag and loose cation (brown) and anion (yellow) beads from Sybron.

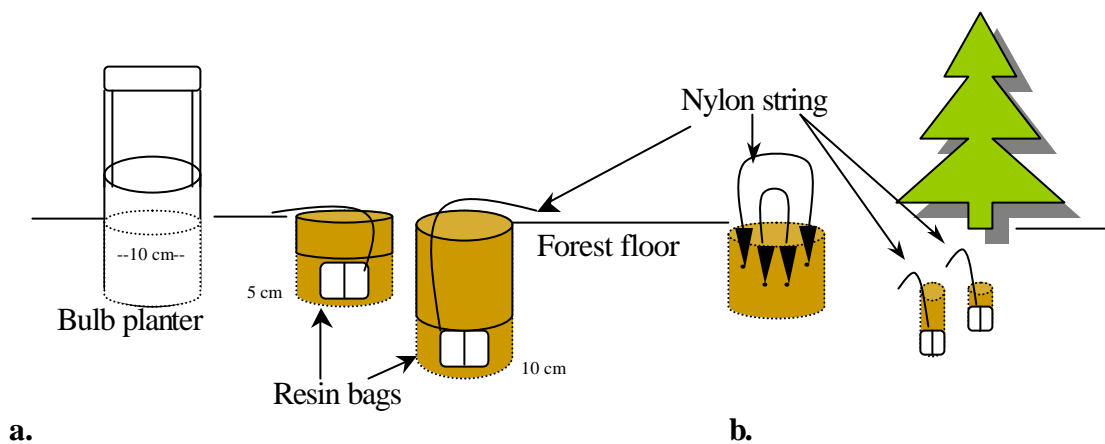


Figure 2.4: a. Depiction of bulb planter being used to sever roots and core soil; IER bags covered with soil cores at depths 5 cm and 10 cm. b. IEM and IER bags in place.

Aerobic incubations:

Soil was collected from the 0-5 cm depth approximately 20 cm away from every PRSTM probe and resin bag sample location in order to perform in-lab aerobic incubations at optimum temperature (23 to 25 C°) and moisture (17 to 27 %). The soil was placed in plastic bags. Extractions with 1 M KCl were made on 10 g sub-samples on the bi-weekly schedule used with the PRSTM probes. This data was used to provide mineralization potentials for each sample location.

Chemical Analysis:

In the laboratory, each PRSTM probe was rinsed with de-ionized water to remove soil particles, put into Ziploc[®] freezer bags, and eluted with 17.5 mL of 1 M KCl solution. The bags were then placed on a side-to-side shaker at low speed for one hour. After collecting and storing the KCl extractant, the PRSTM probes were recharged in a soaking solution of 0.5 M NaHCO₃ and placed on a side-to-side shaker for one hour before discarding the recharging solution. This recharging process was repeated four times before placement of the PRSTM probes in the field to ensure complete regeneration of the IEM exchange sites.

Elutrient from each PRSTM probe and aerobic incubation sample was analyzed for NO₃ and NH₄ on a LACHETTM colorimetry instrument. The resin bags were removed from the soil after eight weeks and sent to Colorado State University for analysis where an eluting solution of 100 mL 2M KCl was used for each IER bag. The elutrient was analyzed for NO₃ and NH₄ using colorimetry techniques.

Statistical Analysis:

The data from the resin bags and PRS™ probes were analyzed using analysis of variance (ANOVA) for a randomized block split-plot design, with three blocks and depth as the split-factor. As no significant depth or depth interaction was found, data was summed over the two depths in the analysis, and depth was removed from the model. Analysis of variance for the aerobic incubation data was analyzed as a randomized block design with sub-sampling and three blocks. The compaction and organic matter removal treatments were considered as strip-plots, the four sampling locations within each plot were considered sub-samples. Duncan's Multiple Range Test was used to compare differences in the effects of organic matter removal on N mineralization when significance was indicated in the ANOVA. All statistical analysis was carried out using SAS software (SAS Institute, 1986).

RESULTS:

PRS™ probes:

During the two-month method comparison study, the PRS™ probes showed significantly different indices of N mineralization rates between blocks ($p < 0.001$), but no treatment effects were found at year ten (Table 2.3). Block 1, consisting primarily of Goldsboro soil, mineralized $63 \mu\text{g N } 10^{-1} \text{ cm}^{-2}$ resin over the two-month period, while blocks 2 and 3, both primarily Lynchburg soil, each mineralized $40 \mu\text{g N } 10^{-1} \text{ cm}^{-2}$ resin (Figure 2.5). Greater nitrification was measured on the drier Goldsboro soil of Block 1, compared with the wetter Lynchburg soil in Blocks 2 and 3 (Figure 2.6).

Table 2.3. Probability values (p>f) for inorganic N by treatment as recovered from PRS™ probes.

Inorganic N	Treatment Effects								r ²
	Block	OM	COMP	OM x COMP	Depth	Depth x OM	Depth x Comp	Depth x OM x Comp	
NH ₄	0.183	0.737	0.455	0.261	0.899	0.968	0.967	0.659	0.34
NO ₃	0.019	0.566	0.184	0.320	0.237	0.656	0.541	0.227	0.50
N _{total}	<0.001	0.685	0.267	0.282	0.616	0.885	0.722	0.996	0.45

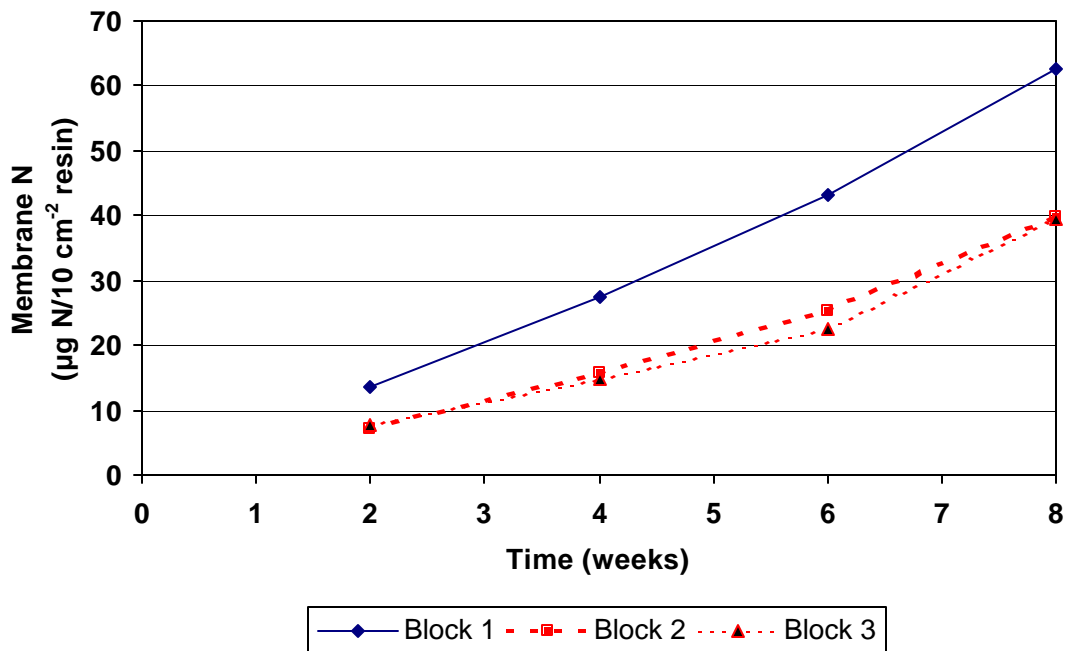


Figure 2.5: Mean membrane-N (NO₃ plus NH₄) accumulation by block during June and July 2001 at the Croatan LTSP site, using the PRS™ probes.

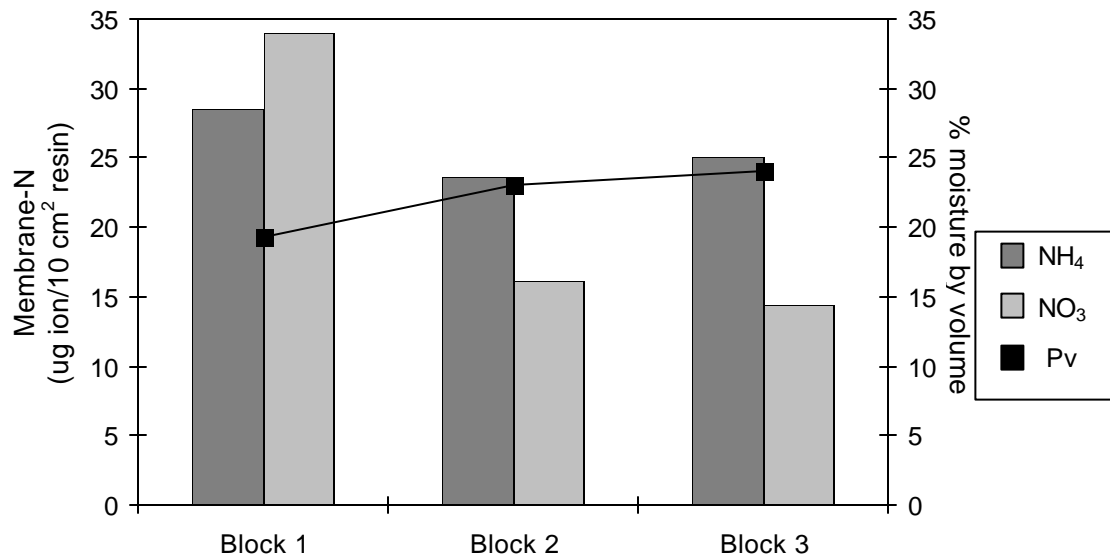


Figure 2.6: Cumulative NO₃ and NH₄ form using PRS™ probes and soil moisture averaged for each block during June and July 2001.

IER bags:

Upon retrieval of the resin bags, resin was lost from 11 of the 144 bags due to holes in the mesh. Decomposition of the nylon material and in some instances, root growth through the bag, made complete recovery of the resin beads problematic. The IER elutriant showed a significant ($p=0.099$) effect of compaction on total inorganic N (Table 2.4). Non-compacted soils mineralized significantly more N than the compacted soils, with 190 and 182 $\mu\text{g N}$ per resin bag measured respectively. It is important to note, however, that of the 133 resin bags analyzed, 56% contained too little NH₄ to be detected. Due to this fact, only total inorganic N was used for comparison.

Table 2.4. Probability values (p>f) for inorganic N by treatment as recovered from IER bags.

Inorganic N	Treatment Effects								
	Block	OM	COMP	OM x COMP	Depth	Depth x OM	Depth x Comp	Depth x OM x Comp	r ²
NH ₄	0.077	0.285	0.064	0.112	0.030	0.270	0.111	0.385	0.65
NO ₃	0.296	0.145	0.227	0.197	0.220	0.153	0.392	0.244	0.51
N _{total}	0.157	0.701	0.099	0.191	0.112	0.195	0.962	0.546	0.59

Aerobic incubations:

A significant (p=0.084) effect of organic matter removal on total inorganic N (Table 2.5 and Figure 2.7) was measured using the aerobic incubation technique. Stem-only and whole-tree removal treatment plots produced similar amounts of inorganic N (44 and 46 $\mu\text{g N g}^{-1}$ soil, respectively) during the eight-week incubation period, while soil N in the whole-tree plus forest floor treatment was significantly lower (28 $\mu\text{g N g}^{-1}$ soil).

Table 2.5. Probability values (p>f) for inorganic N by treatment extracted during the aerobic incubation.

Inorganic N	Block	Treatment Effects				r ²
		OM	COMP	OM x COMP		
NH ₄	0.681	0.066	0.513	0.977	0.46	
NO ₃	0.048	0.732	0.085	0.909	0.56	
N _{total}	0.806	0.084	0.209	0.940	0.47	

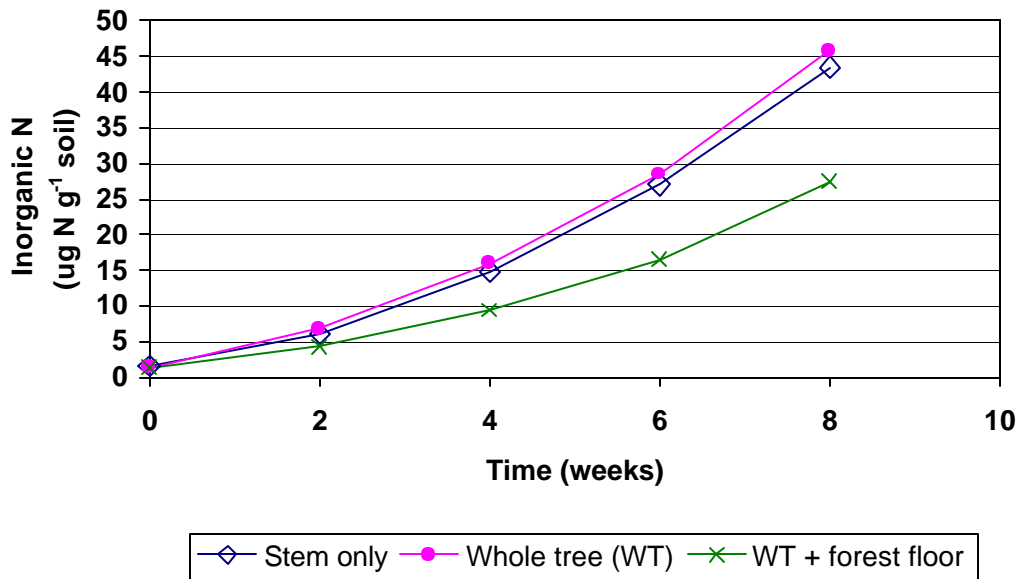


Figure 2.7: Cumulative N mineralization over an eight-week aerobic lab incubation. Samples from the Croatan LTSP site.

Methods comparison:

To compare IER bags and PRS™ probes with aerobic incubation results, sub-sets of the data were re-analyzed, omitting data from the 5 to 10-cm depth. Limited to the 0 to 5-cm depth, the PRS™ probes still showed a significant block effect ($p=0.002$) on N mineralization, but compaction differences were no longer significant using IER bags.

Unlike the PRS™ probe and resin bag data, very little nitrification was measured in the controlled laboratory incubations indicating perhaps higher immobilization rates in the controlled environment. Figure 2.8 shows the cumulative data from the eight-week study for all three techniques, normalized to a scale of 0 to 1 where a value of 1 represents the largest amount of NH_4 or NO_3 recovered from the PRS™ probes or resin bags, or measured during the aerobic incubation. This allows for a more direct comparison

between the methods, as all data are on the same scale. Averages for block and main effect treatments are used because no treatment interactions were found.

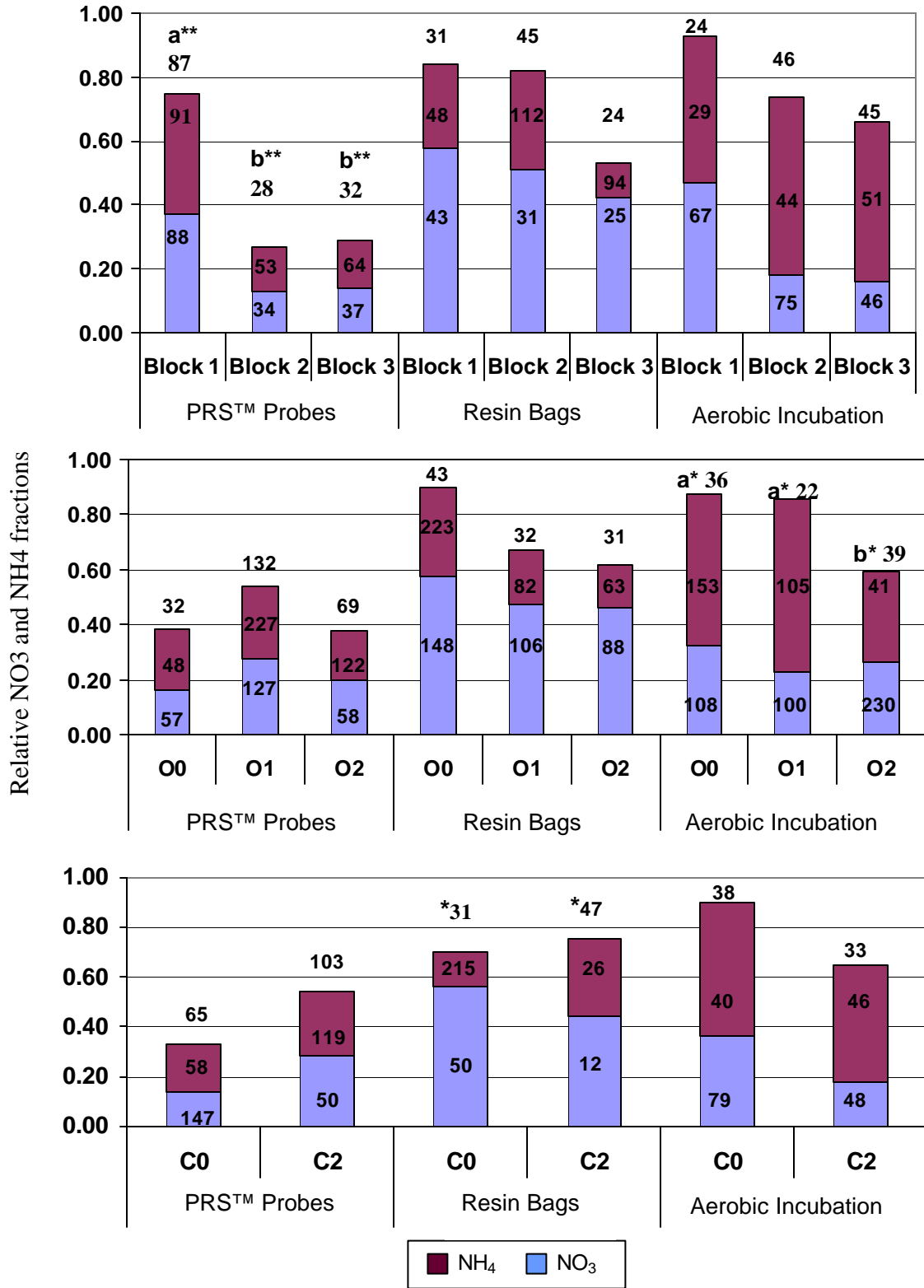


Figure 2.8. Block and main treatment effects on NO₃ and NH₄ measured during the 8-week study with PRSTM probes, resin bags, and during aerobic incubations. Data was normalized to a scale of 0 to 1 to enable comparison of the three techniques. Where appropriate within a method, Duncan's comparison is indicated with a and b. ** indicates significance for total inorganic N at p=0.05, * indicates significance at p=0.1. CVs are included to indicate variability within each method.

A significant correlation between inorganic N measured by IER bags and PRSTM probes was not found during this experiment. Figures 2.9 through 2.11 show regression analysis of the three methods of measuring inorganic N. Because the study was of fairly short duration, and the resin bags were only sampled at the end of the eight-week period, only one data point was available for comparison. The high variation typical of forest soil was also compounded by difficulties encountered when retrieving and processing the resin bags. The majority of the cation resin bags yielded NH₄ concentrations below the analytical detection limit (0.01 mg N L⁻¹). This could be a result of the eluting dilution factor of 100 mL 2M KCl, or an indication that the IER beads are not suitable in lower fertility or unfertilized soils. The three-dimensional physical structure of IER beads may result in lower surface area contact with the soil or lower recovery rates from the beads due to the tortuosity associated with high internal micropore space if there is incomplete ion recovery.

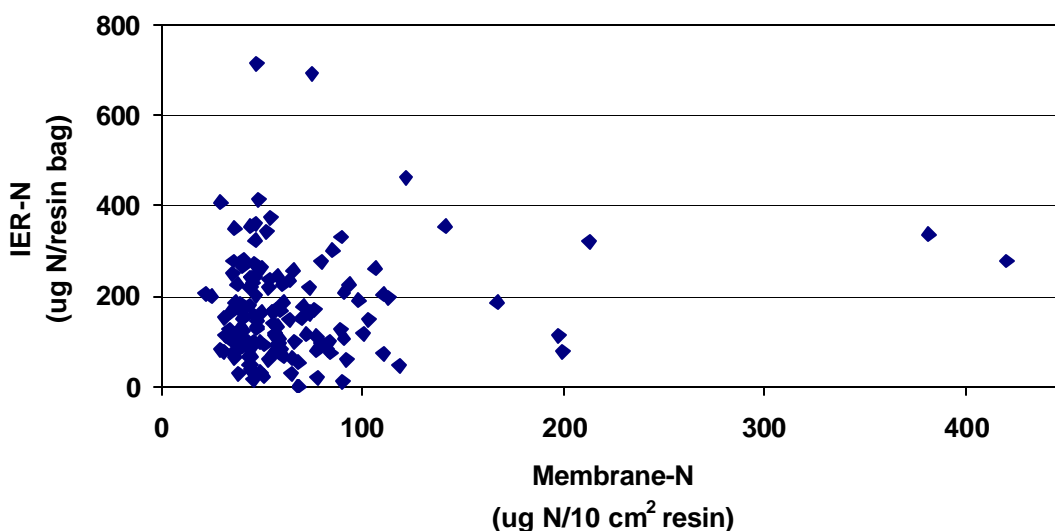


Figure 2.9: Regression analysis of soil inorganic N measured using the resin bag and PRSTM probe techniques in the 0 to 5 cm depth during the 8-week study at the Croatan LTSP site.

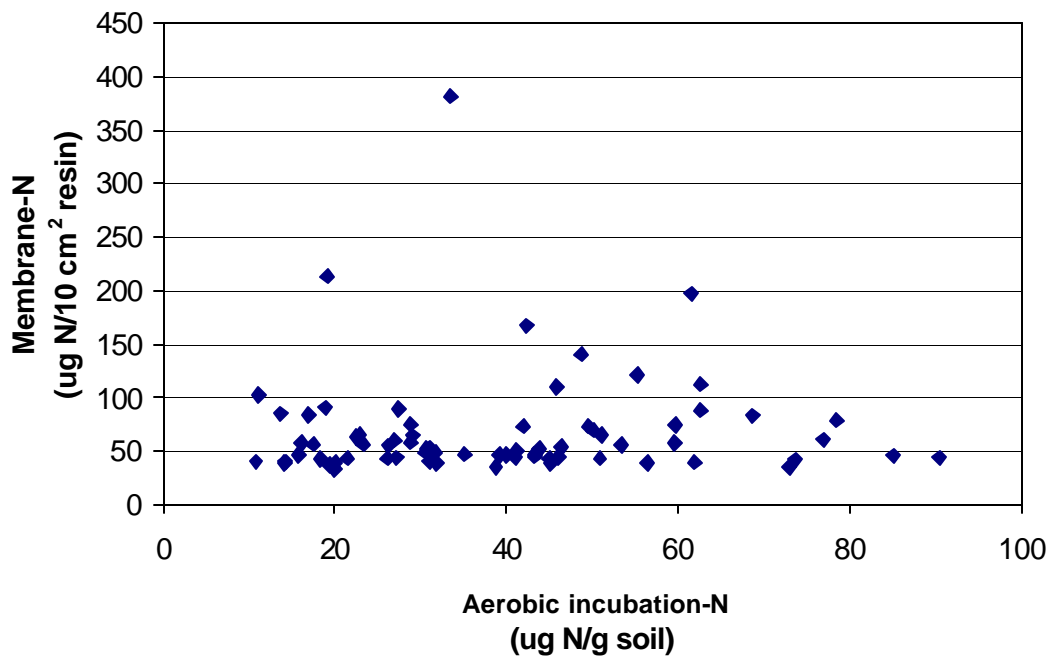


Figure 2.10: Regression analysis of soil inorganic N measured using the PRSTM probe and aerobic incubation techniques in the 0 to 5 cm depth during the 8-week study at the Croatan LTSP site.

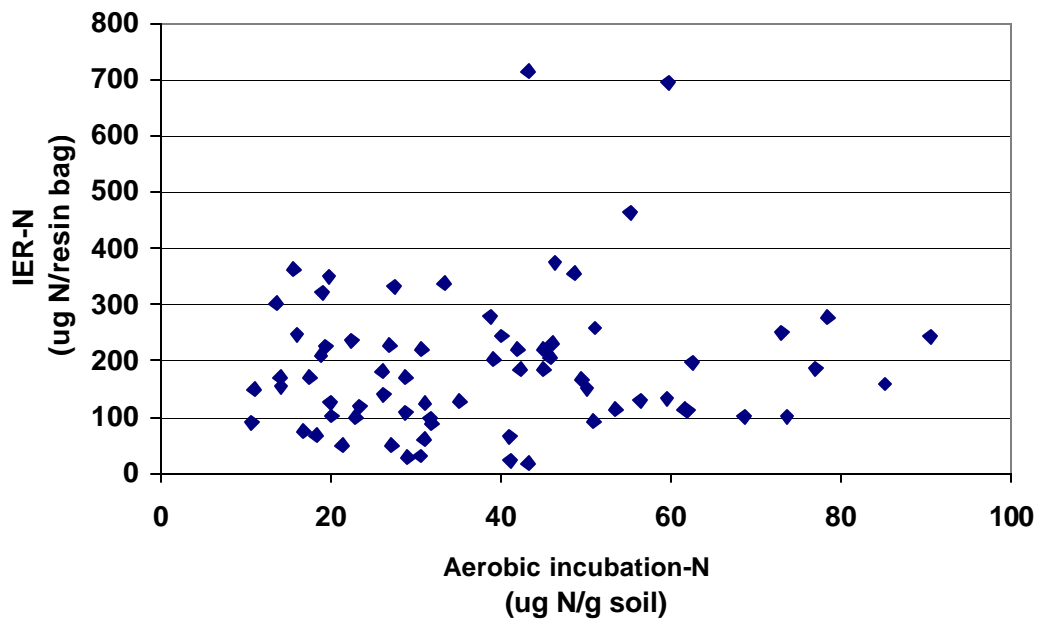


Figure 2.11: Regression analysis of soil inorganic N measured using the resin bag and aerobic incubation techniques in the 0 to 5 cm depth during the 8-week study at the Croatan LTSP site.

DISCUSSION AND CONCLUSIONS:

The planar surface of IEM is similar to the surface area of plant roots, while the physical shape of resin beads likens them more to the shape of a soil particle. These differences in the physical properties of IER bags and PRS™ probes are an important consideration in their use. The benefits of using the membrane form of ion exchange resins include minimizing soil disturbance and simplifying repeated measurements in the same area over time. Though the membranes may tear or the plastic casings may break, only thin slits in soil are necessary for insertion at shallow depths and extraction of the membrane for analysis is always possible. Quantification of recovered ions using PRS™ probes are based on surface area exposure of the ion exchange membrane and are reported as micrograms of ion 10^{-1} cm^{-2} resin. The resin beads used in the bags are spherical with a high degree of porosity, both between beads and internal to the bead, and therefore have a more geometrically complex ion exchange capacity. The necessity of burying the IER bags makes it difficult to sample the same area repeatedly; as a result, resin bags are often left in place for longer periods of time, increasing the chances of deterioration of the bag material.

The standard extraction procedure of using 100 mL 2 M KCl to elute the resin bags has reportedly worked well in fertilized soils (Binkley and Matson, 1983), but in this study, the 100 mL extraction volume diluted the ions collected below the analytical detection limits. Studies using resin beads often report findings as micrograms of ion per resin bag or per gram of dry resin weight, however, resin bead geometry can vary from batch to batch, affecting the total actual surface area and the maximum ion capacity. Though IEM

has no internal exchange sites, the maximum ion capacity of 590 $\mu\text{g NO}_3^- \text{-N}$ and 2740 $\mu\text{g NH}_4^- \text{-N}$ 10^{-1} cm^{-2} resin was never reached in the unfertilized soil during the two-week sampling periods.

Nutrient recovery using IER, in bead or membrane form, is considered an index of plant-available N and not a quantification of ion availability. Results from this study indicate poor correlation among the three methods, and are understandable when the inherent limitations of each method are considered. For example, aerobic incubations reflect N mineralization under optimum temperature and moisture conditions in the laboratory. There is increased soil disturbance associated with soil sample collection with this method, and though the information is useful in providing mineralization potentials, the data does not necessarily reflect field conditions or field nitrogen mineralization rates. Microbial activity in the organic matter layers in the top 5 cm of soil was potentially stimulated by the disturbance and under the ideal environmental conditions of the laboratory. Inherent in the placement of the IER bags (removal of soil cores), increased soil disturbance is associated with this technique than with PRSTM probe placement. Though care was taken during the removal and replacement of the soil cores to minimize disturbance during IER bag installment, it seems probable that additional disturbance occurring during installation may sufficiently alter the compaction treatments enough to alter the results reported. The PRSTM probes have the advantage that they reflect both *in-situ* environmental conditions as well as minimizing soil disturbance.

Correlation of the three methods for estimating plant-available N will be impacted by a number of factors. Laboratory and greenhouse studies typically show high correlation between traditional extraction techniques and IER bags and IEM probes (e.g. Binkley and Matson, 1983; Hubner et al., 1991; Qian et al., 1992; Skogley, 1992; Somasari and Edwards, 1992; Schoenau et al., 1994; McLaughlin et al., 1993; van Raji, 1994). However, when methods performed under controlled laboratory conditions are compared with *in-situ* methods, a correlation usually is not found (Binkley and Matson, 1983). Subtle variations in microclimate, moisture extremes, as well as diurnal environmental fluxes are not relevant in a controlled setting. Environmental variations play a role in determining the type and amount of nutrients available for root uptake *in-situ*, but the causes of variation are inter-related and often confounding. Controlling variation in the laboratory yields valuable information about soil processes, yet data acquired in the field most closely represents the reality of the forest soil system.

This field study has prompted controlled laboratory studies directly comparing the two forms of IER under varying N concentrations and with repeated elutions to measure recovery rates. The benefits of both IER field methods warrant further study. Though IER in membrane-form seems to provide simpler field and lab procedures, the majority of the published research to date is primarily related to the use of IER beads. To validate the use of IER and to ensure appropriate comparisons between methods and across sites can be made, further laboratory and field studies are needed.

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3. Nitrogen form and availability measured with ion exchange resin in a Loblolly pine stand on the Coastal Plain of North Carolina

INTRODUCTION:

Long-term site productivity is a function of both biotic (species and genotype) and abiotic factors (soil productivity, slope, and precipitation) (Morris and Miller, 1994), and can be defined generally as maintaining or increasing biomass productivity on a given site over time. Physical, chemical, and climatic factors interacting within a biological framework characterize a site's productive potential (Powers et al., 1990; Fox, 2000). The most dynamic factor influencing a site's productive potential is soil productivity (Powers et al., 1990). Soil productivity includes the ability of a soil to provide support, water, and nutrients to trees and plants. This, in part, is maintained through the activity of a large range of soil biota that contribute to the development of soil structure, decomposition of organic matter, and nutrient mineralization and transformation.

Forests are subject to large-scale disturbances by harvesting and site preparation. An important question raised by forest soil scientists is whether soils can sustain the long-term needs of forest stands under intensive site preparation practices, shortened rotations, and/or higher utilization standards (Stone, 1987; Powers et al., 1990). Sustaining forest long-term site productivity requires an understanding of the processes that affect the ability of a soil to supply necessary nutrients and water and of the regulation of competition for resources (Kimmins, 1994).

The proportion of soluble nutrients in the soil is low, typically only 1 to 2% of the total quantity is available for plant uptake (Brady and Weil, 1999). Soils differ greatly in their

ability to supply nutrients necessary to sustain forest productivity. The buffering capacity of a soil affects the concentration of plant-available nutrients in the soil solution while the supply of nutrients at any given time is influenced by the net balance of nutrients that are being added and removed from the soil system. Nutrients become available for plant uptake through processes such as mineralization, N_2 fixation, weathering, atmospheric deposition, and fertilization. Nutrients become unavailable for plant uptake through immobilization by soil microorganisms and through chemical and mineralogical reactions including precipitation and adsorption reactions and ionic fixation within the lattice network in clay minerals.

Nitrogen (N) is an essential plant nutrient which plays a role in determining the uptake of other essential nutrients, such as potassium (K) and phosphorous (P). Nitrogen is often a limiting factor in many forest ecosystems and because N availability is relatively sensitive to environmental changes, it is often targeted as a key process or indicator of site disturbance (Keeney, 1980; Munson et al., 1993). Bound mostly within the soil organic matter complexes, N must first be released through microbial decomposition or mineralization, an enzymatic processes through which complex proteins and associated compounds are simplified and hydrolyzed to NH_4 . In oxidizing conditions, NH_4 may be microbially transformed into NO_3 if the soil environment is favorable (temperature, pH, moisture, etc.). Annual net N mineralization has been shown to be an important limiting factor in non-fertilized forest production (Nadelhoffer and Aber, 1984).

The use of ion exchange resins (IER) is gaining interest as a method for determining plant-available N in forest soils. Ion exchange resin in membrane-form (IEM) have chemical structures similar to those of IER beads. They are constructed with reinforcing material that provides dimensional stability and mechanical strength (Skogley and Dobermann, 1996), increasing their durability and potential for reuse.

The ability to accurately measure plant-available N in forest soils is critical to our understanding of management impacts on nutrient availability and long-term site productivity. In an effort to evaluate the fundamental relationships between soil type, long-term productivity, and forest management practices, a standardized experimental design was developed. The USDA Forest Service, in cooperation with the National Forest System, installed research sites in the United States and in Canada across a gradient of site and climatic conditions. The treatments, focusing on organic matter removal and soil compaction, depict the extremes of these factors so that all current management practices would fall within the bounds of the experiment. Management practices, such as site preparation and vegetation control can significantly impact both the quantity and quality of SOM. At the 7th North American Forest Soils Conference, Powers et al. (1990) proposed a Long-Term Soil Productivity (LTSP) program based on the program described by Sollins et al. (1983). From an in-depth review of long-term and retrospective studies, Powers et al. concluded that documented declines in forest productivity were linked with organic matter removal and decreases in soil macroporosity resulting from site management.

The presence of above-ground site organic matter (SOM) affects soil physical properties, such as heat and water flux and erosion. Belowground, SOM affects soil chemical and biological properties by acting as an energy source and nutrient reservoir. The presence of SOM as an energy and nutrient source is associated with microbial decomposition, which drives the nutrient cycling within the system. Site organic matter and activity of both macro- and micro- soil organisms have an impact on the development of soil structure by influencing soil aggregation and porosity.

Soil structure in turn, creates the microenvironment that may enable or hinder microbial activity. Soil porosity at the surface affects water infiltration and interacts with elevation to affect run-off rates and erosion potential. Porosity within a soil horizon affects water storage and release and gas exchange and as an integral part of soil structure plays a role in microbial activity. Porosity, or pore size distribution, can be severely changed by the compaction that takes place with the use of heavy equipment in harvesting and site preparation. As pore size distribution changes with compaction, root penetration and development can be negatively affected (Carter et al., 1998).

Organic matter and soil porosity interact to influence nutrient availability and uptake, which along with atmosphere, heat and light, directly relates to forest productivity (Figure 3.1). The question being addressed by the LTSP program is, will impacts on site organic matter and soil porosity affect forest productivity, and if so, for how long? The objectives of this study were to analyze the effects of harvest intensity and site

preparation on nitrogen availability and tree growth during year ten (2001) of the USDA Forest Service LTSP study in North Carolina.

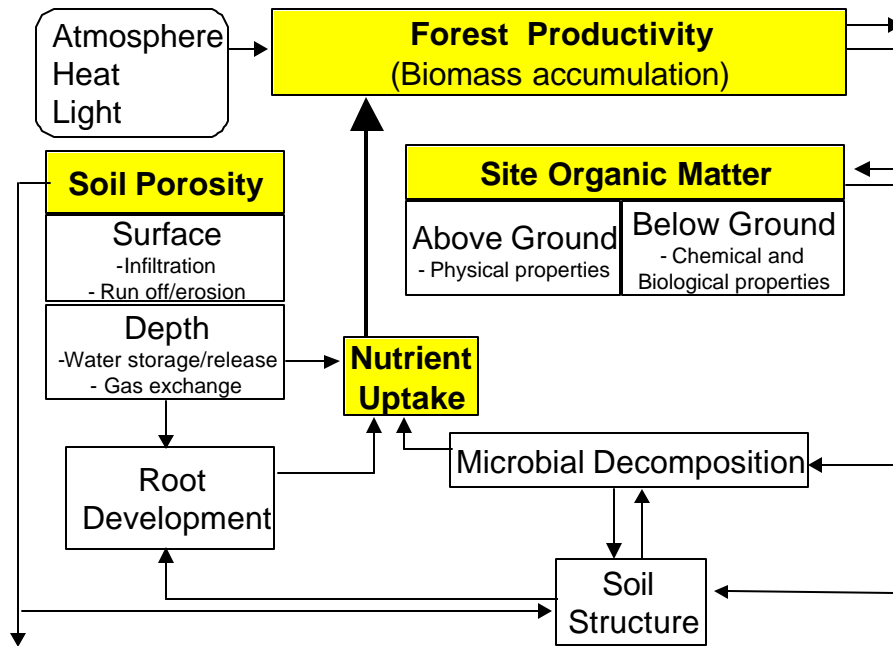


Figure 3.1: Conceptual model of how soil porosity and site organic matter interact to regulate the processes controlling forest growth and site productivity (adapted from Powers et al., 1990).

METHODOLOGY:

Study description:

In 1991 the Southern Forest Research Station cleared a 60-year old natural pine-hardwood stand and established treatment plots on the Croatan National Forest in Craven County, in the Lower Coastal Plain region of North Carolina. Prior to harvest, three 4 - hectare blocks were designated. Nine 0.4-hectare plots were established in each block where three levels of organic matter removal and three levels of compaction were

combined in a 3 x 3 factorial design. Soil compaction levels ranged from no compaction, to moderate and severe compaction. Organic matter removal treatments included stem-only (only useable stems were removed from the plots), whole-tree (all stems, branches and foliage were removed), and whole-tree plus forest floor (all stems, branches, foliage, and forest floor organic material were removed). On the non-compacted plots, tree boles were removed by cranes and the different levels of organic removal were done by hand. On plots receiving moderate compaction, tree boles were removed with skidders and any additional organic removal was done by hand. The forest floor was removed with a bulldozer equipped with a shear blade on the severe compaction treatment plots. Biomass and N removals associated with the organic matter removal were 37,000, 168,000, and 218,000 kg biomass ha⁻¹, and 46, 146, and 500 kg N ha⁻¹, on the stem-only, whole-tree, and whole-tree plus forest floor treatments, respectively (USFS SRS RWU-4154, unpublished data).

The mineral soil was compacted with a vibrating drum roller, without vibration for moderate compaction and with full vibration for severe compaction. To create better conditions for severe compaction on the stem only and whole tree plots, branches, foliage, and other forest floor material were removed prior to compaction and then redistributed by hand. Post-treatment, the average soil bulk density in the surface 15 cm was 1.28 and 1.48 g cm⁻³, for the non-compacted and severely compacted plots, respectively (USFS SRS RWU-4154, unpublished data). There was no statistically significant difference in soil bulk density between the moderately and severely compacted plots.

After the treatments were in place, each 0.4-hectare plot was split into two 0.2-heactare plots for vegetation control treatments (no control and complete control). Complete vegetation control is obtained by repeated applications of Accord herbicide and manual removal of understory growth with a handsaw as necessary. More details regarding the treatments and project design were reported by Powers et al. (1990).

The effects of harvest intensity and site preparation on nitrogen availability and tree growth were assessed for the tenth growing season (2001) using ion exchange resin membranes. In this study, only the no compaction and severe compaction treatments, across all three levels of organic matter removal, in the vegetation-controlled plots, were included (Figure 3.2). Four sampling locations per plot were randomly selected by tree number and ordination, and placed one meter away from the measurement tree.

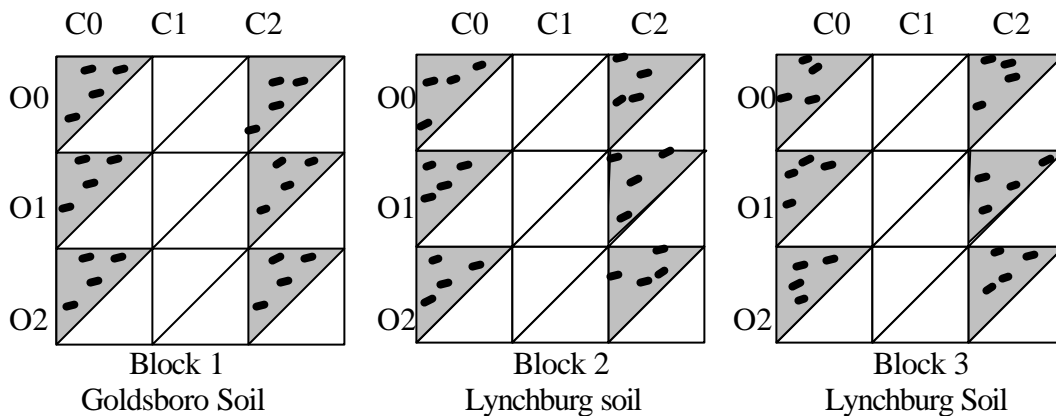


Figure 3.2: Year 10 inorganic N measurements at the Forest Service NC LTSP site in the Croatan National Forest, Craven County, NC. The shaded area indicates the plots receiving complete vegetation control; black dots represent the 4 random sample locations within each plot. C0, C1, and C2 indicate compaction levels of none, moderate, and severe, respectively; O0, O1, and O2 indicate organic matter removal levels stem-only, whole-tree, and whole-tree plus forest floor, respectively.

Site description:

The Croatan LTSP site was blocked to account for soil drainage characteristics. Prior to harvest, three 4–hectare blocks were designated. Block 1 consists primarily of moderately well drained Goldsboro soil (fine-loamy, siliceous, thermic aquic Paleudults) while Blocks 2 and 3 consist of somewhat poorly drained Lynchburg soil (fine-loamy, siliceous, thermic Aeric Paleaquults). Block 3 is more poorly drained than Block 2.

Depths of O and A horizons were measured in December 2001, by augering holes at each sampling location. The average depth of the O horizon at the sample sites varied between the 3 blocks, with the shallowest depth in the drier Goldsboro soil in block 1 and increasing with wetness to the more poorly drained Lynchburg soil in Block 3 (Table 3.1). Depths of O horizon also varied within each block, in reverse order of organic matter removal treatments. Two of the eight sampling locations of the whole tree removal treatment in block 3 were located in depressions, and had deeper than expected O horizons. The texture of A horizons of each treatment plot, in all three blocks, was estimated by the hand-feel method as sandy-loam. The average depths of the A horizon in Block 1, 2, and 3 were 23, 16, and 19 cm, respectively; within each block there was large variation in depth to gray soil, indicating differences in seasonal high water tables.

Average soil pH in the surface 0 to 5 cm also varied between the three blocks (Table 3.1). The Goldsboro soil in Block 1 ranged from a pH of 3.6 to 5.2, and averaged 4.2; the Lynchburg soil in Blocks 2 and 3, ranged from pH values of 3.5 to 4.5 and 3.2 to 4.4 with averages of 3.9 and 3.8, respectively.

Table 3.1. Average depths of O and A horizons, depth to gray soil, and average pH, by block

Block	Ave. depth of O Horizon (cm)	Ave. depth of A Horizon (cm)	Depth to Gray (cm)			Ave. pH (0-5 cm)
			Min.	Max.	Ave.	
1	1	23	5	38+	24.0	4.2
2	2	16	4	25+	12.5	3.9
3	2	19	4	30+	18.7	3.8

Only the A horizon was characterized, therefore ‘+’ indicates the deepest measured A horizon without gleying.

Precipitation and temperature data were collected using a weather station at the Croatan LTSP site. Information from Cherry Point Marine Base was used to supplement on site data. Precipitation for 2001 was 56.9 cm; monthly precipitation and mean monthly temperature data are summarized in Table 3.2.

Table 3.2: Monthly soil and air temperature and precipitation for 2001 at the Forest Service NC LTSP site in the Croatan National Forest, Craven County, NC.

Year 2001	Jan	Feb	Mar**	Apr**	May*	Jun**	Jul	Aug	Sep	Oct	Nov	Dec
-----Average temp (°C)-----												
Soil at 10 cm depth	13.9	10.2	10.7	13.9	15.5	21.3	22.5	23.3	21.5	17.4	14.9	13.9
Air	5.7	9.6	10.1	14.7	18.6	24.7	24.4	25.1	21.3	15.9	13.6	10.9
-----Monthly precipitation (cm)-----												
	2.6	7.6	6.7	3.3	6.7	0.2	11.8	6.8	3.3	2.4	2.8	2.6

*Some temperature data missing for these months

**Some temperature and precipitation data missing for these months

Plant root simulator probes:

Plant root simulator probes (PRSTTM), available from WesternAg Innovations² (Saskatoon, Saskatchewan, Canada), were used to measure plant-available N in the soil solution.

PRSTTM probes are pretreated anion and cation exchange membranes encased in a plastic

²Use of trade names does not constitute an endorsement by either North Carolina State University or the USDA Forest Service.

probe form. The PRSTM probes are 15 cm long and approximately 3 cm wide, each membrane has a total surface area of 17.5 cm². These probes have a maximum ion capacity of 590 µg NO₃ and 2740 µg NH₄ 10⁻¹ cm⁻² anion and cation resin, respectively (WesternAg Innovations Inc., 2001).

At each sampling location, roots were severed with a shovel to a depth of 25 cm in a 25-cm diameter circle to ensure measurement of net N mineralization, as opposed to nutrient surpluses after root uptake. In this way, roots were appropriately hindered while maintaining soil water exchange throughout the sampled area. Roots were re-severed on a monthly basis.

Thin vertical slits were made for 0 to 5-cm and 5 to 10-cm sampling depths, which enabled evaluation of the interface between the Oa and A horizons and the 5 to 10-cm portion of the A horizon. Plant Root Simulator (PRSTM) probes containing anion and cation resin membranes were inserted to each depth (Figure 3.3), and the soil then gently repacked at the surface to ensure contact between the resin membrane and the soil. Each PRSTM probe was collected for laboratory analysis and replaced with a recharged probe every two weeks.

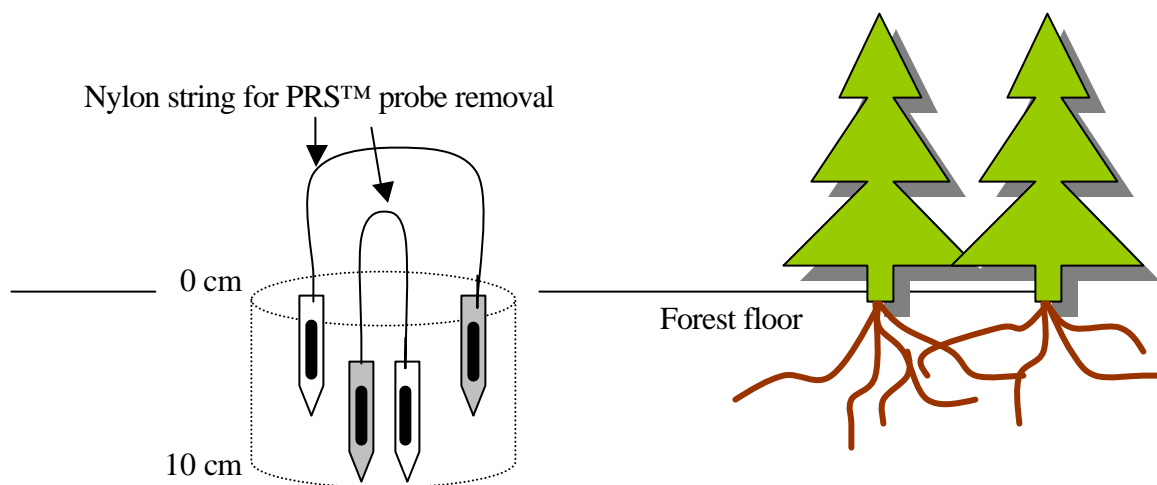


Figure 3.3: Placement of PRS™ probes is depicted within the 25-cm cylinder where roots were severed. The white probes represent the anion exchange membranes and shaded probes represent the cation exchange membranes. (Note that trees are not depicted to scale)

PRS™ probes were collected and replaced every two weeks between February 20 and November 25 2001. In the laboratory, each PRS™ probe was rinsed with de-ionized water to remove soil particles, placed in a Ziploc® freezer bag, and eluted with 17.5 ml per probe of 1 M KCl. The bags were placed on a side-to-side shaker at low speed for one hour. Each KCl elutiant was analyzed for NO₃ and NH₄ using LACHET colorimetric procedures. The PRS™ probes were recharged in a soaking solution of 0.5 M NaHCO₃ and agitated on a side-to-side shaker for one hour. This recharging procedure was repeated four times before placement of probes in the field, to ensure complete regeneration of the IEM exchange sites.

Soil samples from the 0 to 5-cm and 5 to 10-cm depths, adjacent to the probe placement, were collected in October 2001 for total C and N analysis. Soil samples were air-dried, ground, and analyzed on a CarloErba instrument. Volumetric soil moisture was measured on each sample date with a MoisturePoint TDR (Environmental Sciences, G.S.

Gabel Corporation, Canada) automatically calibrated for a sandy-loam texture. The TDR probes are 20 cm in length, and represent average water content over the 20-cm depth.

Tree height and diameter at breast height (DBH) were measured by the Southern Forest Research Station in the fall 2001. From this data, total basal area and total tree volume (Smally and Bower, 1968) were calculated on a per-hectare basis.

Statistical Analysis:

Estimates of total C and N and tree growth were compared using analysis of variance (ANOVA) for a randomized block split-plot design, replicated in three blocks.

Compaction and organic matter removal treatments were applied as factorial combinations of main effect treatments, the four sampling sites within each plot were considered sub-samples, and depth was included as a split-plot factor. Duncan's Multiple Range Test was used where appropriate. All statistical analysis was carried out using SAS software (SAS Institute, 1986).

A 2nd-order polynomial function was fitted using the PROC NLIN procedure with the GAUSS option (SAS, 1986) to estimate the accumulation rate of NO₃ and NH₄ recovered from the PRSTM probes over the 2001 growing season. The model was defined as:

$$[1] \quad NX_{\#} = ax^2 + bx + c + \text{error}$$

where $NX_{\#} = \text{NO}_3$ or NH_4 and $x = \text{day of the year}$. Multivariate analysis of variance and the Wilks' Lambda statistic were used to determine significant differences in parameters due to treatments and treatment interactions.

RESULTS:

I. Total Carbon and Nitrogen:

Total C and N (Table 3.3) were significantly different by soil depth, with a lower C:N ratio in the 0 to 5-cm depth than in the 5 to 10-cm depth (33 and 37, respectively).

Organic matter removal treatment had a significant effect on total N ($p=.077$) while the compaction treatment had a significant effect on total C ($p=.047$). When averaged across treatments, Block 3 had a significantly lower C:N than Blocks 1 and 2.

The differences in total soil C among blocks are most likely linked to soil drainage and the slower decomposition rates associated with wetter soils. Although the organic matter removal treatment had no significant effect on total soil C, trends suggested that soil C decreased as biomass removal intensity increased. At year 2, there was a significant difference in total soil C (Wilson, 1992), but through litter fall and root senescence, the differences in total C in the surface 10 cm are no longer impacted by organic matter removal treatments imposed in 1991.

Total soil N on the stem-only removal (O0) treatment remained significantly higher than on the whole-tree plus forest floor removal (O2) treatment plots, even after 10 years.

Because the whole-tree plus forest floor treatment removed over ten times more N than the stem-only removal (500 vs. 46 kg N ha⁻¹), the impacts on soil N were long lasting.

Development of the forest floor, and perhaps increased microbial biomass were reflected as significant differences in soil N with depth.

Table 3.3: Total soil C, N and C:N after 10 growing seasons, by block and treatment combination at the Croatan LTSP (2001).

Block and Main Treatment	Total C %	Total N %	C:N
Block**			
1:Goldsboro Soil	3.19 ^a	0.09 ^a	38 ^a
2: Lynchburg Soil	4.85 ^b	0.16 ^b	37 ^a
3: Lynchburg Soil	4.61 ^b	0.16 ^b	28 ^b
Organic Matter Removal*			
Stem only	4.82 ^a	0.15 ^a	35 ^a
Whole tree (WT)	4.16 ^a	0.14 ^{ab}	33 ^a
WT+ forest floor	3.66 ^a	0.11 ^b	37 ^a
Compaction**			
None	4.71 ^a	0.14 ^a	37 ^a
Severe	3.72 ^b	0.13 ^a	33 ^a
Depth (cm)**			
0-5	5.7 ^a	0.18 ^a	33 ^a
5-10	2.73 ^b	0.09 ^b	37 ^b

Significance of block and main treatment is indicated as *p=0.1, **p=0.05; Significance within a treatment, by column, are represented with Duncan's Multiple Range Test indicators, a and b.

II. Inorganic Nitrogen:

Total inorganic N, as recovered from the PRSTM probes, was significantly influenced by interactions among block, organic matter removal treatment and compaction level for all three parameters and the model as a whole for (Table 3.4). Figure 3.4 depicts the accumulation rates of total inorganic N on Blocks 1, 2 and 3, respectively. Parameter a and b characterize the rate of accumulation; parameter c represents the y-intercept which provides information regarding the treatment effect on the start of the growing season. Accumulation of total inorganic N was significantly affected (p=.005) by the interaction of block, organic matter removal, and compaction level.

Table 3.4. Probability values (p>f) for cumulative total (NO₃ plus NH₄) inorganic N across three levels of organic matter removal (OM), two levels of compaction (COMP), and across two soil depths

Model Parameters	Block	OM	COMP	Block*		Depth*		Depth*		r ²
				OM*	COMP	OM	Comp	OM*	Comp	
a	0.005	0.298	0.005	0.555	0.104	0.694	0.549	0.370	0.309	0.62
b	0.001	0.874	0.006	0.058	0.099	0.915	0.524	0.580	0.486	0.69
c	<.0001	0.678	0.017	0.021	0.066	0.420	0.829	0.900	0.724	0.75
model	0.001	0.015	0.056	0.057	0.005	0.394	0.777	0.717	0.864	

The accumulation rate of NH₄ was dependent on the interaction of organic matter removal and compaction level (Table 3.5), with higher overall rates on Block 1. Figure 3.5 depicts the accumulation rates of NH₄ for the treatment interactions and by block. More NO₃ than NH₄ was recovered from the PRS™ probes on all three blocks (Figure 3.6), which suggests that this form of N is driving the measured N availability. The rate of NO₃ accumulation was significantly impacted by compaction level but varied among blocks (Table 3.6, Figure 3.7). Accumulation rates were significantly higher in the severely compacted plots of Blocks 1 and 3.

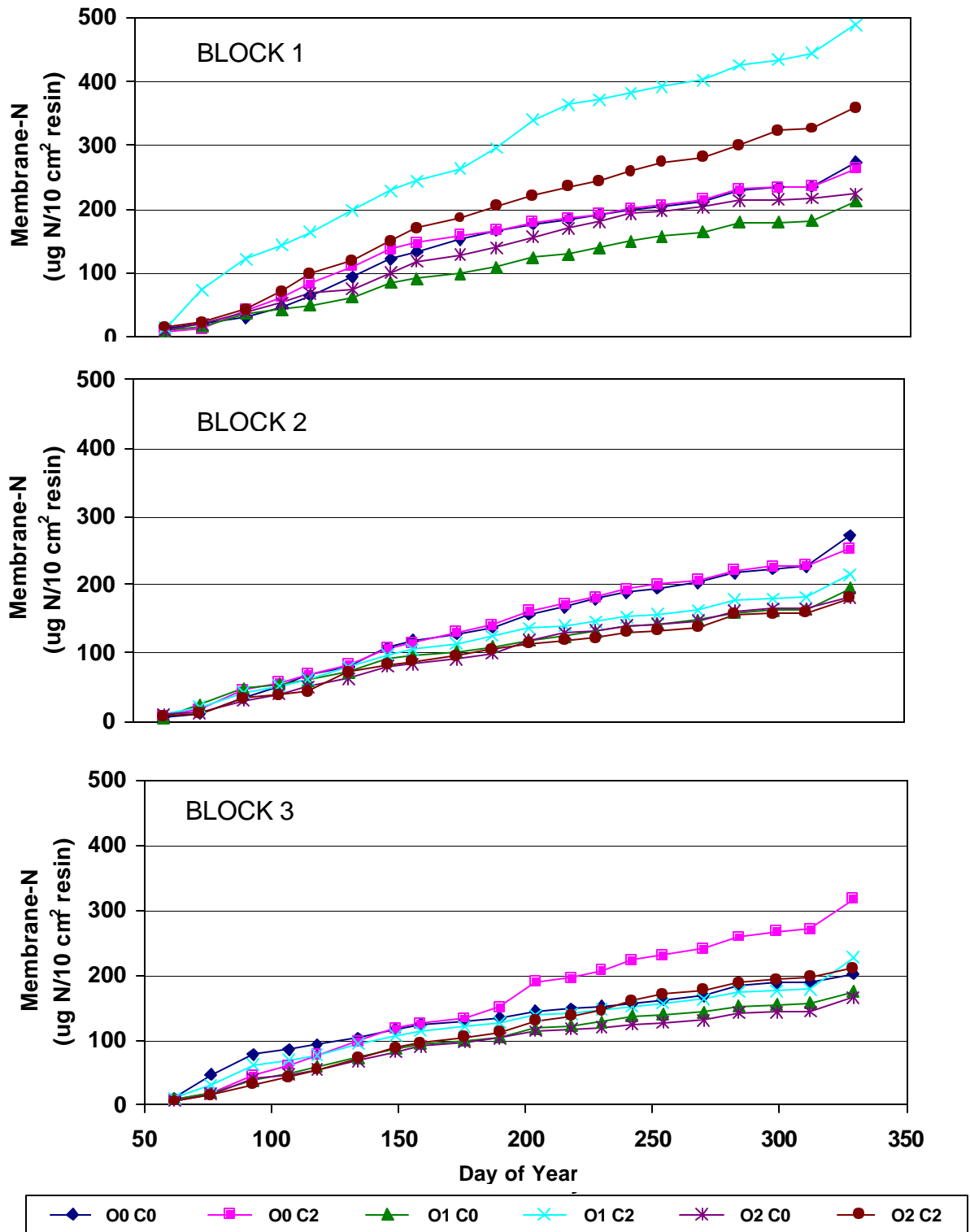


Figure 3.4. Treatment effects on cumulative total inorganic N, averaged over depth, recovered with PRS probes in Blocks 1 (Goldsboro soil), 2 and 3 (Lynchburg soil), Year 10 at the Croatan LTSP site. O0, O1, and O2 indicate organic matter removal levels stem-only, whole-tree (WT), and WT + forest floor. C0 and C2 indicate compaction levels none and severe.

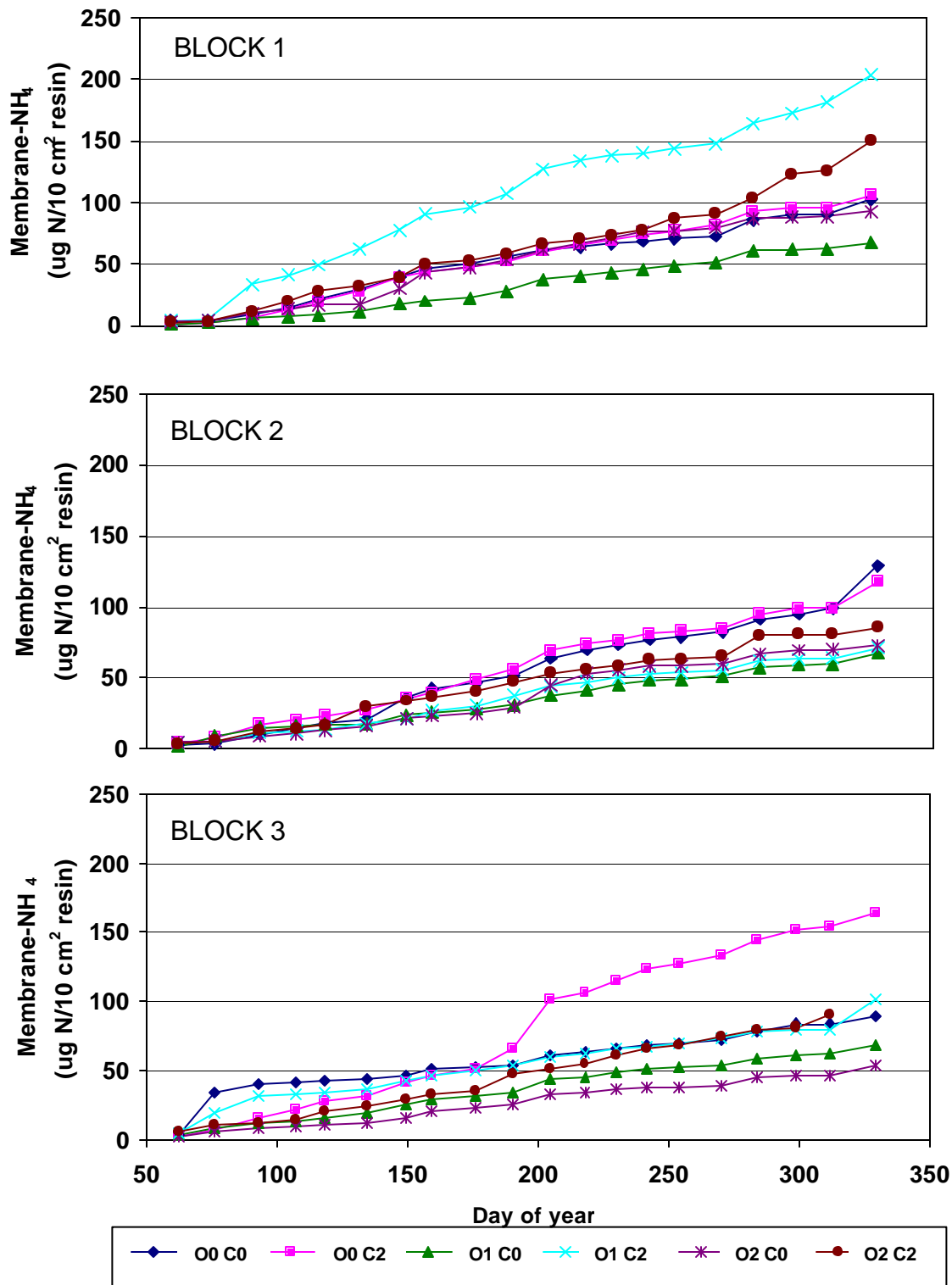


Figure 3.5. Treatment effects on cumulative NH₄, averaged over depth, recovered with PRS probes in Blocks 1 (Goldsboro soil), 2 and 3 (Lynchburg soil), Year 10 at the Croatan LTSP site. O0, O1, and O2 indicate organic matter removal levels stem-only, whole-tree (WT), and WT + forest floor. C0 and C2 indicate compaction levels none and severe.

Table 3.5. Probability values ($p>f$) for cumulative NH_4 across three levels of organic matter removal (OM), two levels of compaction (COMP), and across two soil depths

Model Parameters	Block	OM	COMP	Block*		Depth	Depth*		r^2
				OM*	COMP		OM	Comp	
a	0.314	0.661	0.474	0.293	0.709	0.514	0.527	0.039	0.47
b	0.046	0.748	0.190	0.023	0.172	0.477	0.607	0.132	0.62
c	0.005	0.891	0.465	0.010	0.056	0.322	0.817	0.186	0.68
model	0.048	0.568	0.433	0.090	0.120	0.764	0.845	0.219	0.623

Table 3.6. Probability values ($p>f$) for cumulative NO_3 across three levels of organic matter removal (OM), two levels of compaction (COMP), and across two soil depths

Model Parameters	Block	OM	COMP	Block*		Depth	Depth*		r^2
				OM*	COMP		OM	Comp	
a	0.006	0.434	0.003	0.638	0.107	0.361	0.693	0.811	0.60
b	0.001	0.964	0.003	0.204	0.119	0.543	0.599	0.858	0.66
c	0.0002	0.424	0.009	0.180	0.178	0.070	0.933	0.393	0.71
model	0.001	0.004	0.037	0.019	0.010	0.049	0.883	0.623	0.759

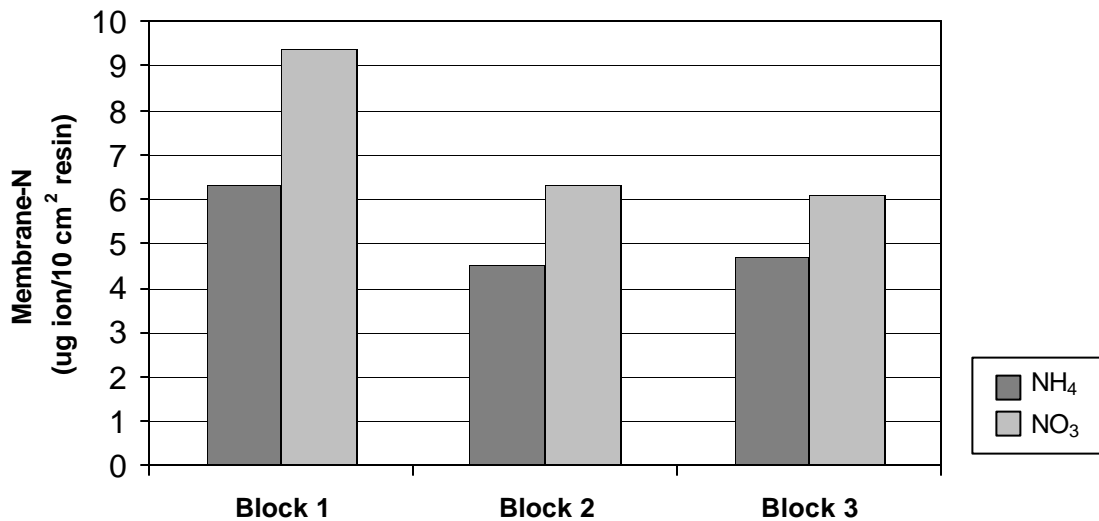


Figure 3.6. Mean NO_3 and NH_4 recovered biweekly from PRS™ probes by block during Year 10 at the Croatan LTSP site.

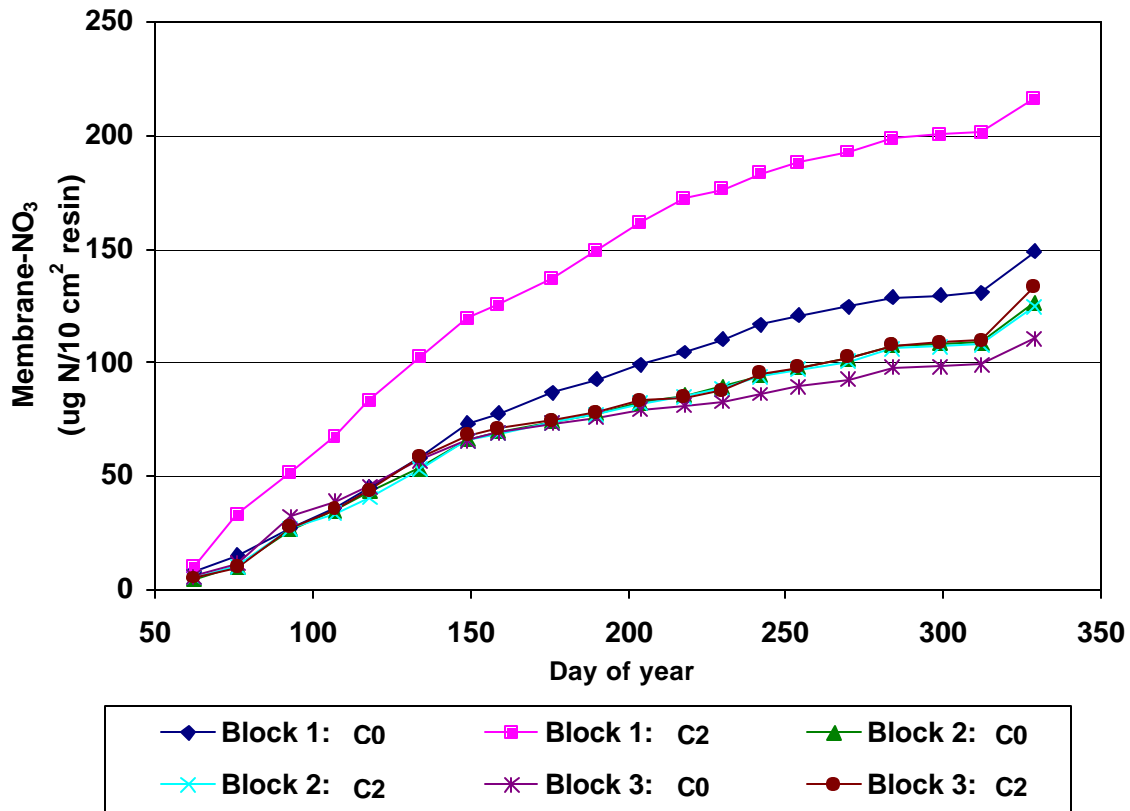


Figure 3.7. Compaction effects on cumulative NO₃ recovered with PRS probes in Blocks 1 (Goldsboro soil), 2 and 3 (Lynchburg soil) during Year 10 at the Croatan LTSP site. C0 and C2 indicate compaction levels none and severe.

III. Tree Growth:

Loblolly pine height, diameter and volume measurements showed no significant response to treatments at the end of the 10th growing season. The average height of loblolly pines at year ten averaged across treatments and blocks was 10 m (sd 0.6). Diameter at breast height (DBH) varied significantly between Block 1 and Blocks 2 and 3 (p=.034) with a means of 15.3 cm (0.8), 16.7 (0.5) and 16.5 (1.2) cm, respectively. Additionally, there were significant block (p=.015) and organic matter removal (p=.032) impacts on total

basal area (BA) (Figure 3.7). Total tree volume averaged across block and treatments was $45.9 \text{ m}^3 \text{ ha}^{-1}$ (14) and showed no significant response to treatment; however, the magnitude of standard deviation seems noteworthy (Table 3.4).

Table 3.7: Mean loblolly pine growth measurements (standard deviations) for the Croatan LTSP (2001).

Block and Main Treatment	Height (m)	DBH (cm)	Total BA ($\text{m}^2 \text{ ha}^{-1}$)	Total volume ($\text{m}^3 \text{ ha}^{-1}$)
Block**				
1:Goldsboro Soil	10 (0.7)	15 (0.8) ^a	20 (3) ^a	48 (21)
2: Lynchburg Soil	11 (0.3)	17 (0.5) ^b	24 (1) ^b	48 (2)
3: Lynchburg Soil	10 (0.7)	17 (1.2) ^b	21 (3) ^a	41 (8)
Organic Matter Removal**				
Stem only	10 (0.6)	16 (1.0)	20 (2) ^a	49 (20)
Whole tree (WT)	11 (0.6)	17 (1.0)	23 (2) ^b	48 (6)
WT+ forest floor	10 (0.7)	16 (1.1)	21 (3) ^a	40 (8)
Compaction**				
None	10 (0.6)	16 (1.2)	21 (3)	47 (17)
Severe	11 (0.7)	16 (0.9)	22 (3)	44 (7)

Significance of block and main treatment is indicated as ** $p=0.05$;
Significance within a treatment, by column, are represented with Duncan's Multiple Range Test indicators, a and b.

The significantly lower DBH and basal area in Block 1 is probably a reflection of fusiform rust impact and mortality that severely affected this Block during the first two years of the study. Total basal area was significantly impacted by organic matter removal treatment and was largest on the whole tree removal treatment plots. Growth rate ($\text{m}^2 \text{ ha}^{-1} \text{ yr}^{-1}$) data was not readily available for analysis, though it is expected that this type of tree growth data, rather than BA and tree volume, would better correspond with the N mineralization data for the growing season.

DISCUSSION AND CONCLUSIONS:

This research addresses one of the primary objectives of the LTSP program which is to understand how soil porosity and soil organic matter interact to regulate long-term site productivity. Nitrogen mineralization rates are critical to our understanding of soil-plant processes.

The significant effect of compaction on the total C pool might reflect fewer lateral and fine roots in the compacted soils, as well as a decrease in soil aeration that would decrease microbial activity. Other researchers at the USDA Forest Service RTP Research and Work Unit have studied root biomass, CO₂ evolution, and microbial activity during the 10th growing season (not reported here), to gain information to relate management treatments to soil processes. Development of the forest floor, and higher input of carbonaceous material to the surface soil is manifest as an effect of depth on N availability.

Decreased soil N concentration may be a reflection of greater microbial activity on the better-aerated soil. Increased microbial activity will increase nutrient cycling, releasing more N for plant uptake and ultimately reducing N concentrations remaining in the soil system.

Chemistry of the plant material left on site will likely impact its decay rate. The biomass left on the plots of the stem-only removal treatment was mostly carbonaceous, while the

whole-tree plus forest floor treatment removed significant amounts of N. The soil C:N ratio for the whole tree removal treatment was the lowest (33) of the three treatment levels. Though C:N did not vary significantly, the impacts of this ratio on microbial decomposition may be significant. The lower ratio indicates more favorable conditions for microbial activity and N mineralization which, over time, could be responsible for the better tree growth.

The compaction effect on nitrification is more likely due to differences in soil environment as opposed to substrate quantity or quality, as there was no significant organic matter removal effect and no treatment interactions found for NO_3 accumulation specifically. Soil porosity, or pore size distribution is the site factor affected by compaction. The average soil bulk density by treatment combination was measured in year 5, but not intensively, leaving the wide variation at the site uncharacterized. Bulk density measurements for year 10 are still underway. Theoretically, even if the soil bulk density had rebounded in the compacted treatment plots over the past ten years, this change would most likely be due to an increase in intermediate-size pores and there would likely still be significantly fewer macropores on the compacted plots. Even subtle changes in pore size distribution affect water retention and release, gas exchange, and heat flux, all of which affect microbial activity. For example, nitrification takes place only in oxidizing conditions and would therefore be impacted by changes in soil aeration.

This theory would suggest higher nitrification rates would generally be found on the non-compacted plots rather than on the severely compacted plots, but this is not supported by

the measurements made during year 10. The 2001 growing season was drier than average and there was no statistically significant difference in soil moisture among compaction treatments. The severely compacted plots in Block 1, however, tended to be wetter than the non-compacted plots. In a dry year, soil moisture rather than aeration may have been the limiting factor on the Goldsboro soil. The higher water-holding capacity of micropores in a compacted soil may have actually provided a more favorable environment for microbial activity and resulted in increased NO_3 availability. The presence of soil moisture also insulates soil, minimizing fluxes in soil temperature. The soil temperature data from the weather station, however, was not gathered in each treatment plot and therefore direct comparison of temperature impacts alone cannot be made.

The effect of treatment interaction on NH_4 accumulation illustrates the fact that N mineralization is reliant not only on the soil environmental conditions governing microbial activity, but also on substrate quantity and quality. There has to be available sources of N compounds for ammonification to take place, and then appropriate conditions for nitrification to occur.

Significant responses to compaction treatments are measurable in total C and NO_3 accumulation ten years after installation of the Croatan LTSP site. Significant responses to organic matter removal treatments could likewise be measured in total soil N and total pine basal area. Significant interactions between soil compaction level and organic matter removal treatment were seen in both NH_4 accumulation and total soil inorganic N. This

may reflect the difference in movement of the NO_3 and NH_4 ions in soil and therefore their capture on the IEM.

The results of this study provide important information to the larger LTSP program. Significant treatment interactions were found, making it more challenging to identify the specific effect driving the differences in N mineralization. Once the results of this N mineralization study are considered as a part of the entire research effort that took place during year ten, additional insights into the overall site management impacts will likely emerge more clear. From this study, we can conclude that N mineralization rates are significantly different when averaged across block and some treatments. This evidence suggests that the impact of soil compaction on the soil physical environment has long-lasting effects on the soil chemical and biological environment.

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4. CONCLUSION:

The increasing world population and demand for a variety of forest products highlight the need for sustainable forestry. The challenge facing the forestry industry is in meeting these growing demands without compromising future supplies (Powers, 1990; Fox, 2000). Increasingly, we will need to rely on intensively managed plantations with higher growth rates in order to supply the world's wood demand (Powers, 1990; Sedjo and Botkin, 1997; Fox, 2000). Our long-term management must maintain or improve site productivity.

Forest management practices cover a broad range of intensity, reflecting a mix of ecological and/or technological constraints (Figure 4.1). Domesticated or intensively managed plantations, where existing site factors can be improved through modifications, lead to increased product returns from less land. This is achieved through increased utilization and shortened rotations that may in turn negatively impact the site's ability to sustain growth over the long-term. Intensively managed forests may not be suited for all sites; high costs of inputs on sites with inherently low productivity, limits domestication to only a small fraction of commercial forest lands (Powers, 1990). Striving to capture more of a site's potential in the short-term may mean that the site's productivity will be degraded over time. This is why a balance must be struck between research focusing on management practices enabling high intensity production and research that identifies the ultimate consequences of these management practices (Powers, 1990; Fox, 2000).

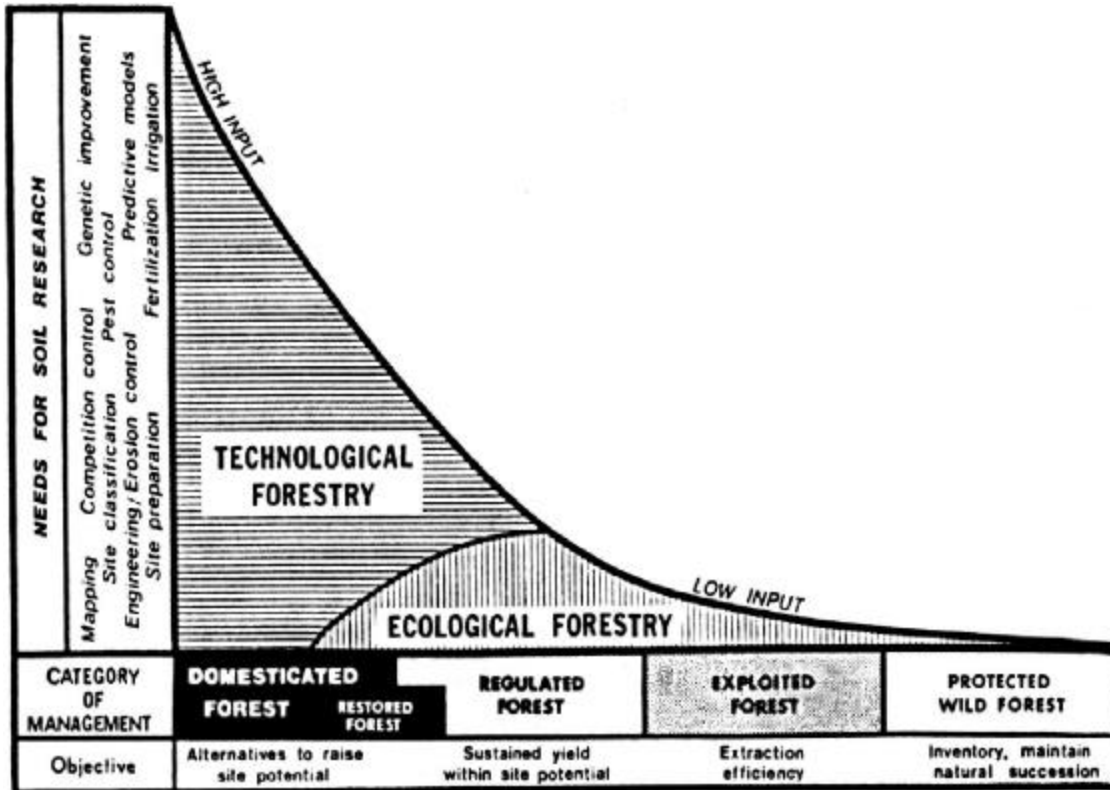


Figure 4.1. Soil research needs relative to forest management practices and their objectives. From Powers (1990).

The USDA Forest Service defines ‘site productivity’ as the carrying capacity of vegetative growth for a site. Carrying capacity is the average dry matter production when a site is fully stocked. A departure from the carrying capacity baseline would have to exceed 15% to be detected and therefore considered significant (Powers, 2002). Because soil is affected by management and is a major factor in determining potential productivity within the constraints of climate, indices of potential long-term site productivity often focus on soil processes (Burger, 1996; Powers, 2002). Measurable soil variables that either reflect or are correlated with important site processes are presented in Table 4.1.

Table 4.1. Site processes and associated soil variables used in determining and monitoring site productivity (adapted from Powers, 2002)

Site process	Key soil monitoring variables
Soil erosion	Soil loss thresholds, & soil cover, presence of rills, etc.
Nutrient availability	Forest floor presence, soil organic matter content, soil chemistry and biology, surface soil loss through erosion or displacement
Water availability	Infiltration, saturated hydraulic conductivity, soil bulk density, soil organic matter, plant water potential, soil moisture, soil texture
Gas exchange	Soil bulk density, air permeability, puddling, presence of mottles, water logging
Root activity	Soil bulk density, soil strength, soils structure, water table depth

This research, conducted during the 2001-growing season, contributes to the larger effort to understand how management practices affect soil processes and the relationship between changes in soil processes and tree growth. Sustainability at this site is still in question. The data presented here shows treatment interactions significantly affect N mineralization during the tenth growing season. To properly evaluate sustainability on this site we will need to compare tree growth rates for this season across treatments and regress them against N availability. If all growth rates are positive and have the same slope then productivity is being sustained.

There is a real need for better soil monitoring tools that will enable researchers to more accurately link changes in the soil to potential changes site productivity. All techniques used to measure plant-available nutrients disrupt soil processes. The more the soil is disturbed, the less accurately the process is portrayed. A relatively new technology to forest soil research, includes utilization of ion exchange resin membranes to estimate

plant-available nutrients in the soil solution. The use of ion exchange resin membranes allows continuous measurements over time with minimal soil disturbance, and maintains the integrity of many linked soil processes. The increased sensitivity to micro-scale environmental variation and the ease of field use and laboratory analysis enhances our ability to monitor soluble nutrient changes and estimate a site's productive potential.

To validate the use of this technology and to ensure appropriate comparisons across sites, further study in both the laboratory and field is needed. This may include intensive laboratory studies to better understand any limitations or constraints of the technology, as well as more field studies comparing ion exchange resin in membrane form with the more established bead form. Strengthening the relationship between measurable indicators and forest soil processes is the ultimate goal.

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Appendix A. Data means for Chapter 2

A.1. Data means for PRS™ probes

PLOT	OM	COMP	DEPTH	8-Jun-01		24-Jun-01		9-Jul-01		23-Jul-01	
				NO ₃	NH ₄	NO ₃	NH ₄	NO ₃	NH ₄	NO ₃	NH ₄
1001	0	0	0	3.60	7.97	23.40	5.59	12.36	6.68	4.11	8.29
1001	0	0	5	6.49	4.34	6.47	1.97	3.94	4.11	5.54	4.65
1021	0	2	0	3.27	3.75	11.21	4.06	2.84	5.92	4.62	8.59
1021	0	2	5	8.77	5.96	4.08	2.64	4.55	3.56	3.53	7.89
1101	1	0	0	2.54	2.68	4.29	2.47	5.34	5.89	7.77	6.29
1101	1	0	5	3.79	1.77	6.70	2.70	3.75	4.65	4.32	12.41
1121	1	2	0	2.84	19.50	14.55	7.25	4.30	16.17	24.11	14.93
1121	1	2	5	4.96	6.60	11.69	3.99	38.67	5.49	22.47	24.91
1201	2	0	0	5.32	19.39	3.47	4.80	3.22	8.03	5.74	8.81
1201	2	0	5	4.46	6.95	9.20	3.14	6.27	5.45	12.18	6.84
1221	2	2	0	8.37	15.64	11.20	3.96	7.96	6.27	11.34	8.95
1221	2	2	5	9.18	6.02	14.70	2.05	17.78	4.54	7.28	6.90
2001	0	0	0	3.67	7.64	5.30	3.47	3.47	4.08	3.64	11.58
2001	0	0	5	5.46	5.21	5.74	5.07	4.99	6.31	7.58	13.37
2021	0	2	0	3.67	4.99	4.07	16.39	4.43	9.73	5.33	14.15
2021	0	2	5	4.88	3.18	6.83	3.17	4.74	4.70	7.26	12.27
2101	1	0	0	3.15	2.28	4.29	2.38	5.15	2.59	2.57	4.77
2101	1	0	5	1.98	1.66	2.63	2.71	2.74	3.06	4.06	7.74
2121	1	2	0	3.10	7.77	4.98	2.25	3.94	4.80	3.84	4.74
2121	1	2	5	3.44	4.02	3.80	4.22	4.03	10.07	4.79	8.40
2201	2	0	0	2.56	1.20	3.95	1.27	3.60	3.05	4.60	8.33
2201	2	0	5	2.10	1.84	4.68	2.67	3.59	5.51	5.07	22.12
2221	2	2	0	2.69	4.03	4.13	5.44	3.55	9.38	3.63	6.22
2221	2	2	5	1.75	2.12	3.99	2.22	2.54	4.04	2.51	5.50
3001	0	0	0	2.88	3.88	3.52	1.41	3.32	1.50	2.89	10.17
3001	0	0	5	4.21	4.84	3.87	2.03	3.13	1.53	2.96	3.76
3021	0	2	0	2.11	4.32	3.16	2.03	2.32	6.68	4.20	30.27
3021	0	2	5	2.87	5.61	2.83	8.47	2.94	22.11	4.51	37.80
3101	1	0	0	2.34	5.63	3.85	2.33	2.09	3.06	4.57	7.75
3101	1	0	5	3.23	2.78	3.66	2.15	2.54	2.05	2.82	11.55
3121	1	2	0	3.22	4.50	3.95	3.31	2.56	4.68	5.50	8.43
3121	1	2	5	3.03	3.44	2.52	4.06	3.30	2.47	2.94	5.68
3201	2	0	0	3.76	5.36	4.04	2.39	2.52	1.78	3.54	7.95
3201	2	0	5	3.13	6.20	4.81	1.80	3.67	2.61	4.17	7.47
3221	2	2	0	2.50	4.16	4.41	3.81	3.84	3.41	6.59	9.12
3221	2	2	5	3.93	4.41	5.33	2.87	5.09	3.77	5.69	13.93

A.2. Data means for IER bags

PLOT	OM	COMP	DEPTH	NO ₃	NH ₄
1001	0	0	0	295.61	18.62
1001	0	0	5	113.43	0.00
1021	0	2	0	168.77	73.77
1021	0	2	5	148.33	26.95
1101	1	0	0	148.23	57.46
1101	1	0	5	240.69	13.67
1121	1	2	0	69.87	42.08
1121	1	2	5	142.17	15.13
1201	2	0	0	195.99	26.23
1201	2	0	5	168.82	2.57
1221	2	2	0	150.70	37.48
1221	2	2	5	52.58	0.00
2001	0	0	0	154.85	20.82
2001	0	0	5	90.38	0.00
2021	0	2	0	187.85	164.21
2021	0	2	5	201.89	0.00
2101	1	0	0	187.44	28.99
2101	1	0	5	104.82	35.68
2121	1	2	0	180.21	50.22
2121	1	2	5	180.72	22.59
2201	2	0	0	126.40	30.01
2201	2	0	5	52.60	11.26
2221	2	2	0	67.24	11.57
2221	2	2	5	49.02	0.00
3001	0	0	0	91.38	16.26
3001	0	0	5	103.70	0.00
3021	0	2	0	126.50	24.48
3021	0	2	5	176.73	0.00
3101	1	0	0	167.55	2.53
3101	1	0	5	195.82	0.00
3121	1	2	0	85.94	12.30
3121	1	2	5	116.66	9.01
3201	2	0	0	137.56	2.62
3201	2	0	5	145.26	0.00
3221	2	2	0	139.37	48.08
3221	2	2	5	54.50	0.00

A.3. Data means for aerobic incubations

PLOT	OM	COMP	DEPTH	29-May-01		8-Jun-01		24-Jun-01		9-Jul-01		23-Jul-01	
				NO ₃	NH ₄	NO ₃	NH ₄	NO ₃	NH ₄	NO ₃	NH ₄	NO ₃	NH ₄
1001	0	0	0	0.15	1.95	0.26	4.36	1.08	8.44	4.36	7.47	10.47	3.27
1021	0	2	0	0.21	1.46	0.29	3.27	0.68	6.81	1.36	11.48	3.70	4.96
1101	1	0	0	0.15	1.16	0.20	3.61	0.78	6.75	2.46	9.70	7.87	6.27
1121	1	2	0	0.17	1.19	0.16	3.93	0.40	8.26	1.29	11.63	2.80	6.72
1201	2	0	0	0.15	1.09	1.01	4.02	3.72	6.69	6.79	5.27	12.60	7.45
1221	2	2	0	0.14	1.08	0.10	2.79	0.36	4.23	1.59	4.82	3.19	7.61
2001	0	0	0	0.20	1.29	0.28	6.36	0.77	17.70	1.47	17.60	3.51	8.64
2021	0	2	0	0.18	1.41	0.34	4.45	0.61	6.94	1.46	10.21	3.85	9.74
2101	1	0	0	0.18	1.23	0.25	4.49	0.75	9.95	2.00	11.77	5.90	10.84
2121	1	2	0	0.20	1.15	0.12	3.59	0.27	6.19	0.41	7.75	0.78	11.05
2201	2	0	0	0.26	1.74	0.14	2.23	0.24	5.52	0.47	7.39	0.99	11.11
2221	2	2	0	0.13	1.32	0.17	2.31	0.19	3.03	0.21	5.36	0.17	11.32
3001	0	0	0	0.10	1.12	0.24	2.54	0.48	4.14	1.59	3.69	3.29	13.80
3021	0	2	0	0.14	1.41	0.44	3.92	0.64	4.48	1.92	10.33	2.86	13.95
3101	1	0	0	0.18	1.21	0.21	7.61	0.35	11.52	0.78	14.64	1.51	14.88
3121	1	2	0	0.14	1.75	0.21	7.61	0.36	9.78	0.65	12.03	1.57	17.61
3201	2	0	0	0.14	1.12	0.14	2.39	0.18	3.83	0.27	5.47	0.67	20.32
3221	2	2	0	0.15	0.89	0.16	2.25	0.42	2.38	1.67	3.40	1.97	21.25

Appendix B. Data means for Chapter 3

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
03/03/01	1001	0	0	0	10.6	5.5	15.4
03/03/01	1001	0	0	5	8.6	2.2	
03/03/01	1021	0	2	0	6.8	1.9	24.0
03/03/01	1021	0	2	5	5.7	1.4	
03/03/01	1101	1	0	0	7.8	3.3	15.9
03/03/01	1101	1	0	5	7.3	0.5	
03/03/01	1121	1	2	0	12.6	3.0	18.1
03/03/01	1121	1	2	5	7.9	5.3	
03/03/01	1201	1	0	0	6.5	5.3	15.8
03/03/01	1201	2	0	5	6.3	2.0	
03/03/01	1221	2	2	0	13.8	1.7	19.1
03/03/01	1221	2	2	5	11.7	4.2	
03/03/01	2001	0	0	0	2.9	2.7	16.0
03/03/01	2001	0	0	5	4.5	3.1	
03/03/01	2021	0	2	0	6.4	2.2	16.2
03/03/01	2021	0	2	5	3.1	5.3	
03/03/01	2101	1	0	0	5.0	1.3	15.6
03/03/01	2101	1	0	5	3.4	1.7	
03/03/01	2121	1	2	0	7.8	5.1	15.6
03/03/01	2121	1	2	5	4.2	3.8	
03/03/01	2201	2	0	0	7.0	6.7	16.2
03/03/01	2201	2	0	5	3.7	3.1	
03/03/01	2221	2	2	0	6.4	5.0	16.0
03/03/01	2221	2	2	5	2.9	2.3	
03/03/01	3001	0	0	0	8.8	2.1	28.5
03/03/01	3001	0	0	5	4.9	4.4	
03/03/01	3021	0	2	0	5.7	2.4	29.6
03/03/01	3021	0	2	5	5.1	2.2	
03/03/01	3101	1	0	0	6.7	2.4	26.3
03/03/01	3101	1	0	5	6.1	3.8	
03/03/01	3121	1	2	0	5.2	3.1	28.9
03/03/01	3121	1	2	5	5.6	6.6	
03/03/01	3201	2	0	0	3.9	1.5	26.6
03/03/01	3201	2	0	5	4.1	2.4	
03/03/01	3221	2	2	0	5.9	1.5	15.8
03/03/01	3221	2	2	5	1.9	2.8	
03/17/01	1001	0	0	0	7.5	0.5	15.6
03/17/01	1001	0	0	5	4.0	0.5	
03/17/01	1021	0	2	0	7.2	1.1	16.9
03/17/01	1021	0	2	5	1.2	0.5	
03/17/01	1101	1	0	0	1.4	0.6	23.6
03/17/01	1101	1	0	5	9.5	0.7	
03/17/01	1121	1	2	0	104.4	1.0	28.9
03/17/01	1121	1	2	5	12.4	0.7	
03/17/01	1201	1	0	0	8.0	0.8	17.7
03/17/01	1201	2	0	5	11.0	0.9	
03/17/01	1221	2	2	0	11.0	0.7	19.5
03/17/01	1221	2	2	5	2.7	0.6	

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
03/17/01	2001	0	0	0	2.2	0.4	20.5
03/17/01	2001	0	0	5	5.3	0.7	
03/17/01	2021	0	2	0	4.8	2.8	24.4
03/17/01	2021	0	2	5	4.4	5.1	
03/17/01	2101	1	0	0	12.4	8.6	21.6
03/17/01	2101	1	0	5	9.3	6.4	
03/17/01	2121	1	2	0	10.7	0.7	20.7
03/17/01	2121	1	2	5	7.4	0.9	
03/17/01	2201	2	0	0	1.6	0.6	24.1
03/17/01	2201	2	0	5	2.6	0.5	
03/17/01	2221	2	2	0	2.5	1.6	22.9
03/17/01	2221	2	2	5	0.9	1.7	
03/17/01	3001	0	0	0	4.2	6.2	19.1
03/17/01	3001	0	0	5	7.1	56.1	
03/17/01	3021	0	2	0	2.5	2.4	24.1
03/17/01	3021	0	2	5	8.4	7.5	
03/17/01	3101	1	0	0	5.3	6.3	27.2
03/17/01	3101	1	0	5	3.1	3.8	
03/17/01	3121	1	2	0	6.6	9.9	29.1
03/17/01	3121	1	2	5	2.5	20.9	
03/17/01	3201	2	0	0	10.7	5.1	26.8
03/17/01	3201	2	0	5	2.9	3.3	
03/17/01	3221	2	2	0	6.7	5.7	28.1
03/17/01	3221	2	2	5	2.4	3.0	
04/03/01	1001	0	0	0	6.0	4.2	17.9
04/03/01	1001	0	0	5	5.9	4.4	
04/03/01	1021	0	2	0	13.3	3.2	19.7
04/03/01	1021	0	2	5	35.5	4.7	
04/03/01	1101	1	0	0	16.3	3.5	17.6
04/03/01	1101	1	0	5	17.6	4.6	
04/03/01	1121	1	2	0	28.3	42.0	19.9
04/03/01	1121	1	2	5	10.8	16.3	
04/03/01	1201	2	0	0	14.3	7.9	22.7
04/03/01	1201	2	0	5	11.4	4.4	
04/03/01	1221	2	2	0	12.6	12.8	28.6
04/03/01	1221	2	2	5	9.9	4.0	
04/03/01	2001	0	0	0	8.4	6.8	25.4
04/03/01	2001	0	0	5	24.2	6.3	
04/03/01	2021	0	2	0	28.7	12.1	25.9
04/03/01	2021	0	2	5	8.9	6.8	
04/03/01	2101	1	0	0	23.9	7.9	29.3
04/03/01	2101	1	0	5	12.6	4.0	
04/03/01	2121	1	2	0	19.3	5.7	27.4
04/03/01	2121	1	2	5	12.4	6.0	
04/03/01	2201	2	0	0	16.2	3.2	26.4
04/03/01	2201	2	0	5	13.1	3.0	
04/03/01	2221	2	2	0	14.2	10.8	25.1
04/03/01	2221	2	2	5	15.2	3.9	
04/03/01	3001	0	0	0	41.3	8.2	182.4

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
04/03/01	3001	0	0	5	9.7	3.7	
04/03/01	3021	0	2	0	23.2	7.4	25.3
04/03/01	3021	0	2	5	15.5	9.1	
04/03/01	3101	1	0	0	24.8	4.7	21.6
04/03/01	3101	1	0	5	6.7	2.4	
04/03/01	3121	1	2	0	11.7	16.2	26.8
04/03/01	3121	1	2	5	28.3	7.5	
04/03/01	3201	2	0	0	27.9	3.0	27.1
04/03/01	3201	2	0	5	14.2	2.6	
04/03/01	3221	2	2	0	9.3	2.1	26.7
04/03/01	3221	2	2	5	16.8	6.0	
04/17/01	1001	0	0	0	14.1	9.4	
04/17/01	1001	0	0	5	7.2	4.0	
04/17/01	1021	0	2	0	16.7	9.1	
04/17/01	1021	0	2	5	13.1	4.6	
04/17/01	1101	1	0	0	4.4	1.6	
04/17/01	1101	1	0	5	6.1	0.7	
04/17/01	1121	1	2	0	14.5	11.9	
04/17/01	1121	1	2	5	11.9	3.5	
04/17/01	1201	2	0	0	9.0	2.4	
04/17/01	1201	2	0	5	13.5	4.2	
04/17/01	1221	2	2	0	6.3	2.6	
04/17/01	1221	2	2	5	33.6	14.0	
04/17/01	2001	0	0	0	6.8	1.8	
04/17/01	2001	0	0	5	18.2	6.5	
04/17/01	2021	0	2	0	13.3	3.4	
04/17/01	2021	0	2	5	3.3	2.9	
04/17/01	2101	1	0	0	5.2	1.0	
04/17/01	2101	1	0	5	4.6	1.0	
04/17/01	2121	1	2	0	7.1	0.4	
04/17/01	2121	1	2	5	9.9	2.1	
04/17/01	2201	2	0	0	5.7	1.1	
04/17/01	2201	2	0	5	9.4	3.3	
04/17/01	2221	2	2	0	3.3	0.3	
04/17/01	2221	2	2	5	3.5	3.3	
04/17/01	3001	0	0	0	4.8	0.8	
04/17/01	3001	0	0	5	6.5	2.2	
04/17/01	3021	0	2	0	6.1	8.8	
04/17/01	3021	0	2	5	12.3	3.3	
04/17/01	3101	1	0	0	5.1	1.7	
04/17/01	3101	1	0	5	11.9	3.2	
04/17/01	3121	1	2	0	4.6	1.6	
04/17/01	3121	1	2	5	7.6	1.3	
04/17/01	3201	2	0	0	5.0	0.7	
04/17/01	3201	2	0	5	6.8	1.0	
04/17/01	3221	2	2	0	5.1	0.8	
04/17/01	3221	2	2	5	13.0	3.0	
04/28/01	1001	0	0	0	14.1	9.4	11.8
04/28/01	1001	0	0	5	7.2	4.0	

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
04/28/01	1021	0	2	0	16.7	9.1	12.8
04/28/01	1021	0	2	5	13.1	4.6	
04/28/01	1101	1	0	0	4.4	1.6	10.2
04/28/01	1101	1	0	5	6.1	0.7	
04/28/01	1121	1	2	0	14.5	11.9	12.4
04/28/01	1121	1	2	5	11.9	3.5	
04/28/01	1201	2	0	0	9.0	2.4	19.5
04/28/01	1201	2	0	5	13.5	4.2	
04/28/01	1221	2	2	0	6.3	2.6	24.2
04/28/01	1221	2	2	5	33.6	14.0	
04/28/01	2001	0	0	0	6.8	1.8	22.7
04/28/01	2001	0	0	5	18.2	6.5	
04/28/01	2021	0	2	0	13.3	3.4	23.9
04/28/01	2021	0	2	5	3.3	2.9	
04/28/01	2101	1	0	0	5.2	1.0	23.1
04/28/01	2101	1	0	5	4.6	1.0	
04/28/01	2121	1	2	0	7.1	0.4	26.2
04/28/01	2121	1	2	5	9.9	2.1	
04/28/01	2201	2	0	0	5.7	1.1	23.4
04/28/01	2201	2	0	5	9.4	3.3	
04/28/01	2221	2	2	0	3.3	0.3	21.3
04/28/01	2221	2	2	5	3.5	3.3	
04/28/01	3001	0	0	0	4.8	0.8	27.5
04/28/01	3001	0	0	5	6.5	2.2	
04/28/01	3021	0	2	0	6.1	8.8	18.0
04/28/01	3021	0	2	5	12.3	3.3	
04/28/01	3101	1	0	0	5.1	1.7	22.8
04/28/01	3101	1	0	5	11.9	3.2	
04/28/01	3121	1	2	0	4.6	1.6	24.6
04/28/01	3121	1	2	5	7.6	1.3	
04/28/01	3201	2	0	0	4.9	0.8	24.0
04/28/01	3201	2	0	5	6.6	1.0	
04/28/01	3221	2	2	0	5.1	0.8	22.1
04/28/01	3221	2	2	5	13.0	3.0	
05/14/01	1001	0	0	0	18.2	4.3	8.6
05/14/01	1001	0	0	5	26.6	11.2	
05/14/01	1021	0	2	0	16.2	7.8	9.3
05/14/01	1021	0	2	5	19.9	8.4	
05/14/01	1101	1	0	0	9.7	0.9	8.9
05/14/01	1101	1	0	5	10.3	4.7	
05/14/01	1121	1	2	0	25.9	12.1	10.1
05/14/01	1121	1	2	5	16.4	14.3	
05/14/01	1201	2	0	0	8.3	1.4	13.6
05/14/01	1201	2	0	5	4.1	0.6	
05/14/01	1221	2	2	0	15.4	4.2	23.2
05/14/01	1221	2	2	5	18.4	2.7	
05/14/01	2001	0	0	0	9.3	3.8	14.4
05/14/01	2001	0	0	5	10.2	1.1	
05/14/01	2021	0	2	0	11.9	5.4	18.5

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
05/14/01	2021	0	2	5	7.9	2.4	
05/14/01	2101	1	0	0	13.9	0.2	17.0
05/14/01	2101	1	0	5	9.5	0.2	
05/14/01	2121	1	2	0	7.8	5.0	16.1
05/14/01	2121	1	2	5	20.5	2.9	
05/14/01	2201	2	0	0	8.5	3.6	16.2
05/14/01	2201	2	0	5	10.1	2.3	
05/14/01	2221	2	2	0	15.7	6.1	14.3
05/14/01	2221	2	2	5	13.4	20.2	
05/14/01	3001	0	0	0	6.4	0.1	17.9
05/14/01	3001	0	0	5	15.1	0.6	
05/14/01	3021	0	2	0	16.1	4.9	14.1
05/14/01	3021	0	2	5	20.6	2.9	
05/14/01	3101	1	0	0	11.0	1.5	21.5
05/14/01	3101	1	0	5	8.8	4.4	
05/14/01	3121	1	2	0	22.6	4.3	16.1
05/14/01	3121	1	2	5	6.4	0.7	
05/14/01	3201	2	0	0	2.9	0.7	15.1
05/14/01	3201	2	0	5	22.9	2.6	
05/14/01	3221	2	2	0	16.0	0.9	16.9
05/14/01	3221	2	2	5	6.2	12.7	
05/29/01	1001	0	0	0	11.0	12.8	20.8
05/29/01	1001	0	0	5	23.9	7.8	
05/29/01	1021	0	2	0	13.2	14.2	16.7
05/29/01	1021	0	2	5	15.3	8.7	
05/29/01	1101	1	0	0	21.8	6.1	17.2
05/29/01	1101	1	0	5	12.7	7.0	
05/29/01	1121	1	2	0	15.1	15.7	22.0
05/29/01	1121	1	2	5	13.9	14.9	
05/29/01	1201	2	0	0	16.9	19.0	29.3
05/29/01	1201	2	0	5	7.5	5.0	
05/29/01	1221	2	2	0	24.7	4.9	27.3
05/29/01	1221	2	2	5	22.0	9.9	
05/29/01	2001	0	0	0	13.1	14.5	21.2
05/29/01	2001	0	0	5	13.7	15.8	
05/29/01	2021	0	2	0	16.2	8.2	23.3
05/29/01	2021	0	2	5	17.6	6.9	
05/29/01	2101	1	0	0	17.7	8.0	21.4
05/29/01	2101	1	0	5	7.8	5.4	
05/29/01	2121	1	2	0	11.1	3.2	27.2
05/29/01	2121	1	2	5	17.1	3.5	
05/29/01	2201	2	0	0	14.8	6.8	24.9
05/29/01	2201	2	0	5	10.0	4.7	
05/29/01	2221	2	2	0	6.4	5.4	20.7
05/29/01	2221	2	2	5	6.2	3.2	
05/29/01	3001	0	0	0	9.8	2.8	29.0
05/29/01	3001	0	0	5	10.0	3.1	
05/29/01	3021	0	2	0	8.7	7.0	24.2
05/29/01	3021	0	2	5	10.5	13.3	

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
05/29/01	3101	1	0	0	8.5	7.6	22.1
05/29/01	3101	1	0	5	8.2	3.9	
05/29/01	3121	1	2	0	8.1	6.2	21.0
05/29/01	3121	1	2	5	6.7	4.3	
05/29/01	3201	2	0	0	11.1	3.0	25.1
05/29/01	3201	2	0	5	7.3	3.7	
05/29/01	3221	2	2	0	12.4	4.2	26.3
05/29/01	3221	2	2	5	13.2	3.5	
06/08/01	1001	0	0	0	3.6	8.0	13.6
06/08/01	1001	0	0	5	6.5	4.3	
06/08/01	1021	0	2	0	3.3	3.7	12.8
06/08/01	1021	0	2	5	8.8	6.0	
06/08/01	1101	1	0	0	2.5	2.7	11.6
06/08/01	1101	1	0	5	3.8	1.8	
06/08/01	1121	1	2	0	2.8	19.5	13.0
06/08/01	1121	1	2	5	5.0	6.6	
06/08/01	1201	2	0	0	5.3	19.4	16.8
06/08/01	1201	2	0	5	4.5	7.0	
06/08/01	1221	2	2	0	8.4	15.6	25.6
06/08/01	1221	2	2	5	9.2	6.0	
06/08/01	2001	0	0	0	3.7	7.6	16.7
06/08/01	2001	0	0	5	5.5	5.2	
06/08/01	2021	0	2	0	3.7	5.0	18.8
06/08/01	2021	0	2	5	4.9	3.2	
06/08/01	2101	1	0	0	3.2	2.3	15.9
06/08/01	2101	1	0	5	2.0	1.7	
06/08/01	2121	1	2	0	3.1	7.8	23.0
06/08/01	2121	1	2	5	3.4	4.0	
06/08/01	2201	2	0	0	2.6	1.2	21.7
06/08/01	2201	2	0	5	2.1	1.8	
06/08/01	2221	2	2	0	2.7	4.0	16.5
06/08/01	2221	2	2	5	1.7	2.1	
06/08/01	3001	0	0	0	2.9	3.9	20.2
06/08/01	3001	0	0	5	4.2	4.8	
06/08/01	3021	0	2	0	2.1	4.3	18.6
06/08/01	3021	0	2	5	2.9	5.6	
06/08/01	3101	1	0	0	2.3	5.6	19.0
06/08/01	3101	1	0	5	3.2	2.8	
06/08/01	3121	1	2	0	3.2	4.5	19.0
06/08/01	3121	1	2	5	3.0	3.4	
06/08/01	3201	2	0	0	3.8	5.4	17.2
06/08/01	3201	2	0	5	3.1	6.2	
06/08/01	3221	2	2	0	2.5	4.2	23.4
06/08/01	3221	2	2	5	3.9	4.4	
06/24/01	1001	0	0	0	23.4	5.6	20.8
06/24/01	1001	0	0	5	6.5	2.0	
06/24/01	1021	0	2	0	11.2	4.1	23.9
06/24/01	1021	0	2	5	4.1	2.6	
06/24/01	1101	1	0	0	4.3	2.5	19.2

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
06/24/01	1101	1	0	5	6.7	2.7	
06/24/01	1121	1	2	0	14.6	7.2	27.6
06/24/01	1121	1	2	5	11.7	4.0	
06/24/01	1201	2	0	0	3.5	4.8	23.9
06/24/01	1201	2	0	5	9.2	3.1	
06/24/01	1221	2	2	0	11.2	4.0	35.9
06/24/01	1221	2	2	5	14.7	2.1	
06/24/01	2001	0	0	0	5.3	3.5	27.4
06/24/01	2001	0	0	5	5.7	5.1	
06/24/01	2021	0	2	0	4.1	16.4	26.9
06/24/01	2021	0	2	5	6.8	3.2	
06/24/01	2101	1	0	0	4.3	2.4	26.4
06/24/01	2101	1	0	5	2.6	2.7	
06/24/01	2121	1	2	0	5.0	2.3	32.2
06/24/01	2121	1	2	5	3.8	4.2	
06/24/01	2201	2	0	0	3.9	1.3	31.6
06/24/01	2201	2	0	5	4.7	2.7	
06/24/01	2221	2	2	0	4.1	5.4	23.8
06/24/01	2221	2	2	5	4.0	2.2	
06/24/01	3001	0	0	0	3.5	1.4	30.4
06/24/01	3001	0	0	5	3.9	2.0	
06/24/01	3021	0	2	0	3.2	2.0	27.6
06/24/01	3021	0	2	5	2.8	8.5	
06/24/01	3101	1	0	0	3.9	2.3	30.9
06/24/01	3101	1	0	5	3.7	2.2	
06/24/01	3121	1	2	0	3.9	3.3	24.5
06/24/01	3121	1	2	5	2.5	4.1	
06/24/01	3201	2	0	0	4.0	2.4	30.3
06/24/01	3201	2	0	5	4.8	1.8	
06/24/01	3221	2	2	0	4.4	3.8	32.3
06/24/01	3221	2	2	5	5.3	2.9	
07/09/01	1001	0	0	0	12.4	6.7	12.9
07/09/01	1001	0	0	5	3.9	4.1	
07/09/01	1021	0	2	0	2.8	5.9	14.4
07/09/01	1021	0	2	5	4.6	3.6	
07/09/01	1101	1	0	0	5.3	5.9	14.0
07/09/01	1101	1	0	5	3.7	4.7	
07/09/01	1121	1	2	0	4.3	16.2	18.7
07/09/01	1121	1	2	5	38.7	5.5	
07/09/01	1201	2	0	0	3.2	8.0	22.3
07/09/01	1201	2	0	5	6.3	5.5	
07/09/01	1221	2	2	0	8.0	6.3	27.1
07/09/01	1221	2	2	5	17.8	4.5	
07/09/01	2001	0	0	0	3.5	4.1	22.7
07/09/01	2001	0	0	5	5.0	6.3	
07/09/01	2021	0	2	0	4.4	9.7	29.6
07/09/01	2021	0	2	5	4.7	4.7	
07/09/01	2101	1	0	0	5.2	2.6	21.9
07/09/01	2101	1	0	5	2.7	3.1	

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
07/09/01	2121	1	2	0	3.9	4.8	28.1
07/09/01	2121	1	2	5	4.0	10.1	
07/09/01	2201	2	0	0	3.6	3.0	25.8
07/09/01	2201	2	0	5	3.6	5.5	
07/09/01	2221	2	2	0	3.6	9.4	24.4
07/09/01	2221	2	2	5	2.5	4.0	
07/09/01	3001	0	0	0	3.3	1.5	29.4
07/09/01	3001	0	0	5	3.1	1.5	
07/09/01	3021	0	2	0	2.3	6.7	23.3
07/09/01	3021	0	2	5	2.9	22.1	
07/09/01	3101	1	0	0	2.2	3.1	24.9
07/09/01	3101	1	0	5	2.5	2.1	
07/09/01	3121	1	2	0	2.6	4.7	25.1
07/09/01	3121	1	2	5	3.3	2.5	
07/09/01	3201	2	0	0	2.5	1.8	26.0
07/09/01	3201	2	0	5	3.7	2.6	
07/09/01	3221	2	2	0	3.8	3.4	26.6
07/09/01	3221	2	2	5	5.1	3.8	
07/23/01	1001	0	0	0	4.1	8.3	14.4
07/23/01	1001	0	0	5	5.5	4.7	
07/23/01	1021	0	2	0	4.6	8.6	14.2
07/23/01	1021	0	2	5	3.5	7.9	
07/23/01	1101	1	0	0	7.8	6.3	14.7
07/23/01	1101	1	0	5	4.3	12.4	
07/23/01	1121	1	2	0	24.1	14.9	17.1
07/23/01	1121	1	2	5	22.5	24.9	
07/23/01	1201	2	0	0	5.7	8.8	19.7
07/23/01	1201	2	0	5	12.2	6.8	
07/23/01	1221	2	2	0	11.3	8.9	29.2
07/23/01	1221	2	2	5	7.3	6.9	
07/23/01	2001	0	0	0	3.6	11.6	20.7
07/23/01	2001	0	0	5	7.6	13.4	
07/23/01	2021	0	2	0	5.3	14.2	20.0
07/23/01	2021	0	2	5	7.3	12.3	
07/23/01	2101	1	0	0	2.6	4.8	15.6
07/23/01	2101	1	0	5	4.1	7.7	
07/23/01	2121	1	2	0	3.8	4.7	25.4
07/23/01	2121	1	2	5	4.8	8.4	
07/23/01	2201	2	0	0	4.6	8.3	15.9
07/23/01	2201	2	0	5	5.1	22.1	
07/23/01	2221	2	2	0	3.6	6.2	20.8
07/23/01	2221	2	2	5	2.5	5.5	
07/23/01	3001	0	0	0	2.9	10.2	25.8
07/23/01	3001	0	0	5	3.0	3.9	
07/23/01	3021	0	2	0	4.2	30.3	21.3
07/23/01	3021	0	2	5	4.5	37.8	
07/23/01	3101	1	0	0	4.6	7.7	20.7
07/23/01	3101	1	0	5	2.8	11.6	
07/23/01	3121	1	2	0	5.5	8.4	17.5

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
07/23/01	3121	1	2	5	2.9	5.7	
07/23/01	3201	2	0	0	3.5	7.9	19.5
07/23/01	3201	2	0	5	4.2	7.5	
07/23/01	3221	2	2	0	6.6	9.1	22.6
07/23/01	3221	2	2	5	5.7	13.9	
08/06/01	1001	0	0	0	7.0	3.3	17.9
08/06/01	1001	0	0	5	4.4	1.3	
08/06/01	1021	0	2	0	2.6	7.8	9.6
08/06/01	1021	0	2	5	1.8	3.2	
08/06/01	1101	1	0	0	2.0	2.9	13.1
08/06/01	1101	1	0	5	2.9	2.9	
08/06/01	1121	1	2	0	8.9	6.8	13.7
08/06/01	1121	1	2	5	28.4	6.8	
08/06/01	1201	2	0	0	6.7	5.2	19.8
08/06/01	1201	2	0	5	11.3	4.4	
08/06/01	1221	2	2	0	13.4	4.3	25.3
08/06/01	1221	2	2	5	7.9	3.7	
08/06/01	2001	0	0	0	4.5	6.2	20.5
08/06/01	2001	0	0	5	7.9	4.5	
08/06/01	2021	0	2	0	5.0	4.3	21.0
08/06/01	2021	0	2	5	7.4	5.2	
08/06/01	2101	1	0	0	1.6	3.2	21.0
08/06/01	2101	1	0	5	3.3	3.9	
08/06/01	2121	1	2	0	1.5	3.1	24.6
08/06/01	2121	1	2	5	1.2	3.2	
08/06/01	2201	2	0	0	2.4	4.0	25.1
08/06/01	2201	2	0	5	1.1	12.5	
08/06/01	2221	2	2	0	1.8	2.8	17.5
08/06/01	2221	2	2	5	1.2	3.5	
08/06/01	3001	0	0	0	1.1	2.9	23.2
08/06/01	3001	0	0	5	1.2	1.9	
08/06/01	3021	0	2	0	1.3	4.8	13.7
08/06/01	3021	0	2	5	1.1	4.9	
08/06/01	3101	1	0	0	1.1	1.8	17.7
08/06/01	3101	1	0	5	4.3	1.9	
08/06/01	3121	1	2	0	1.0	1.2	20.1
08/06/01	3121	1	2	5	1.0	1.6	
08/06/01	3201	2	0	0	0.9	1.9	16.4
08/06/01	3201	2	0	5	1.1	1.3	
08/06/01	3221	2	2	0	3.0	3.2	16.8
08/06/01	3221	2	2	5	2.6	4.6	
08/18/01	1001	0	0	0	5.0	2.2	15.8
08/18/01	1001	0	0	5	3.0	2.8	
08/18/01	1021	0	2	0	2.7	3.7	11.8
08/18/01	1021	0	2	5	1.8	2.7	
08/18/01	1101	1	0	0	9.9	2.2	12.0
08/18/01	1101	1	0	5	3.3	3.2	
08/18/01	1121	1	2	0	2.1	3.1	16.2
08/18/01	1121	1	2	5	5.3	5.8	

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
08/18/01	1201	2	0	0	6.6	3.9	20.7
08/18/01	1201	2	0	5	5.0	5.2	
08/18/01	1221	2	2	0	8.5	4.0	24.4
08/18/01	1221	2	2	5	2.7	2.5	
08/18/01	2001	0	0	0	7.5	3.8	20.8
08/18/01	2001	0	0	5	5.6	4.6	
08/18/01	2021	0	2	0	7.3	2.8	21.8
08/18/01	2021	0	2	5	6.6	2.3	
08/18/01	2101	1	0	0	2.5	5.5	16.2
08/18/01	2101	1	0	5	3.1	3.0	
08/18/01	2121	1	2	0	2.5	2.2	24.3
08/18/01	2121	1	2	5	2.4	3.6	
08/18/01	2201	2	0	0	1.6	1.2	25.1
08/18/01	2201	2	0	5	2.1	5.0	
08/18/01	2221	2	2	0	1.6	2.6	22.8
08/18/01	2221	2	2	5	1.4	2.3	
08/18/01	3001	0	0	0	1.6	3.3	24.3
08/18/01	3001	0	0	5	1.6	2.2	
08/18/01	3021	0	2	0	2.6	8.8	18.1
08/18/01	3021	0	2	5	2.5	8.7	
08/18/01	3101	1	0	0	1.6	2.4	22.9
08/18/01	3101	1	0	5	1.9	3.6	
08/18/01	3121	1	2	0	2.0	4.9	21.8
08/18/01	3121	1	2	5	2.0	3.9	
08/18/01	3201	2	0	0	1.4	1.8	18.6
08/18/01	3201	2	0	5	1.5	2.2	
08/18/01	3221	2	2	0	5.1	4.0	22.5
08/18/01	3221	2	2	5	4.6	4.4	
08/30/01	1001	0	0	0	2.8	2.4	10.3
08/30/01	1001	0	0	5	7.1	1.9	
08/30/01	1021	0	2	0	4.9	4.3	10.8
08/30/01	1021	0	2	5	2.6	5.6	
08/30/01	1101	1	0	0	10.2	2.7	8.5
08/30/01	1101	1	0	5	5.5	3.4	
08/30/01	1121	1	2	0	8.8	2.2	12.8
08/30/01	1121	1	2	5	5.8	2.2	
08/30/01	1201	2	0	0	4.8	5.2	16.5
08/30/01	1201	2	0	5	9.4	6.0	
08/30/01	1221	2	2	0	13.2	3.8	21.3
08/30/01	1221	2	2	5	7.4	3.9	
08/30/01	2001	0	0	0	6.7	2.5	16.4
08/30/01	2001	0	0	5	6.8	4.8	
08/30/01	2021	0	2	0	8.8	5.7	19.8
08/30/01	2021	0	2	5	6.4	3.3	
08/30/01	2101	1	0	0	2.9	3.8	14.5
08/30/01	2101	1	0	5	5.3	2.7	
08/30/01	2121	1	2	0	5.0	3.5	19.4
08/30/01	2121	1	2	5	4.5	1.3	
08/30/01	2201	2	0	0	3.3	2.7	21.2

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
08/30/01	2201	2	0	5	3.9	2.1	
08/30/01	2221	2	2	0	5.4	1.6	17.8
08/30/01	2221	2	2	5	2.0	6.7	
08/30/01	3001	0	0	0	2.4	1.5	18.8
08/30/01	3001	0	0	5	1.8	2.2	
08/30/01	3021	0	2	0	2.7	4.5	17.9
08/30/01	3021	0	2	5	12.5	13.7	
08/30/01	3101	1	0	0	10.4	5.8	20.6
08/30/01	3101	1	0	5	1.7	0.4	
08/30/01	3121	1	2	0	3.5	1.7	19.2
08/30/01	3121	1	2	5	4.0	1.3	
08/30/01	3201	2	0	0	2.0	1.2	18.3
08/30/01	3201	2	0	5	3.6	1.2	
08/30/01	3221	2	2	0	5.1	2.7	18.3
08/30/01	3221	2	2	5	15.5	7.4	
09/11/01	1001	0	0	0	3.1	2.0	10.0
09/11/01	1001	0	0	5	3.9	2.1	
09/11/01	1021	0	2	0	4.3	3.2	7.4
09/11/01	1021	0	2	5	2.7	2.3	
09/11/01	1101	1	0	0	4.2	0.9	7.1
09/11/01	1101	1	0	5	4.2	4.5	
09/11/01	1121	1	2	0	4.1	6.5	10.9
09/11/01	1121	1	2	5	9.7	0.2	
09/11/01	1201	2	0	0	4.2	0.9	13.8
09/11/01	1201	2	0	5	3.4	0.4	
09/11/01	1221	2	2	0	7.5	13.8	21.8
09/11/01	1221	2	2	5	3.0	5.7	
09/11/01	2001	0	0	0	4.1	0.4	18.0
09/11/01	2001	0	0	5	5.0	1.7	
09/11/01	2021	0	2	0	5.5	3.8	19.8
09/11/01	2021	0	2	5	3.9	0.3	
09/11/01	2101	1	0	0	2.6	0.1	15.4
09/11/01	2101	1	0	5	3.1	1.3	
09/11/01	2121	1	2	0	2.2	0.0	21.4
09/11/01	2121	1	2	5	2.8	1.8	
09/11/01	2201	2	0	0	2.9	0.1	19.4
09/11/01	2201	2	0	5	2.1	0.1	
09/11/01	2221	2	2	0	2.0	0.2	16.2
09/11/01	2221	2	2	5	2.3	0.6	
09/11/01	3001	0	0	0	6.5	2.7	21.1
09/11/01	3001	0	0	5	2.4	0.0	
09/11/01	3021	0	2	0	3.3	0.4	12.6
09/11/01	3021	0	2	5	2.7	7.0	
09/11/01	3101	1	0	0	2.1	1.9	19.5
09/11/01	3101	1	0	5	2.1	0.0	
09/11/01	3121	1	2	0	2.2	2.9	13.4
09/11/01	3121	1	2	5	2.3	0.0	
09/11/01	3201	2	0	0	3.5	0.2	15.7
09/11/01	3201	2	0	5	2.2	0.1	

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
09/11/01	3221	2	2	0	3.6	0.2	18.1
09/11/01	3221	2	2	5	2.9	11.9	
09/27/01	1001	0	0	0	4.6	2.6	5.0
09/27/01	1001	0	0	5	6.3	1.3	
09/27/01	1021	0	2	0	4.0	5.7	5.0
09/27/01	1021	0	2	5	3.1	5.0	
09/27/01	1101	1	0	0	4.4	3.8	5.0
09/27/01	1101	1	0	5	3.3	1.9	
09/27/01	1121	1	2	0	9.7	5.3	5.0
09/27/01	1121	1	2	5	3.1	3.0	
09/27/01	1201	2	0	0	3.5	3.1	5.0
09/27/01	1201	2	0	5	2.9	1.5	
09/27/01	1221	2	2	0	3.5	5.3	5.0
09/27/01	1221	2	2	5	3.6	1.2	
09/27/01	2001	0	0	0	4.6	4.8	5.0
09/27/01	2001	0	0	5	5.2	3.1	
09/27/01	2021	0	2	0	4.4	3.1	5.0
09/27/01	2021	0	2	5	3.4	1.1	
09/27/01	2101	1	0	0	3.8	2.2	5.0
09/27/01	2101	1	0	5	4.5	1.9	
09/27/01	2121	1	2	0	4.4	2.4	5.0
09/27/01	2121	1	2	5	4.5	1.7	
09/27/01	2201	2	0	0	4.1	1.3	5.0
09/27/01	2201	2	0	5	3.5	1.0	
09/27/01	2221	2	2	0	2.9	2.6	5.0
09/27/01	2221	2	2	5	2.8	1.2	
09/27/01	3001	0	0	0	3.4	3.1	5.0
09/27/01	3001	0	0	5	3.9	1.7	
09/27/01	3021	0	2	0	4.4	7.9	5.0
09/27/01	3021	0	2	5	4.6	3.7	
09/27/01	3101	1	0	0	2.7	0.4	5.0
09/27/01	3101	1	0	5	2.5	1.3	
09/27/01	3121	1	2	0	4.0	2.5	5.0
09/27/01	3121	1	2	5	3.5	5.5	
09/27/01	3201	2	0	0	2.8	0.8	5.0
09/27/01	3201	2	0	5	3.1	1.0	
09/27/01	3221	2	2	0	4.3	2.2	5.0
09/27/01	3221	2	2	5	5.0	1.9	
10/11/01	1001	0	0	0	4.7	14.3	7.1
10/11/01	1001	0	0	5	3.1	12.4	
10/11/01	1021	0	2	0	6.9	6.2	7.0
10/11/01	1021	0	2	5	2.6	14.7	
10/11/01	1101	1	0	0	8.1	12.3	8.3
10/11/01	1101	1	0	5	3.1	6.9	
10/11/01	1121	1	2	0	7.7	12.4	7.1
10/11/01	1121	1	2	5	5.6	20.7	
10/11/01	1201	2	0	0	3.8	8.1	11.1
10/11/01	1201	2	0	5	2.6	7.5	
10/11/01	1221	2	2	0	6.7	8.4	20.2

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
10/11/01	1221	2	2	5	4.9	17.9	
10/11/01	2001	0	0	0	5.8	5.5	13.9
10/11/01	2001	0	0	5	4.2	13.0	
10/11/01	2021	0	2	0	5.5	14.1	11.2
10/11/01	2021	0	2	5	4.3	5.4	
10/11/01	2101	1	0	0	3.4	7.5	11.1
10/11/01	2101	1	0	5	6.4	4.9	
10/11/01	2121	1	2	0	7.8	6.1	11.3
10/11/01	2121	1	2	5	9.0	7.4	
10/11/01	2201	2	0	0	7.8	8.6	14.0
10/11/01	2201	2	0	5	6.1	5.5	
10/11/01	2221	2	2	0	4.0	6.3	14.2
10/11/01	2221	2	2	5	2.9	23.0	
10/11/01	3001	0	0	0	6.6	6.9	13.2
10/11/01	3001	0	0	5	9.2	7.0	
10/11/01	3021	0	2	0	8.6	7.7	8.9
10/11/01	3021	0	2	5	5.7	15.3	
10/11/01	3101	1	0	0	4.4	8.0	15.9
10/11/01	3101	1	0	5	3.7	3.0	
10/11/01	3121	1	2	0	6.9	7.9	9.2
10/11/01	3121	1	2	5	3.6	2.7	
10/11/01	3201	2	0	0	4.1	6.9	11.5
10/11/01	3201	2	0	5	4.7	6.1	
10/11/01	3221	2	2	0	6.6	8.9	14.0
10/11/01	3221	2	2	5	3.2	3.8	
10/26/01	1001	0	0	0	1.0	6.7	5.9
10/26/01	1001	0	0	5	1.4	1.2	
10/26/01	1021	0	2	0	0.8	2.0	5.4
10/26/01	1021	0	2	5	1.0	3.0	
10/26/01	1101	1	0	0	0.6	0.6	5.4
10/26/01	1101	1	0	5	0.2	0.3	
10/26/01	1121	1	2	0	1.0	12.6	5.2
10/26/01	1121	1	2	5	0.7	3.2	
10/26/01	1201	2	0	0	1.0	1.0	7.8
10/26/01	1201	2	0	5	0.3	0.6	
10/26/01	1221	2	2	0	7.0	24.0	11.3
10/26/01	1221	2	2	5	0.4	14.9	
10/26/01	2001	0	0	0	1.8	4.2	10.5
10/26/01	2001	0	0	5	1.2	3.3	
10/26/01	2021	0	2	0	1.1	6.6	10.8
10/26/01	2021	0	2	5	1.0	1.7	
10/26/01	2101	1	0	0	0.7	0.3	8.0
10/26/01	2101	1	0	5	0.6	3.2	
10/26/01	2121	1	2	0	0.1	1.4	6.4
10/26/01	2121	1	2	5	0.8	0.4	
10/26/01	2201	2	0	0	0.4	4.0	8.5
10/26/01	2201	2	0	5	0.4	1.6	
10/26/01	2221	2	2	0	1.4	1.2	5.8
10/26/01	2221	2	2	5	1.4	0.3	

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
10/26/01	3001	0	0	0	0.2	0.2	6.4
10/26/01	3001	0	0	5	1.2	8.0	
10/26/01	3021	0	2	0	0.8	6.6	5.9
10/26/01	3021	0	2	5	0.4	7.9	
10/26/01	3101	1	0	0	0.2	3.8	10.9
10/26/01	3101	1	0	5	0.1	0.8	
10/26/01	3121	1	2	0	0.2	1.6	6.4
10/26/01	3121	1	2	5	0.7	0.2	
10/26/01	3201	2	0	0	0.6	0.7	11.0
10/26/01	3201	2	0	5	0.3	0.5	
10/26/01	3221	2	2	0	1.5	2.0	6.3
10/26/01	3221	2	2	5	1.0	7.0	
11/08/01	1001	0	0	0	1.1	0.6	5.0
11/08/01	1001	0	0	5	0.8	0.4	
11/08/01	1021	0	2	0	1.1	0.2	5.0
11/08/01	1021	0	2	5	1.0	0.5	
11/08/01	1101	1	0	0	1.1	1.0	5.0
11/08/01	1101	1	0	5	0.7	1.2	
11/08/01	1121	1	2	0	1.0	1.9	5.0
11/08/01	1121	1	2	5	0.7	16.8	
11/08/01	1201	2	0	0	0.9	0.2	5.0
11/08/01	1201	2	0	5	1.2	0.8	
11/08/01	1221	2	2	0	0.7	0.4	5.0
11/08/01	1221	2	2	5	1.0	5.5	
11/08/01	2001	0	0	0	1.0	5.2	5.0
11/08/01	2001	0	0	5	0.7	2.2	
11/08/01	2021	0	2	0	0.8	0.3	5.0
11/08/01	2021	0	2	5	0.7	0.6	
11/08/01	2101	1	0	0	0.6	1.3	5.0
11/08/01	2101	1	0	5	0.5	0.2	
11/08/01	2121	1	2	0	0.9	0.2	5.0
11/08/01	2121	1	2	5	0.5	2.0	
11/08/01	2201	2	0	0	0.8	0.1	5.0
11/08/01	2201	2	0	5	0.4	0.5	
11/08/01	2221	2	2	0	0.9	0.2	5.0
11/08/01	2221	2	2	5	0.6	0.1	
11/08/01	3001	0	0	0	0.8	0.2	5.0
11/08/01	3001	0	0	5	0.9	0.8	
11/08/01	3021	0	2	0	1.1	0.9	5.0
11/08/01	3021	0	2	5	1.2	3.9	
11/08/01	3101	1	0	0	1.0	1.0	5.0
11/08/01	3101	1	0	5	0.6	0.7	
11/08/01	3121	1	2	0	1.1	0.2	5.0
11/08/01	3121	1	2	5	1.4	0.9	
11/08/01	3201	2	0	0	1.0	0.2	5.0
11/08/01	3201	2	0	5	0.8	0.0	
11/08/01	3221	2	2	0	1.5	1.0	5.0
11/08/01	3221	2	2	5	1.0	2.1	
11/25/01	1001	0	0	0	35.2	9.9	9.6

DATE	PLOT	OM	COMP	DEPTH	NO ₃	NH ₄	Pv
11/25/01	1001	0	0	5	17.0	13.9	
11/25/01	1021	0	2	0	24.4	12.4	11.9
11/25/01	1021	0	2	5	10.1	9.2	
11/25/01	1101	1	0	0	32.5	3.7	10.6
11/25/01	1101	1	0	5	20.3	4.7	
11/25/01	1121	1	2	0	29.1	10.5	12.8
11/25/01	1121	1	2	5	13.4	33.8	
11/25/01	1201	2	0	0	2.5	4.5	16.1
11/25/01	1201	2	0	5	2.0	4.0	
11/25/01	1221	2	2	0	11.2	40.5	22.2
11/25/01	1221	2	2	5	6.2	7.3	
11/25/01	2001	0	0	0	15.3	54.8	16.5
11/25/01	2001	0	0	5	15.3	4.7	
11/25/01	2021	0	2	0	10.7	32.9	18.9
11/25/01	2021	0	2	5	3.4	4.6	
11/25/01	2101	1	0	0	33.6	12.8	13.2
11/25/01	2101	1	0	5	14.3	2.0	
11/25/01	2121	1	2	0	24.1	5.9	18.6
11/25/01	2121	1	2	5	29.6	7.1	
11/25/01	2201	2	0	0	13.0	4.9	17.0
11/25/01	2201	2	0	5	13.6	1.9	
11/25/01	2221	2	2	0	20.9	5.4	16.5
11/25/01	2221	2	2	5	11.7	3.6	
11/25/01	3001	0	0	0	8.2	3.6	15.2
11/25/01	3001	0	0	5	9.3	5.4	
11/25/01	3021	0	2	0	37.7	8.0	17.2
11/25/01	3021	0	2	5	35.3	12.2	
11/25/01	3101	1	0	0	13.1	12.1	17.1
11/25/01	3101	1	0	5	10.3	1.4	
11/25/01	3121	1	2	0	37.4	7.7	18.5
11/25/01	3121	1	2	5	21.8	32.8	
11/25/01	3201	2	0	0	9.9	5.3	15.3
11/25/01	3201	2	0	5	19.2	9.7	
11/25/01	3221	2	2	0	4.7	5.3	22.7
11/25/01	3221	2	2	5	5.4	11.7	

Appendix C: Percent ion recovery from PRS™ probes and IER bags in solutions of different concentrations and with two elutions. The numbers –1 and –2 indicate the first and second elutions.

NO ₃ or NH ₄	Ion	Resin-1	Resin-2	PRS™-1	PRS™-2
3 ug L ⁻¹	NO ₃	73%	45%	67%	0%
	NH ₄	39%	20%	61%	6%
5 ug L ⁻¹	NO ₃	74%	41%	80%	8%
	NH ₄	100%	30%	97%	7%
35 ug L ⁻¹	NO ₃	38%	45%	59%	9%
	NH ₄	74%	34%	85%	4%
65 ug L ⁻¹	NO ₃	54%	31%	31%	5%
	NH ₄	75%	16%	75%	4%
95 ug L ⁻¹	NO ₃	49%	27%	23%	4%
	NH ₄	76%	18%	71%	5%
125 ug L ⁻¹	NO ₃	52%	28%	17%	3%
	NH ₄	75%	22%	65%	6%

In some of the samples, contamination resulted in 100⁺ % recovery.