ABSTRACT

CHAPMAN, LEEANNA YOUNG. Estimating Net Nitrogen Mineralization in Natural Ecosystems across the Conterminous U.S. (Under the direction Drs. Yang Zhang and Steven McNulty).

Nitrogen is the primary nutrient limiting ecosystem productivity over most of the U.S. Although soil nitrogen content is important, knowledge about its spatial extent at the continental scale is rather limited. The objective of this study was to estimate net nitrogen mineralization for the conterminous U.S. (CONUS) using an empirical modeling approach by scaling up site level measurements. Net nitrogen mineralization and total soil nitrogen data across the CONUS were obtained via publications for different ecosystems: low elevation forests, high elevation forests, and grasslands. Equations to predict net nitrogen mineralization were developed through stepwise multiple linear regression using total kjeldahl nitrogen, average growing season air temperature, total growing season precipitation, and wet plus dry nitrogen deposition as predictor variables for four categories: low elevation high temperature forests (coefficient of determination, $R^2 = 0.83$), low elevation low temperature forests ($R^2 = 0.74$), high elevation forests ($R^2 = 0.80$), and grasslands ($R^2 = 0.88$).

A map of net nitrogen mineralization was developed through GIS utilizing these equations and national-scale databases of total kjeldahl nitrogen, air temperature, precipitation, and nitrogen deposition for the CONUS. The result shows that net nitrogen mineralization varies widely across the U.S. Grasslands were predicted to have the lowest net nitrogen mineralization, while low elevation forests in the east were predicted to have the highest. Mean values were 14.3 kg ha^{-1} yr^{-1} for grasslands, 22.6 kg ha^{-1} yr^{-1} for high elevation forests, 58 kg ha^{-1} yr^{-1} for low elevation low temperature forests, and 82.9 kg ha^{-1}

yr^{-1} for low elevation high temperature forests. This continental scale estimation of net nitrogen mineralization provides a means of comparing net nitrogen mineralization across regions, and the databases developed from this study are useful for accounting for nitrogen limitations in large scale ecosystem modeling.

Estimating Net Nitrogen Mineralization in Natural Ecosystems across
the Conterminous U.S.

by
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DEDICATION

To Momaw- who always enjoyed and never tired of hearing my many “grad school stories.”

BIOGRAPHY

LeeAnna Tiffany Young Chapman grew up in the small town of Vale, North Carolina. She graduated from West Lincoln High School in 2006. She received the Park Scholarship at NC State University where she graduated with a B.S. in Natural Resources-Ecosystems Assessment in 2010. LeeAnna worked for the Utilities Unit of NC Department of Transportation before returning to NC State for her graduate education. In the fall of 2011, she joined the Air Quality Forecasting Lab at NCSU to receive a M.S. in atmospheric sciences. During her time in graduate school, LeeAnna has served as a lab instructor for Introduction to Weather and Climate. LeeAnna has also completed requirements for a graduate minor in Geographic Information Systems.

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CHAPTER 1

1. INTRODUCTION

1.1 Background and Motivation

The net primary production of terrestrial ecosystems is constrained by nutrient availability (Kenney, 1980; Vitousek and Howard, 1991; Reich et al., 1997; LeBauer and Treseder, 2008) in addition to sunlight and water. Nitrogen is the nutrient that most often limits plant growth in ecosystems (Epstein, 1972; Chapin, 1980). Soil nitrogen limitations impact many components of an ecosystem, including limiting forest growth and yield and constraining carbon sequestration (Oren et al., 2001). However, too much nitrogen leaving soils can cause air pollution as well as water pollution problems in watersheds (Aber et al., 1989; Fenn et al., 1998). Total soil nitrogen includes nitrogen in all organic and inorganic forms, but is not an indicator of plant available nitrogen. Total soil nitrogen is often referred to as total kjeldahl nitrogen (TKN) because it is primarily measured by the Kjeldahl method, a wet oxidation laboratory procedure used for the quantitative determination of nitrogen in a substance (Bremner and Mulvaney, 1982). Nitrogen mineralization, the conversion of organic nitrogen to ammonium, represents most of the nitrogen availability in unfertilized soils (Pastor et al., 1984), and provides an index of plant available nitrogen (Nadelhoffer et al., 1983). Factors controlling nitrogen mineralization vary spatially and temporally and include temperature and soil moisture, among other variables (Swift et al., 1979; Knoepp and Swank, 2002).

Ecological modeling requires accurate soil nutrient information (O'Neill et al., 1989; Cramer et al., 2001). Campbell et al. (1984) reported that a way to extrapolate soil nitrogen availability from field data was urgently needed; such a resource is still unavailable. Modeling simulations have shown that carbon sequestration under higher carbon dioxide (CO_2) conditions and future climate change conditions are likely overestimated when nitrogen limitations are omitted (Wang and Houlton, 2009; Wang et al., 2011). Piao et al. (2013) suggested that new terrestrial biosphere models include nutrient limitations to account for the substantial effect of carbon-nitrogen interactions of climate variability and atmospheric CO_2 concentration on modeled carbon cycle. Fan et al. (1998) proposed that better predictions of forest ecosystem dynamics at the regional scale could be provided by using different nitrogen mineralization equations to relate to different regions and scales.

Although net nitrogen mineralization is important to ecosystem productivity, a national scale database of soil nitrogen that could be used for ecosystem model development is lacking, primarily due to lack of spatial data at a continental scale. In this work, data were synthesized from previous studies measuring *in situ* nitrogen mineralization. Net annual nitrogen mineralization was calculated as the sum of monthly incubated sample nitrogen (NH_4-N + NO_3-N) minus initial monthly sample nitrogen (NH_4-N + NO_3-N). Stepwise multiple linear regressions were performed for four data categories: high elevation forests, low elevation low temperature forests, low elevation high temperature forests, and grasslands (including prairies, grasslands, shrublands, and woodlands) to generate equations estimating net nitrogen mineralization based on total kjeldahl nitrogen, air temperature, precipitation, and nitrogen deposition. These equations were applied to existing national scale databases to generate a map of net nitrogen mineralization for the conterminous U.S. (CONUS) because a national scale database of nitrogen availability does not currently exist.

1.2 Objectives

The objectives of this study were:

1. To create and validate a set of empirical models for net nitrogen mineralization based on total kjeldahl nitrogen and other environmental variables;
2. To apply models to generate a map of net nitrogen mineralization for the continental U.S.;
3. To assess mean and variability of net nitrogen mineralization for different ecosystems.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Overview of Nitrogen Cycle

Although the atmosphere is approximately 78 percent nitrogen gas, this form of nitrogen is not biologically available to plants. Nitrogen is only available to plants in inorganic forms, i.e., ammonium and nitrate. The nitrogen cycle describes the way nitrogen generally moves from the atmosphere to the soil and back (Figure 2.1). Nitrogen gas from the atmosphere undergoes either industrial fixation into fertilizers or biological fixation through legumes, where it is converted to organic nitrogen ($N_2 \rightarrow NH_3 \rightarrow R\text{-}NH_2$). Through mineralization, this organic nitrogen is then decomposed by microbes (i.e., a variety of bacteria, actinomycetes, and fungi) into ammonium ($R\text{-}NH_2 \rightarrow NH_3 \rightarrow NH_4^+$). Nitrate is formed when microorganisms convert ammonium into nitrate ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) through nitrification. Nitrate is the form of nitrogen most susceptible to leaching, causing pollution via runoff when there is excess nitrate. Immobilization, the opposite of mineralization, occurs when nitrate and ammonium are up taken by soil organisms and are thus not available to plants. Volatilization is the conversion of ammonium to ammonia gas, which occurs during hot and windy times when evaporation rates are high. Completing the cycle, denitrification occurs when nitrate is converted into nitrogen gas, which occurs when the soil is saturated ($NO_3^- \rightarrow NO_2^- \rightarrow NO \leftrightarrow N_2O \leftrightarrow N_2$).

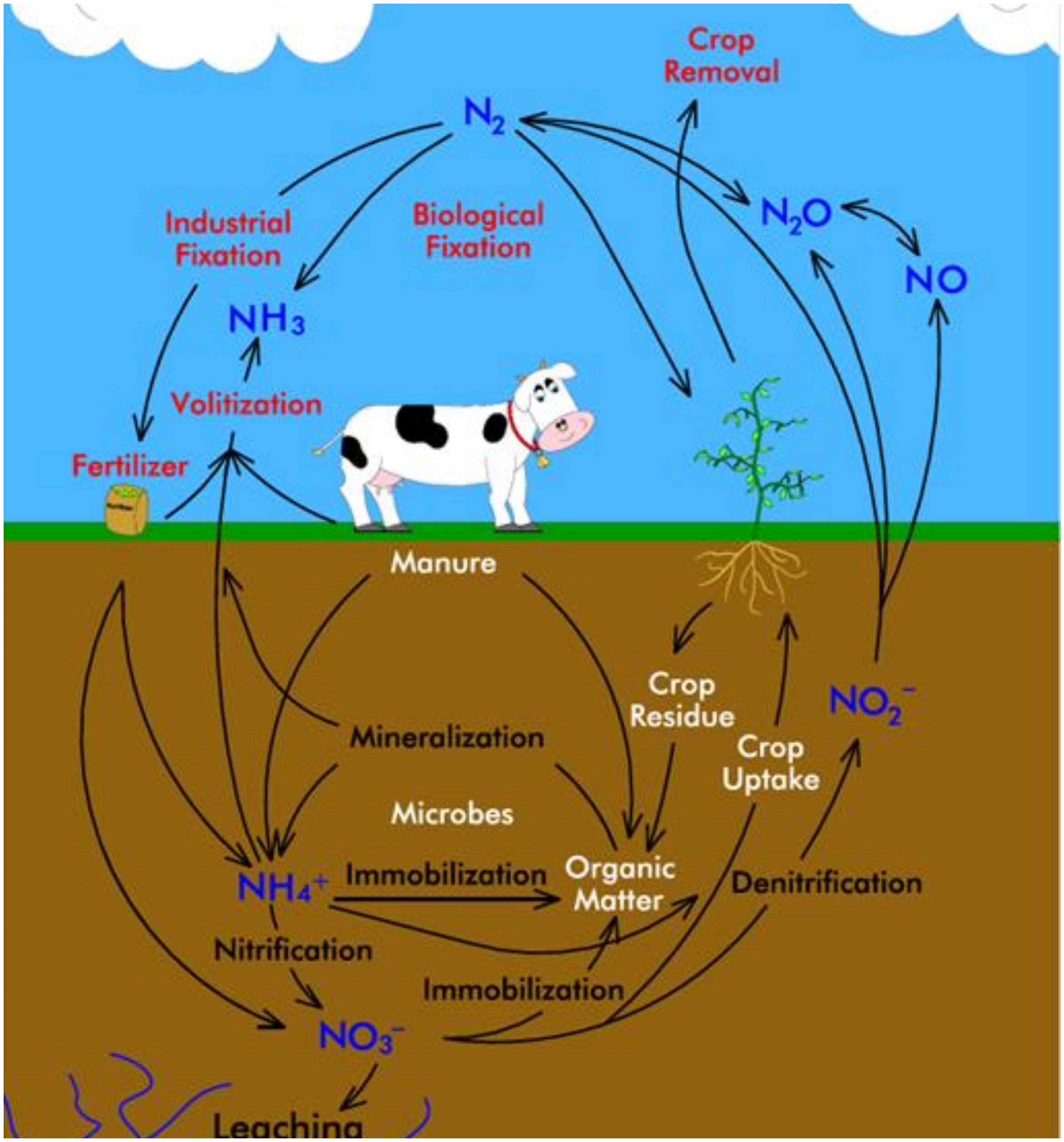

Figure 2.1. The nitrogen cycle.

Micro-environmental conditions strongly affect nitrogen mineralization (Binkley and Hart, 1989). Total soil nitrogen, temperature, precipitation, and nitrogen deposition were chosen as variables in this study because each influences nitrogen mineralization.

Temperature and soil moisture each has been widely shown through experimentation to impact nitrogen mineralization (Powers, 1990). Cold and dry climates have low nitrogen mineralization and low plant nitrogen use efficiency due to slow enzyme activity (Lloyd and Taylor, 1994). An increase in total soil nitrogen has been shown to correlate to increased nitrogen mineralization (Vlassak, 1970; Pastor, 1987). Binkley and Hart (1989) indicated that in broad comparisons where macro-climatic differences surpass micro-environmental differences, the amount of total nitrogen present in soils may be useful for the determination of nitrogen availability. Increased nitrogen deposition is correlated to increased nitrogen availability (McNulty et al., 1990; Schindler and Bayley, 1993) due to nitrogen enriched soil, as well as increased net primary production (Cole and Rapp, 1981).

Other factors influencing nitrogen mineralization exist but were not included in this study due to its large scale. At a smaller scale (i.e., regional or watershed), other important controlling factors include soil pH, soil aeration, specific vegetation type (i.e., species), quality of soil organic matter, and litter quality. Through past experiments, each of these factors has been shown to influence net nitrogen mineralization at a small scale such as a point level.

2.2 Importance of Plant Available Nitrogen

Nitrogen is an essential nutrient for the growth of plants, including both crops and trees. However, plant growth in ecosystems is most often limited by nitrogen (Epstein, 1972;

Chapin, 1980). Forest ecosystems are typically considered nitrogen-limited (Gilliam et al., 1996). Chapin et al. (1986) defined nitrogen limitation by the extent that a limited supply of available nitrogen constrains plant production. If a plant is nitrogen deficient, both root systems and plant growth are stunted. Nitrogen deficient plants have lower chlorophyll, causing the plant to appear yellow instead of dark green. The protein content of nitrogen deficient plants is also reduced, lessening the health effects of crops like legumes. Linder et al. (1981) discovered that the photosynthetic rates of many deciduous trees such as *Betula pendula* increase by up to five times when their nitrogen content is increased. Increased nitrogen content in conifers is likely to produce greater foliage (Waring and Schlesinger, 1985). Soil nitrogen limitations impact many components of an ecosystem, including limiting forest growth and yield and constraining carbon sequestration (Oren et al., 2001). Wang et al. (2009) revealed that global models significantly overestimate carbon uptake when nutrient limitations are not included. Net annual nitrogen mineralization has been shown to be an important limiting factor in non-fertilized forest production (Nadelhoffer and Aber, 1984). Nitrogen mineralization has also been shown to be correlated at multiple scales (including local, regional, and interbiome) with aboveground net primary productivity (Joshi et al., 2003).

A fundamental link between the mineralization of nitrogen and forest productivity has been discovered to exist, causing attention to shift from static measurements of available nitrogen to more dynamic measurements (Powers, 1990). Nitrogen mineralization has been found to strongly correlate with net ecosystem production (NEP) and annual above-ground net primary production (ANPP) (Curtis et al., 2002). Nitrogen mineralization is used as an index of plant available nitrogen (Nadelhoffer et al., 1983). Mineralized nitrogen can be predicted and spatially represented in roughly the same way as total nitrogen due to both concentrating near the surface where fine roots are more abundant and decreasing with increasing depth (Powers, 1980).

2.3 Previous Studies

Although many methods exist to estimate nitrogen availability (Kenney, 1980; Binkley, 1986; Binkley and Vitousek, 1989), none are considered a complete and accurate assessment of nutrient supply rate (Binkley and Hart, 1989). However, many studies measure nitrogen mineralization which is considered as an index, allowing nitrogen availability to be estimated. Net nitrogen mineralization studies are conducted primarily using *in situ* incubations or laboratory incubations. Each method has benefits and drawbacks. The method for measuring nitrogen mineralization should be chosen based on study objectives. The most widely used method for *in situ* studies is the buried bag procedure following Eno (1960), in which soil is incubated in the field via polyethylene bags, although the exact methodology varies by experiment. In a buried bag incubation, a soil core is placed in a polyethylene bag that prevents water loss but allows transfer of carbon dioxide and oxygen. The bag is then buried in the soil floor and incubated for a predetermined period. Net nitrogen mineralization is calculated as the difference in the current level of nitrate and ammonium and the initial level of nitrate and ammonium. The resin core method of

DiStefano and Gholz (1983) is also a common method, in which ion exchange resin is placed on the top and bottom of open tubes, allowing moisture to fluctuate. Studies involving laboratory incubations measure potential nitrogen mineralization, most often utilizing aerobic incubations with constant air temperature and soil moisture content. Laboratory incubations are not as time consuming or as expensive as *in situ* techniques and are thus often the method of choice. *In situ* methods are influenced by ambient air temperature and precipitation of the study site, whereas laboratory incubations are kept at constant air temperature and soil moisture content. Soils incubated in a laboratory do not show seasonal patterns (Knoepp and Swank, 2002). Potential mineralization depends on other factors such as incubation method and time, which vary greatly by experiment and have large impacts on nitrogen availability estimates (Binkley and Hart, 1989). Buried bag incubations are considered superior to laboratory incubations due to this sensitivity to on-site temperature (Binkley and Hart, 1989).

Many studies measuring nitrogen mineralization at the point level have been conducted, most occurring at single sites with uniform soils and climate (Scott and Binkley, 1997). The outcomes of these point level experiments vary by study and often have conflicting results. Factors such as soil type, vegetation type, and climate are extremely influential at the small scale these experiments are conducted. However, the positive relationship of nitrogen mineralization to increased temperature and soil moisture has been repeatedly proven through experiments in a variety of ecosystems (Cassman and Munns, 1980; Knoepp and Swank, 2002). Cassman and Munns (1980) studied nitrogen mineralization in a Yolo soil profile in California and determined nitrogen mineralization was highly correlated to temperature and moisture. An equation was generated via multiple regression utilizing soil temperature and moisture to predict net nitrogen mineralization. Powers (1990) measured *in situ* net nitrogen mineralization in northern California for six vegetation types along a 2000-m altitudinal gradient. Results indicated that nitrogen release is strongly impacted by soil temperature and soil moisture, with net nitrogen mineralization varying from 19.9 to 58.5 kgN ha^{-1}. The mid-elevation mixed-conifer forest had the highest aerobic nitrogen mineralization rate, while the high-elevation red fir site had the lowest. The red fir site had the lowest number of potential growth days due to snow cover, while the mixed conifer had the greatest number of potential growth days. Net nitrogen mineralization increased directly with potential growth days. Nitrogen mineralization was reduced at higher elevations by cold temperature and by soil drought at lower elevations. Powers noted that absolute nitrogen mineralization did not correlate with site variables such as TKN and soil organic matter due to the broad range of data. Therefore, data was normalized and temperature became the singularly important factor influencing nitrogen mineralization. Knoepp and Swank (2002) utilized laboratory incubations to study how soil temperature and moisture influence nitrogen mineralization for three mixed-oak forest sites. Net soil nitrogen mineralization was found to be significantly affected by temperature and temperature-moisture interactions. Equations were then generated for net nitrogen mineralization based on temperature and moisture and used to calculate nitrogen mineralization for similar sites. Measured rates were higher than predicted rates, showing that temperature and moisture significantly influenced nitrogen mineralization, but other factors were also influential. Dou et al. (1997) measured nitrogen mineralization for two ages of citrus trees on two soil types in Florida. This study conducted both *in situ* and laboratory incubations. *In situ* measurements were significantly correlated to the laboratory measured potential nitrogen mineralization. Net nitrogen mineralization was greater for older trees at each site. The well-drained Tavares fine sand had higher mineralization rates than the poorly-drained Wabasso sand. Mean temperature and cumulative rainfall were significantly correlated with net nitrogen mineralization in this study. Curtis et al. (2002) studied five deciduous forests in the AmeriFlux network. Nitrogen mineralization was positively correlated to NEP and ANPP. When sites had low precipitation and low temperature, they had low nitrogen mineralization.

Frequently, studies focusing on nitrogen mineralization measure effects on mineralization due to a single factor such as temperature, moisture, vegetation type, elevation, or leaf litter (Powers, 1990). The variation of nitrogen mineralization among different plant species is a common research topic. Fisk and Schmidt (1995) measured *in situ* net nitrogen mineralization in three alpine tundra communities in Niwot Ridge containing various vegetation types. Although soil properties differed among the communities, there was no difference in yearly nitrogen mineralization rate. Each community's net nitrogen mineralization rate varied seasonally, although the variation was attributed to a different variable in each community. Wedin and Tilman (1990) compared mineralization rates of five perennial grasses and observed that most nitrogen mineralization occurred in summer and that nitrogen mineralization was highly correlated with belowground litter quality. Their study also indicated that grass species can affect nitrogen mineralization. Wedin and Pastor

(1993) expanded on the study by Wedin and Tilman (1990). In contrast to the previous study, grass species did not significantly affect nitrogen mineralization in a year-long aerobic laboratory incubation study. However, grass species did affect short-term nitrogen mineralization rates in days 1 through 17. Grass species also did not impact total soil nitrogen amounts. After one year, for all grass species in this study, cumulative nitrogen mineralization was approximately 10 percent of total soil nitrogen. Greater than 99 percent of the nitrogen mineralized was nitrate. Their results indicated that cumulative nitrogen mineralization is significantly correlated with total soil nitrogen. Pastor et al. (1984) measured *in situ* nitrogen mineralization in various forest sites in Wisconsin. Conifer dominated sites were revealed to have lower nitrogen mineralization, with the red pine stand having the lowest. Intermediate nitrogen mineralization was located in oak stands while sugar maple stands had the highest. According to their study, net primary production (annual litterfall plus woody biomass) and litter production are positively correlated to nitrogen mineralization. Nitrogen mineralization rate was most related to net aboveground production. Hibbard et al. (2001) studied properties of herbaceous patches versus woody plant patches in Texas. Mean annual nitrogen mineralization and percent soil nitrogen were much higher in woody patches than herbaceous patches. Mean annual nitrogen mineralization rates varied from 6 g m^{-2} in herbaceous patches to 22 g m^{-2} in discrete cluster woodland patches. Zak et al. (1989) conducted a study determining potential net nitrogen mineralization of nine forest (mainly oak and maple dominated) ecosystems in lower Michigan. Potential net nitrogen mineralization was the lowest in the xeric oak dominated site and the highest in the mesic northern hardwood site. Sites with moraine soil type had high mineralization. Their results showed that potential mineralization is highly correlated with overstory biomass and annual biomass increment. Zak et al. (1990) studied three different forest types (black and white oak, sugar maple and red oak, and sugar maple and basswood) in Michigan to determine how nitrogen cycling differed among ecosystems. *In situ* nitrogen mineralization was significantly lower in the oak dominated forest and was the highest in the sugar maple-basswood forest. Maximum mineralization occurred in the growing season, with very little occurring during winter. Knoepp and Swank (1998) measured *in situ* net nitrogen mineralization across a vegetation and elevation gradient in Coweeta Hydrologic Laboratory in North Carolina. The results indicated that mineralization is influenced primarily by vegetation type, not climate. Oak-pine and mixed oak sites had the lowest nitrogen mineralization rate, while northern hardwoods, the highest elevation site, had the highest mineralization rate. Strong seasonal variation occurred in nitrogen mineralization, with mineralization the highest in the summer and the lowest in the winter at all sites. Liu and Muller (1993) conducted a study in eastern Kentucky to determine if ANPP in forests is related to nitrogen mineralization and species composition. In this experiment, nitrogen mineralization varied significantly among forest types. The mixed mesophytic forest had the highest mineralization, while the lowest was in the oak forest. Litter production, woody increment, and above-ground net primary productivity were not correlated with nitrogen mineralization rate. Evans et al. (1998) measured net nitrogen mineralization in high elevation birch or fir dominated forests in New Hampshire. Results showed that net nitrogen mineralization is influenced by species feedbacks. In the birch plots, net nitrogen mineralization was significantly correlated with total soil nitrogen. However, in the fir plots, net nitrogen mineralization was correlated with soil moisture.

Fertilization is often used in silviculture to promote stand establishment and productivity, especially in intensive forest management practices. Many experiments focus on the response of nitrogen mineralization to nitrogen inputs, either by fertilization or increased nitrogen deposition. Pastor et al. (1987) studied nitrogen mineralization in four old fields (16 to > 100 years old) in Minnesota to determine the response of nitrogen availability to fertilizer. Net nitrogen mineralization increased with field age, with older forests having greater amounts of net nitrogen mineralization. Net nitrogen mineralization in the youngest field was 4.4 g m^{-2} compared to 6.5 g m^{-2} in the oldest field. Their results indicate that there is a significant correlation between average annual nitrogen mineralization and total nitrogen soil content. The vast majority (> 90%) of mineralized nitrogen mineralized was nitrified. Gillian et al. (1996) also studied nutrient responses of forests to nitrogen inputs. It was discovered that there was little difference in nitrogen content and mineralization in Fernow Experimental Forest in West Virginia due to high amounts of nitrogen deposition causing nitrogen saturation in untreated watersheds. McNulty and Aber (1993) examined the effects of nitrogen additions on *in situ* nitrogen mineralization on a high-elevation spruce-fir stand in Vermont. With higher nitrogen fertilization, net forest floor nitrogen mineralization and first year net nitrogen mineralization increased. Net nitrogen mineralization was the greatest in the second year of fertilization. During the third year of the study, sites with low nitrogen additions resulted in increased net nitrogen mineralization rates, while net nitrogen mineralization rates for sites with high nitrogen addition were constant or decreased. The authors suggested that the additional nitrogen no longer increasing nitrogen mineralization was due to a carbon limitation.

Another common research topic is the impact of elevation on nitrogen mineralization. Strader et al. (1989) studied the influence of elevation on *in situ* nitrogen mineralization of spruce-fir forests in the Southern Appalachian Mountains. Average annual nitrogen mineralization rates varied greatly from 26 to 180 kg ha^{-1}. Study results indicate nitrogen mineralization rates are not related to elevation or total soil nitrogen. Douglas et al. (1998) measured nitrogen mineralization via laboratory incubation for a climosequence of < 250 to > 700 mm annual precipitation in northeastern Oregon. In general, increased precipitation increased nitrogen mineralization, which varied from 28 to 61 mg N kg^{-1}. Uncultivated silt loam soils at moderate and high rainfall sites had twice the nitrogen mineralization of cultivated silt loam soils. Native soils had higher total soil nitrogen and nitrogen mineralization than cropped soils. McCulley et al. (2009) also studied nitrogen across a precipitation gradient. Net nitrogen mineralization along with other nitrogen dynamics was measured *in situ* for five sites in the Central Great Plains with differing grassland vegetation. Total growing season net nitrogen mineralization was not significantly different among sites, although total soil nitrogen increased from west to east. Net nitrogen mineralization was not highly significant with environmental parameters including precipitation and temperature. A strong seasonal variation in nitrogen mineralization was observed, with the highest nitrogen mineralization occurring in June for most sites. At Whiteface Mountain, New York, Joshi et al. (2003) studied nitrogen availability of deciduous and coniferous forests along an elevation gradient. Nitrogen mineralization generally decreased with increasing elevation. ANPP and soil growing season degree-days (the combination of mean daily air temperature and growing season) were correlated with nitrogen mineralization. Nitrogen mineralization was seasonal, with the highest occurring in July and August. Deciduous forests were found to have higher nitrogen mineralization than coniferous.

Other studies measure the effects of site changes such as timber harvest on nitrogen mineralization. Piatek and Allen (1999) measured the impact of mid-rotation harvesting and site preparation on nitrogen availability on a loblolly pine planation in North Carolina. Harvest treatments were either stem-only or whole-tree and site preparation was chop and burn or shear, pile, and disk. Harvest intensity affected nitrogen mineralization, with stem-only harvest plots having higher nitrogen mineralization than whole-tree harvest. Site preparation did not significantly impact nitrogen mineralization. Soil temperature positively correlated with mid-rotation nitrogen mineralization. Frazer et al. (1990) examined the response of soil nitrogen dynamics to timber harvesting in three Sierra Nevada mixed-conifer stands. Nitrogen mineralization rates were the highest in the clearcut forest (cut in 1978), intermediate in the regeneration stand (cut in 1966) and the lowest in the uncut forest. Fisk et al. (2002) conducted a study in Michigan to determine if greater nitrogen retention is found in old growth forests than second-growth forests. Net nitrogen mineralization did not differ in the two forest types, but ranged widely among individual stands, varying from 44 to 129 kg ha^{-1}. Total nitrogen was similar in old and young growth forests and varied little among forest stands. Grady and Hart (2006) studied the effects of thinning, prescribed burning, and wildfire on ecosystem processes in northern Arizona. The study revealed that unmanaged stands had higher *in situ* annual net nitrogen mineralization than thinning or thinning plus burning stands. High-severity wildfire stands had much higher (~60%) net nitrogen mineralization rates than unmanaged stands. Zhu and Ehrenfeld (1999) conducted a laboratory incubation study in developed and undeveloped Atlantic White Cedar wetlands in New Jersey. Nitrogen mineralization was much higher in developed sites than undeveloped sites, but neither TKN nor water content was significantly correlated to nitrogen mineralization rate.

Another common experiment is the influence of leaf litter on nitrogen mineralization. Nadelhoffer et al. (1983) measured *in situ* annual net nitrogen mineralization on nine forest stands in Southern Wisconsin to determine how leaf litter production impacts soil dynamics. Net nitrogen mineralization varied greatly by season; rates peaked in June at all sites while rates were low from December through April. At all sites, nitrification accounted for more than 50 percent of annual net nitrogen mineralization. Overall, hardwoods had a higher nitrogen mineralization than conifers, with oak dominated sites the highest. The red pine dominated site had the lowest nitrogen mineralization. Annual leaf and needle litter production was significantly correlated to annual nitrogen uptake, and appeared to be correlated to annual mineralization. Nitrogen uptake was also correlated with nitrogen returned in leaf litter. Results from this study indicated that total soil nitrogen is not significantly correlated with mineralization; the site with the greatest total soil nitrogen did not have the greatest nitrogen mineralization. Instead, the site with the lowest soil nitrogen (black oak dominate) had the highest nitrogen mineralization rate. Soil temperature remained relatively constant across all sites and did thus not impact nitrogen mineralization in this study. The study concludes that nitrogen availability may be impacted by litter quality and quantity.

Studies examining multiple soil and environmental variables exist but are not as common as those testing a single relationship. Perakis and Sinkhorn (2011) conducted a study in the Oregon Coast Range measuring various nitrogen dynamics, including gross and net nitrogen mineralization rates, litterfall nitrogen uptake and return, and hydrologic nitrogen losses of nine Douglas-fir forests. Soil nitrogen varied from 0.29% to 0.78% N in the study area and was linearly correlated with net nitrogen mineralization. Annual net nitrogen mineralization rates varied from 8 to 82 kg ha^{-1}. In this study, temperature, precipitation, soil texture, and soil C:N were unrelated to net nitrogen mineralization. Groffman et al. (2006) studied the impact of land use and fertility on carbon and nitrogen cycling processes in eight forest stands in Maryland. Net nitrogen mineralization did not differ between rural and urban forest sites. Soil with high fertility had significantly greater net nitrogen mineralization rates than low fertility soil.

Data are often gathered from many point level sites to examine broader relationships. Reich et al. (1997) compiled data from multiple studies, including 50 conifer and hardwood forest stands in Wisconsin and Minnesota. Forests with higher ANPP had higher nitrogen mineralization; this was a significant linear relationship for all sites. On average, nitrogen mineralization was the highest in the natural oak sites. Nitrogen mineralization differed more among soils than among forest type, with the highest occurring on fine-textured Alfisols. Their results indicate that for natural stands, 81 percent of the variance in annual nitrogen mineralization is explained by soil texture, litterfall nitrogen, and mean annual temperature. The study concluded that annual net nitrogen mineralization variation can explain at least half of the variation in ANPP at a regional scale. Scott and Binkley (1997) utilized data from 11 studies to find the relationship between litter quality and nitrogen mineralization. Data indicated that in forest ecosystems, as the litter lignin : N ratio increased, nitrogen mineralization strongly decreased. Net nitrogen mineralization also decreased as litter lignin concentration increased. Results revealed neither litter nitrogen content, litter nitrogen concentration, nor litterfall quantity are correlated with nitrogen mineralization. In this study, variation in net nitrogen mineralization was more strongly influenced by litter lignin : N ratio than by climatic factors. LeBauer and Treseder (2008) combined data from 126 nitrogen addition experiments to determine if nitrogen limitation is influenced by climate and geography. The nitrogen addition experiments showed that most ecosystems are nitrogen-limited and have an average growth in response to added nitrogen of 29 percent. Response to nitrogen additions varied by biome. All biomes except desert responded positivity to nitrogen fertilizer. The correlation of nitrogen response and latitude was not significant.

Studies reporting total soil nitrogen and nitrogen mineralization are not always nitrogen mineralization specific studies. Many are soil warming or elevated carbon dioxide studies. Rustad et al. (2001) combined data from 32 sites to determine how experimental ecosystem warming influences soil respiration, net nitrogen mineralization, and aboveground plant productivity. At all sites, net nitrogen mineralization rates were significantly increased by 46 percent with 0.3 to 6.0 ^{o}C experimental warming. Garten and Miegroet (1994) conducted a study to determine if naturally occurring nitrogen isotope ratios in foliage are an indicator of soil nitrogen dynamics. The study included eight forest stands in the Great Smoky Mountains that ranged from low elevation nitrogen poor sites to high elevation nitrogen rich sites. After conducting laboratory incubations, results showed that high elevation sites had greater net nitrogen mineralization than low elevation sites. Potential net nitrogen mineralization values were the lowest at the pine site and highest at the spruce-fir dominated site.

Clearly, nitrogen mineralization is influenced by a plethora of site characteristics which vary by a variety of factors including ecosystem type and location. Temperature, soil moisture, nitrogen addition, and total soil nitrogen (TKN) have been repeatedly shown to influence nitrogen mineralization and was thus used as variables in this study. Soil moisture is not directly measurable. Therefore, precipitation was used as an indicator of soil moisture because it is directly measurable and nitrogen deposition will represent nitrogen addition. Vegetation type and elevation are also very influential to nitrogen mineralization and was used to separate data into categories to best characterize nitrogen relationships.

2.4 Estimating Nitrogen Mineralization

Very little data exist on regional or large-scale nitrogen availability (Burke et al., 1997). Although many models have been developed to predict potential nitrogen mineralization (Stanford et al., 1974; Dou et al., 1996), these models are not influenced by environmental factors because data are obtained via laboratory incubations. Few studies have scaled up field measurements and have estimated nitrogen mineralization at a regional scale (Fan et al., 1998; Hope et al., 2005). These studies used different methods to estimate nitrogen mineralization. Table 2.1 summarizes several methods used in the literature along with their strengths and limitations.

Burke et al. (1997) utilized the CENTURY ecosystem model to estimate nitrogen mineralization for the Central Grassland region of the U.S. using a database of input variables including precipitation, temperature, and soils. In this study, net nitrogen mineralization increased with increased mean annual precipitation and increased slightly with increased temperature across the study region. Fan et al. (1998) estimated nitrogen mineralization for forest ecosystems across the Midwestern Great Lakes region based on leaf litter, evapotranspiration, and soil texture using GIS. Net nitrogen mineralization varied widely across this region, from 15 kg ha^{-1} yr^{-1} to 140 kg ha^{-1} yr^{-1}. Lower nitrogen mineralization was found in coniferous forests, while higher nitrogen mineralization was predicted in deciduous forests and wetlands. Sites that had lower actual evapotranspiration (AET) and lower litterfall were predicted to have lower nitrogen mineralization. Gonclaves and Carlyle (1994) created a simple linear model predicting net nitrogen mineralization in

South Australia. The model, based on only soil temperature and soil moisture, was compared to *in situ* measurements and had good agreement for three out of four measurement periods.

Some nutrient cycling studies are conducted on a global scale. Bouwman et al. (1997) utilized carbon to nitrogen (C/N) ratios to calculate net nitrogen mineralization for different vegetation types. Estimated nitrogen mineralization values were reported as a total per ecosystem (i.e., 119 Tg yr^{-1} for temperate forests). The calculated values were similar to rates measured by Nadelhoffer et al. (1991) for artic soils. Fisher et al. (2012) created a global map of total nutrient limitation. Nutrient limitation was calculated from the ratio of normalized difference vegetation index to actual evapotranspiration and did not include actual nutrient measurements. The majority of land was discovered to have some degree of nutrient limitation.

Table 2.1. Summary of methods estimating nitrogen mineralization

Region	Variables	Strengths	Limitations	Reference
Central Grasslands of U.S.	Temperature, precipitation, soil data	Good predictions for study area	Applicable only to a small area	Burke et al. (1997)
Great Lakes Region of U.S.	Leaf litter, evapo-transpiration, soil texture	Good predictions for study area	Applicable only to a small area	Fan et al. (1998)
South Australia	Soil temperature, soil moisture	Simple linear model; easy to apply	May not suit well for all areas in study region	Gonclaves and Carlyle (1994)
Global	C/N ratios	Estimates N mineralization by vegetation type	Only one variable used; other variables are likely influential	Bouwman et al. (1997)

CHAPTER 3

3. METHODOLOGY

Data were obtained from publications reporting both net nitrogen mineralization and total soil nitrogen data across the CONUS for low elevation low temperature forests, low elevation high temperature forests, high elevation forests, and grasslands. Through stepwise multiple linear regression, equations to predict net nitrogen mineralization were developed for each category using TKN, average air temperature during growing season, total precipitation during growing season, and nitrogen deposition as predictor variables and net nitrogen mineralization as the dependent variable. Using these equations and national-scale databases of TKN, air temperature, precipitation, and nitrogen deposition for the CONUS, a map of plant available soil nitrogen was developed in GIS. Figure 3.1 shows the methodology diagram.

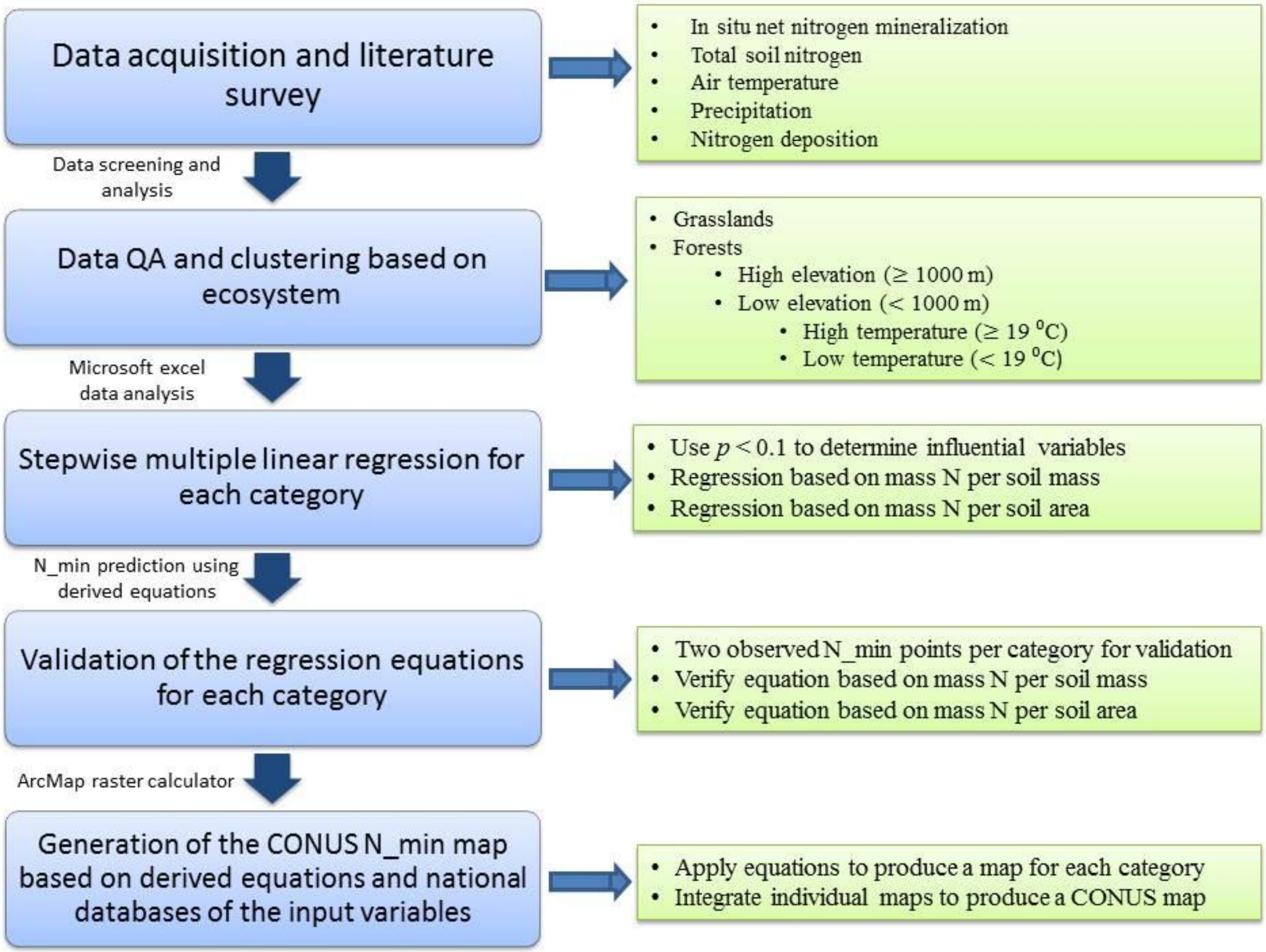

Figure 3.1. Methodology diagram.

3.1 Factors Impacting Nitrogen Availability

A literature review was first conducted to locate studies reporting both total soil nitrogen and net nitrogen mineralization rate across the CONUS. Often, studies reporting total soil nitrogen and nitrogen mineralization are soil warming, elevated carbon dioxide, or nitrogen fertilization experiments. Only data from control plots were included from these studies to reflect ambient conditions in natural ecosystems. The data obtained was used to develop net nitrogen mineralization equations based on parameters influencing net nitrogen mineralization that included total soil nitrogen, air temperature, precipitation, and nitrogen deposition (Table 1).

The study locations produced by the literature review were widely distributed and represent many ecosystems developed under a variety of climate regimes (Figure 3.2). Effort was made to equally represent all areas of the CONUS. Some areas (such as Colorado) had a large number of data available. In these areas where extensive research has been conducted, data from all studies were not recorded to avoid skewing. The focus for the generation of the net nitrogen mineralization equations in this study was *in situ* incubation data rather than laboratory incubations because of its more accurate representation of site conditions including temperature and soil moisture. Most studies utilized the buried bag method of measurement, but some used the resin bag method. Results from the resin technique have been found to correlate well with the buried bag (Binkley et al., 1986) and there is no evidence of a systemic bias (Zou et al., 1990; Binkley et al., 1992). We followed previous studies that have utilized data from different *in situ* nitrogen mineralization measurement methods (Scott and Binkley, 1997) and included studies even if they did not have identical methodology.

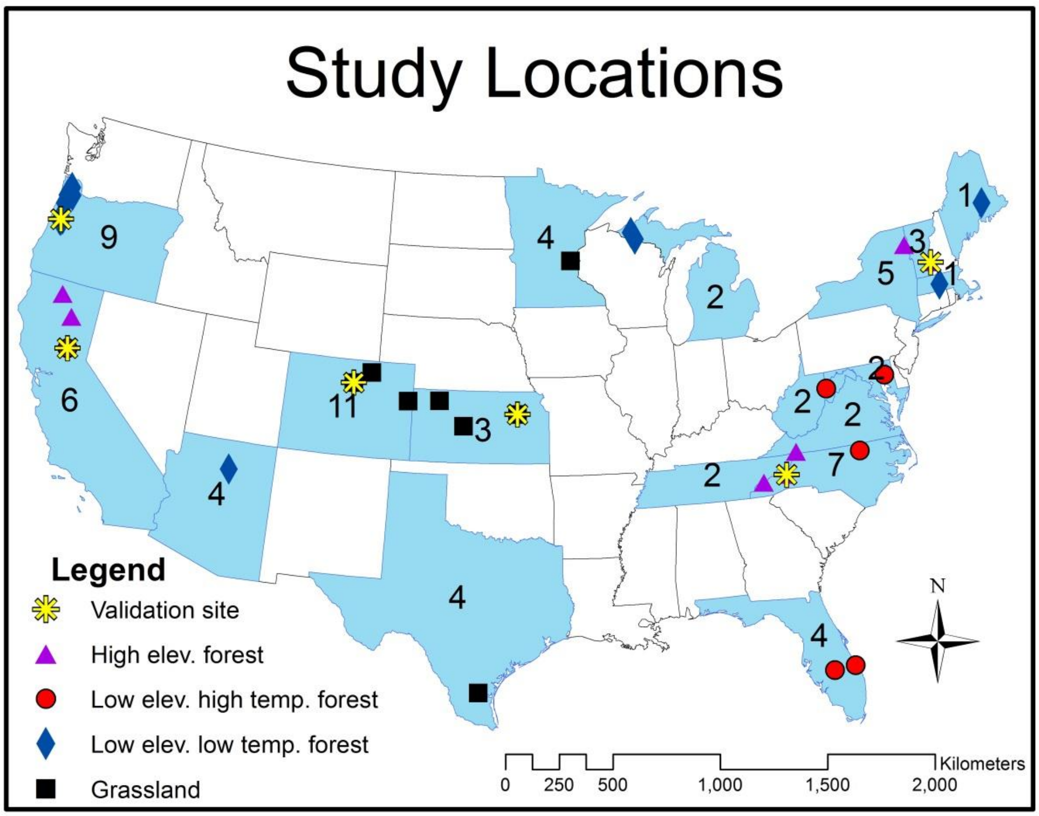

Figure 3.2. Map of study locations. The number of data points in each state is also shown. Symbols indicate the category of the data.

Differences in methodology among experiments required data to be sorted by measurement method to allow more accurate comparison of soil nitrogen availability between sites. In experiments, total soil nitrogen and nitrogen mineralization rates are either measured on a mass of N per area of soil (e.g., kgN ha^{-1} yr^{-1}) or mass of N per mass of soil basis (e.g., gN kg $soil^{-1}$ yr^{-1}). Data were converted to common units of kg ha^{-1} for per area measurements and g kg^{-1} for per mass measurements using appropriate conversion units. If data were reported as a percentage, it was converted into g kg^{-1}. After collecting data, it was determined that total soil nitrogen data measured in mass N per mass of soil would be the focus of this study as this measurement method contains the greatest number of data points and represents the greatest variety of ecosystems.

Data used in this study represented many ecosystems and a variety of climates (Figure 3.2). Across the study area, total soil nitrogen varied from 0.3 to 17 g kg^{-1}, average growing season air temperature ranged from 12.8 to 28.3 °C, total growing season precipitation ranged from 44 to 908 mm, nitrogen deposition ranged from 84 to 777 eqN ha^{-1} yr^{-1}, and net nitrogen mineralization ranged from 1.2 to 220 kg ha^{-1} yr^{-1}. Other studies have shown that vegetation influences net nitrogen mineralization (Pastor et al., 1984). Given the variability in site conditions among the studies, models were formulated for different land uses, resulting in several net nitrogen mineralization equations for different data categories (Figure 3.1). High elevation ecosystems contain unique characteristics, such as low air temperature but high TKN (Joshi et al., 2003) and are thus separated from low elevation ecosystems. Similarly, forest and grassland ecosystems were separated to account for their diverse climatic, soil, and vegetation characteristics. Data were divided by high elevation forests, low elevation forests, and grasslands (including prairies, grasslands, shrublands and woodlands) to account for differences (e.g., vegetation, soil type) among ecosystems. Data clustering of previous studies of temperature and net primary productivity (NPP) (Waring and Schlesinger, 1985; Burke et al., 1997) and soil respiration (Lloyd and Taylor, 1994), reveals a data division around a temperature of 19 °C. Below 19 °C, net NPP and soil respiration rate increase linearly with temperature. Above 19 °C, a strong linear relationship between temperature and these processes is no longer observed. Thus, the low elevation forest category was further divided by temperature due to differences in productivity at high and low forest temperatures with a division threshold of 19 °C.

To better represent nitrogen availability, total soil nitrogen on a per area basis (kg ha^{-1}) was needed. An estimate of total soil nitrogen in kg ha^{-1} was obtained using bulk density either from publications or by soil type and location (Table 1) when the publication was missing or had incomplete bulk density values (Unkovich et al., 2008). Only the upper mineral soil was examined in most nitrogen mineralization studies (Binkley and Hart, 1989) because the upper soil is where the majority of nutrient cycling occurs due to clustering of fine roots (Powers, 1980). Nitrogen mineralization generally decreases with depth; half or more of nitrogen mineralization in forests occurs in the forest floor and first 15 cm of soil. Therefore, when converting from mass per mass to mass per area, soil depth was kept constant at 10 cm for all data points to provide standardization among studies. The estimated value of total soil nitrogen was used for all locations in this study for consistent treatment

(Table 3.1) because per area total soil nitrogen is not given in all publications. The resulting total soil nitrogen values from 0-10 cm depth were used for regression analysis and mapping at the continental scale.

Monthly total precipitation and mean air temperature data for the year 2010 were downloaded from the National Climatic Data Center (NCDC) for a nearby station for each of the research areas recorded in the *in situ* nitrogen mineralization studies (Table 3.1). The majority of nitrogen mineralization occurs during the growing season due to higher temperature and greater soil moisture. For each station, total precipitation data were downloaded for each month in the growing season of 2010 (i.e., May-September) and were summed to obtain total precipitation during the growing season. Monthly mean temperatures were also downloaded from NCDC for the growing season and the five monthly-mean values were averaged to obtain one value for the growing season (Table 3.1). The wet and dry nitrogen deposition data were derived from a 1 km^2 resolution map compiled by McNulty et al. (2007), who combined the nitrate wet deposition map of Grimm and Lynch (2004), isopleth maps of the wet deposition fluxes of nitrate and ammonium from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (NADP, 2005), and the dry deposition fluxes of nitric acid, ammonium, and nitrate from the Clean Air Status and Trends Network (CASTNET) (U.S. EPA, 2007).

Table 3.1. Observations utilized in the development and validation of *in situ* nitrogen mineralization equations in this work

State	Ecosystem	[1]Soil N g kg^{-1}	[2]Est. Soil N kg ha^{-1}	[3]Temp °C	[4]N dep eqN $ha^{-1} yr^{-1}$	[5]Precip mm	[6]N_min kg ha^{-1} yr^{-1}	Reference
Florida	Forest	0.3	450[a]	27.7	319	908	127	Dou et al. (1997)
Florida[7]	Forest	0.3	450[a]	27.7	319	908	43	Dou et al. (1997)
Florida	Forest	0.6	870[a]	27.8	359	519	89	Dou et al. (1997)
Florida	Forest	0.6	870[a]	27.8	359	519	42	Dou et al. (1997)
Colorado	Grassland	13.6	20536[a]	19.1	249	246	9.4	Fisk and Schmidt (1995)
Colorado	Grassland	14	21140[a]	19.1	249	246	7.9	Fisk and Schmidt (1995)
Colorado	Grassland	13.6	20536[a]	19.1	249	246	11.5	Fisk and Schmidt (1995)
Colorado	Grassland	8.1	12231[a]	19.1	249	246	6.2	Fisk and Schmidt (1995)
Colorado	Grassland	10.2	15402[a]	19.1	249	246	15.8	Fisk and Schmidt (1995)
Colorado[7]	Grassland	14.9	22499[a]	19.1	249	246	16.6	Fisk and Schmidt (1995)
Colorado	Grassland	8.3	12533[a]	19.1	249	246	11.2	Fisk and Schmidt (1995)
Colorado	Grassland	10.2	15402[a]	19.1	249	246	7.9	Fisk and Schmidt (1995)
Colorado	Grassland	11.9	17969[a]	19.1	249	246	8	Fisk and Schmidt (1995)

Table 3.1 (Continued)

Michigan[7]	Forest	1.6	1728[a]	17.1	430	503	93	Fisk et al. (2002)
Michigan	Forest	1.7	1836[a]	16.3	459	678	91	Fisk et al. (2002)
California	Forest	2	3140[a]	23.6	203	44	49	Frazer et al. (1990)
California[7]	Forest	1.6	2512[a]	23.6	203	44	31	Frazer et al. (1990)
California	Forest	1.5	2355[a]	23.6	203	44	12	Frazer et al. (1990)
West Virginia	Forest	4.2	5502[a]	19.7	777	553	77	Gilliam et al. (1996)
West Virginia	Forest	4.7	6157[a]	19.7	777	553	78	Gilliam et al. (1996)
Arizona	Forest	1.4	1453[a]	14.0	167	239	18	Grady and Hart (2006)
Arizona	Forest	1.6	1660[a]	14.0	167	239	13	Grady and Hart (2006)
Arizona	Forest	1.5	1557[a]	14.0	167	239	11	Grady and Hart (2006)
Arizona	Forest	1.2	1245[a]	14.0	167	239	27	Grady and Hart (2006)
Maryland	Forest	3.35	4355[b]	14.0	580	560	61	Groffman et al. (2006)
Maryland	Forest	3.35	4355[b]	14.0	580	560	71	Groffman et al. (2006)
Texas	Grassland	0.7	980[b]	28.3	309	757	60	Hibbard et al. (2001)
Texas	Grassland	1.8	1980[b]	28.3	309	757	220	Hibbard et al. (2001)
Texas	Grassland	1.2	1320[b]	28.3	309	757	160	Hibbard et al. (2001)

Table 3.1 (Continued)

Texas	Grassland	2	2200[b]	28.3	309	757	140	Hibbard et al. (2001)
New York	High elevation forest	11.5	11040[a]	17.0	410	569	37.3	Joshi et al. (2003)
New York	High elevation forest	16.1	15456[a]	17.0	410	569	28.99	Joshi et al. (2003)
New York	High elevation forest	13.8	13248[a]	17.0	410	569	21.82	Joshi et al. (2003)
New York	High elevation forest	13.2	12672[a]	17.0	410	569	25.29	Joshi et al. (2003)
New York	High elevation forest	15.2	14592[a]	17.0	410	569	19.85	Joshi et al. (2003)
Colorado	Grassland	1.946	1759[b]	18.5	261	229	14.9	McCulley et al. (2009)
Colorado	Grassland	1.185	1386[b]	20.2	291	322	30.4	McCulley et al. (2009)
Kansas	Grassland	3.151	3299[b]	22.8	355	417	30	McCulley et al. (2009)
Kansas[7]	Grassland	2.697	2729[b]	22.8	393	417	24.5	McCulley et al. (2009)
Kansas	Grassland	1.881	1836[b]	23.5	521	448	14.8	McCulley et al. (2009)
Vermont	High elevation forest	12.2	13786[a]	17.9	503	372	13.7	McNulty and Aber (1993)
Vermont[7]	High elevation forest	12.2	13786[a]	17.9	503	372	15.7	McNulty and Aber (1993)
Vermont	High elevation forest	12.2	13786[a]	17.9	503	372	16	McNulty and Aber (1993)
Minnesota	Grassland	0.59	888[a]	18.5	452	685	44	Pastor et al. (1987)

Table 3.1 (Continued)

Minnesota	Grassland	0.54	802[a]	18.5	452	685	45	Pastor et al. (1987)
Minnesota	Grassland	0.80	1203[a]	18.5	452	685	48	Pastor et al. (1987)
Minnesota	Grassland	1.05	1581[a]	18.5	452	685	65	Pastor et al. (1987)
Oregon	Forest	2.90	1552[a]	13.1	155	520	8	Perakis and Sinkhorn (2011)
Oregon	Forest	3.10	1659[a]	13.1	155	520	12	Perakis and Sinkhorn (2011)
Oregon[7]	Forest	3.30	1766[a]	16.0	96	249	25	Perakis and Sinkhorn (2011)
Oregon	Forest	3.30	1766[a]	16.0	96	249	22	Perakis and Sinkhorn (2011)
Oregon	Forest	3.40	1819[a]	16.0	97	249	37	Perakis and Sinkhorn (2011)
Oregon	Forest	3.80	2033[a]	16.0	96	249	42	Perakis and Sinkhorn (2011)
Oregon	Forest	5.70	3050[a]	13.1	114	520	51	Perakis and Sinkhorn (2011)
Oregon	Forest	7.80	4173[a]	13.1	136	520	82	Perakis and Sinkhorn (2011)
North Carolina	Forest	0.70	812[b]	24.1	525	513	34.4	Piatek and Allen (1999)
North Carolina	Forest	0.70	812[b]	24.1	525	513	22.3	Piatek and Allen (1999)
North Carolina	Forest	0.70	812[b]	24.1	525	513	34.4	Piatek and Allen (1999)
North Carolina	Forest	0.60	696[b]	24.1	525	513	19.1	Piatek and Allen (1999)

Table 3.1 (Continued)

California	Forest	1.80	1869[a]	23.2	118	130	21.2	Powers (1990)
California	High elevation forest	1.70	3174[a]	23.2	85	130	40.4	Powers (1990)
California	High elevation forest	1.57	1628[a]	23.2	118	130	1.2	Powers (1990)
Massachusetts	Forest	17.00	19550[a]	18.5	514	424	16.1	Rustad et al. (2001)
Maine	Forest	10.00	9400[a]	18.4	280	403	41.3	Rustad et al. (2001)
Tennessee	High elevation forest	5.37	6766[a]	21.8	533	430	152	Strader et al. (1989)
Tennessee	High elevation forest	5.50	6930[a]	21.8	533	430	87	Strader et al. (1989)
North Carolina	High elevation forest	6.10	7137[a]	15.0	463	576	134	Strader et al. (1989)
North Carolina[7]	High elevation forest	9.03	10565[a]	15.0	463	576	82	Strader et al. (1989)
North Carolina	High elevation forest	8.97	10491[a]	15.0	463	576	98	Strader et al. (1989)
Virginia	High elevation forest	8.80	12144[a]	21.9	531	460	73	Strader et al. (1989)
Virginia	High elevation forest	6.85	9453[a]	21.9	531	460	93	Strader et al. (1989)

[1]Soil N: measured total soil nitrogen (g kg^{-1})

[2]Estimated soil N: total soil nitrogen estimated using bulk density (kg ha^{-1})

[3]Temp: average growing season air temperature (°C) from NCDC

[4]N dep: nitrogen deposition (eqN ha^{-1} yr^{-1}) from McNulty et al. (2007)

[5]Precip: total growing season precipitation (mm) from NCDC

[6]N_min: measured nitrogen mineralization (kg ha^{-1} yr^{-1})

[7]Data used for validation of regression equations

[a]Bulk density determined by soil type for use in estimating mass per area total soil nitrogen

[b]Complete bulk density given in publication and used for estimating mass per area total soil nitrogen

3.2 Linear Regression Models

Stepwise multiple linear regressions were performed independently in Microsoft Excel for each data category (i.e., high elevation forests, low elevation high temperature forests, low elevation low temperature forests, and grasslands) with annual net nitrogen mineralization as the dependent variable and four independent variables: total soil nitrogen from 0 to 10 cm depth, average air temperature during growing season (°C), total precipitation during growing season (mm), and wet plus dry nitrogen deposition (eqN ha^{-1} yr^{-1}). Independent variables were only included in the final equations if they were statistically significant (i.e., *p*-value < 0.1). Two sets of equations were created: one using provided total soil nitrogen in mass N per mass of soil and the other utilizing estimated total soil nitrogen values in mass N per area to provide equations for each measurement method. The coefficient of determination (R^2) and adjusted coefficient of determination (adjusted R^2) are given for each category. R^2 assumes that every independent variable in the model helps to explain variation in the dependent variables and indicates how well the regression line predicts actual data points. The adjusted R^2 accounts for only the independent variables that truly affect the dependent variable and thus represents the percentage of variation explained by the influential independent variables.

3.3 Mapping Plant-Available Soil Nitrogen

The equations developed were used to calculate national scale net nitrogen mineralization from existing CONUS databases of total kjeldahl nitrogen, average growing season air temperature, total growing season precipitation, and nitrogen deposition. The total kjeldahl nitrogen map was developed at a 1 km^2 resolution using soil taxonomic relationships to link data from the National Soil Characterization Database to spatial information in STATSGO (State Soil Geographic Database) (Hargrove and Hoffman, 2004). Averages from 1960-2010 Parameter-elevation Regressions on Independent Slopes Model (PRISM) data at a 1-km^2 resolution (http://www.prism.oregonstate.edu/) were used to obtain average growing season temperature and total growing season precipitation. The map aggregated to a 1-km^2 resolution compiled by McNulty et al. (2007) used for equation development was also used for wet and dry nitrogen deposition in the map creation.

Equations in mass per area measurements were utilized for map creation as the total kjeldahl nitrogen map is in units of kg ha^{-1}. The 2006 National Land Cover Database (Fry et al., 2011) was used to determine which areas are forests and grasslands. Forested land cover types included deciduous, evergreen, and mixed forests. Grasslands, pastures, and shrublands were included in the grassland category. PRISM average growing season air temperature data was used to determine forest areas above and below 19 °C for use in separating high temperature forests from low temperature forests. High elevation in this study indicates an elevation of 304.8 m (i.e., 1000 ft) or greater (Fisher and Wood, 1998). The National Elevation Dataset (Data available from the U.S. Geological Survey) was utilized to determine elevation. Spatially distributed net nitrogen mineralization was computed within ArcMap raster calculator as functions of total kjeldahl nitrogen, nitrogen deposition, temperature, and precipitation. Net nitrogen mineralization for each data category was calculated separately using the appropriate equation, and then summed to obtain a complete map for the CONUS.

3.4 Validation of the Linear Regression Models

In each of the four data categories (i.e., high elevation forests, low elevation high temperature forests, low elevation low temperature forests, and grasslands), two net nitrogen mineralization data points were randomly excluded from regression for use in validation of the derived regression equations (Table 3.1 and Figure 3.2). After stepwise multiple linear regression was performed and statistically significant variables were identified (p-value < 0.1), the corresponding equation was used to predict nitrogen mineralization for these two excluded sites in each data category. The predicted nitrogen mineralization values were compared to the measured nitrogen mineralization values to verify if the equations were representative of different site conditions. A value was considered significantly different if the predicted value did not fall within the measured value plus or minus the standard error of the category (Ott and Longnecker, 2001). If the predicted net nitrogen mineralization was significantly different from the measured value, factors causing the discrepancy are explored and discussed. For consistency, the same two data points in each category were excluded for validation in both of the equation sets (g kg^{-1} and kg ha^{-1}).

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1 Independent Variable Relationships

To determine the overall relationship of each of the variables to net nitrogen mineralization, data from all categories were combined. Net nitrogen mineralization was graphed as a function of average growing season temperature (Figure 4.1), total growing season precipitation (Figure 4.2), nitrogen deposition (Figure 4.3), and total soil nitrogen (Figure 4.4). As expected from past experiments, net nitrogen mineralization increased with increasing temperature, precipitation, and nitrogen deposition. Although the relationships were not strong ($R^2 < 0.4$), the general trends are shown. The low R^2, as well as outliers, imply that additional variables other than the one graphed explain the increase in net nitrogen mineralization. For example, the low R^2 for temperature indicates that other variables, such as precipitation, are responsible for the change in net nitrogen mineralization. Net nitrogen mineralization decreased slightly with increasing TKN. This relationship is due to very different net nitrogen mineralization rates in different ecosystems. For example, high elevation areas often have very high TKN, but their net nitrogen mineralization is low due to low temperature. This resulted in a negative TKN versus net nitrogen mineralization relationship with all data categories combined. Regression performed with the data combined resulted in a low correlation ($R^2 = 0.37$ and adjusted $R^2 = 0.33$). Precipitation was the primary predicting variable (p-value $= 7 \times 10^{-3}$). Data separation into the discussed categories (grasslands, high elevation forests, low elevation low temperature forests, and low elevation high temperature forests) greatly improved the predictive quality of these variables. The regressions performed with data separation were the focus of this study.

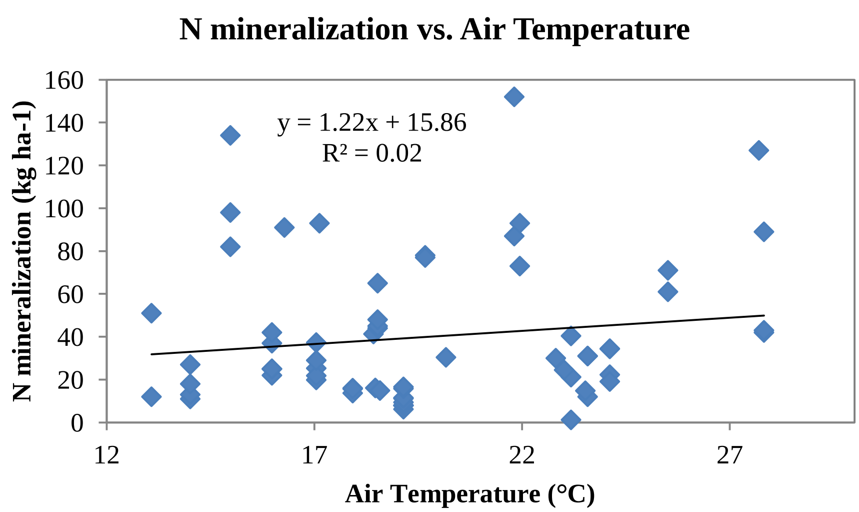

Figure 4.1. Nitrogen mineralization in response to average growing season temperature.

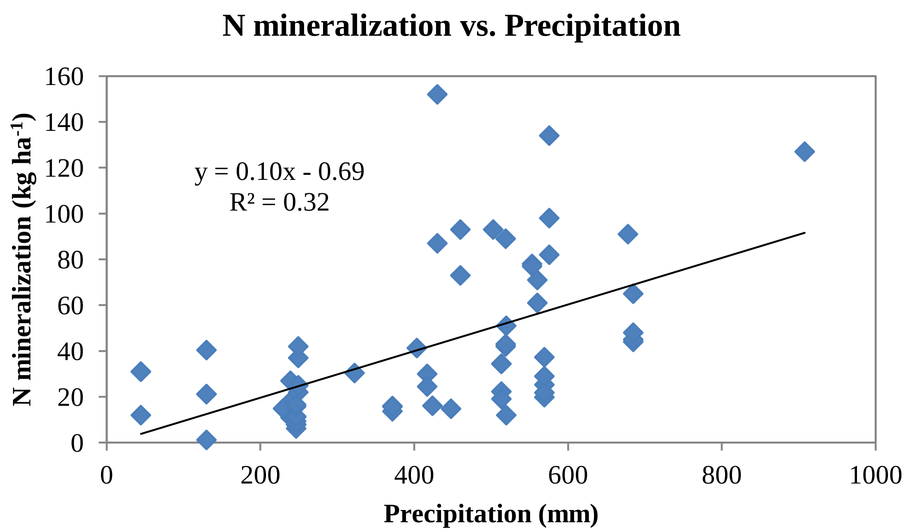

Figure 4.2. Nitrogen mineralization in response to total growing season precipitation.

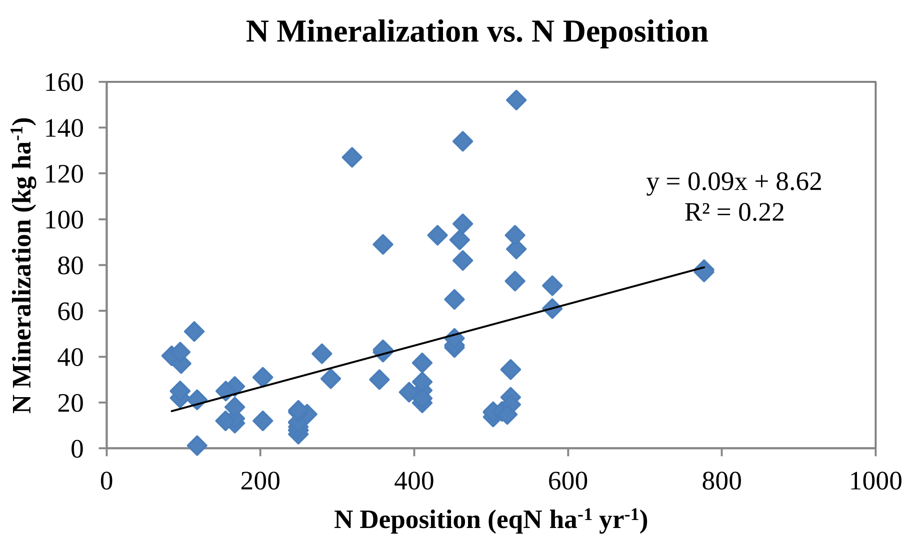

Figure 4.3. Nitrogen mineralization in response to nitrogen deposition.

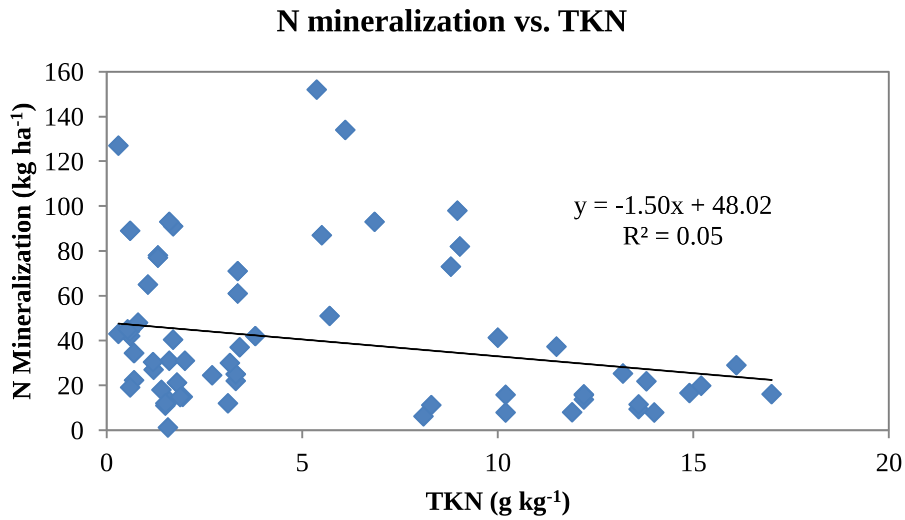

Figure 4.4. Nitrogen mineralization in response to total soil nitrogen.

4.2 Nitrogen Mineralization Equations using Total Soil Nitrogen Units of Mass per Mass (g kg^{-1})

In the publications used in this study, the provided total soil nitrogen value was measured and reported in mass per mass terms (g kg^{-1}). Using these units, data were analyzed, stepwise multiple linear regressions were performed, and equations created for each category. The equations in this section can be used for net nitrogen mineralization prediction when total soil nitrogen is measured and recorded on a per mass basis.

4.2.1 High Elevation Forest Category on Mass per Mass Basis

In the high elevation forest mass per mass category, the regression model for net nitrogen mineralization had a R^2 of 0.86, adjusted R^2 of 0.82, and standard error (S.E.) of 11.54 (sample size, n = 16) (Table 4.1). Significant variables were total soil nitrogen (*p*-value = 1.16×10^{-5}), nitrogen deposition (*p*-value = 1.08×10^{-2}), and precipitation (*p*-value = 1.79×10^{-2}). The equation resulting from stepwise multiple linear regression was used to predict net nitrogen mineralization for high elevation forest locations included in regression and compared to their corresponding measured value (Figure 4.5). Validation sites in Vermont and North Carolina were predicted to have net nitrogen mineralization rates of 16 kg ha^{-1} yr^{-1} (vs. observed value of 15.7 kg ha^{-1} yr^{-1}) and 93 kg ha^{-1} yr^{-1} (vs. observed value of 82 kg ha^{-1} yr^{-1}), respectively. These predictions fall within one standard error of the measured value. The formula for net nitrogen mineralization in the high elevation forest category is presented below (Equation 1).

$$N\_min_{highelev} = -5.61 - 11.34 \times SoilN + 0.15 \times Depo + 0.23 \times Precip \qquad (1)$$

where N_min is predicted net nitrogen mineralization (kg ha^{-1} yr^{-1}), SoilN is total soil nitrogen (g kg^{-1}), Depo is nitrogen deposition (eqN ha^{-1} yr^{-1}), and Precip is total growing season precipitation (mm).

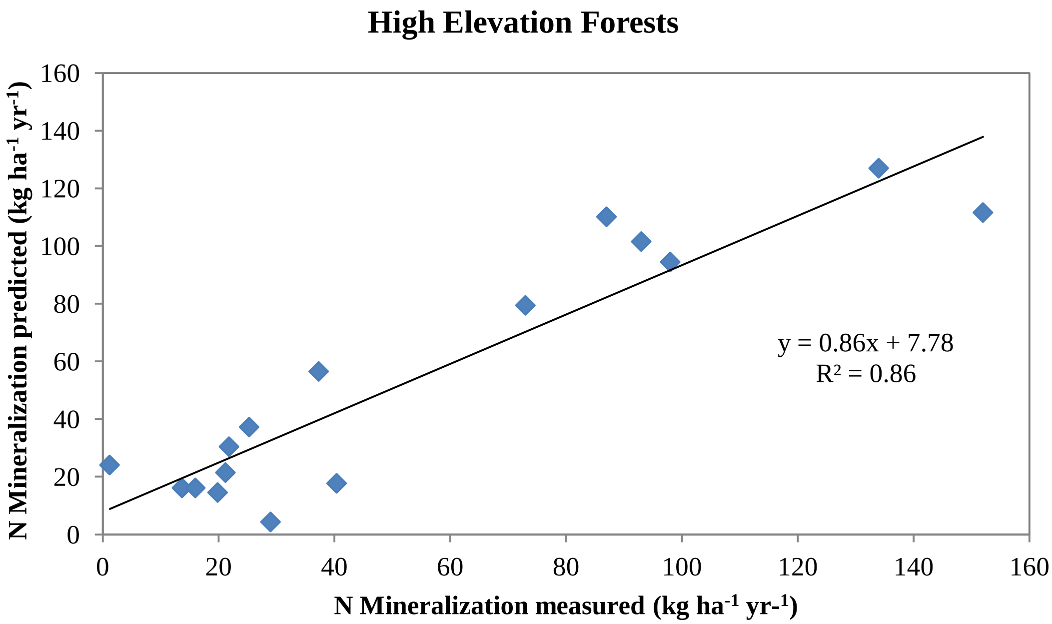

Figure 4.5. Measured and predicted nitrogen mineralization in the per mass high elevation forest category.

4.2.2 Grassland Category on Mass per Mass Basis

After graphing net nitrogen mineralization for grasslands (R^2 = 0.73), it was apparent that the data from Hibbard et al. (2001) was an outlier, as measured net nitrogen mineralization values were much greater than those in other areas. Further investigation revealed that this study was conducted on a site with heavy livestock grazing, possibly resulting in the fertilization of the soil. Previous studies have shown that nitrogen dynamics can be altered by long-term livestock grazing (Welker et al., 2004). Thus, this study was omitted in further calculations. The net nitrogen mineralization regression equation for grasslands had a high correlation (R^2 = 0.88, adjusted R^2 = 0.86, n=16) and S.E. of 4.77. Only two variables were significant: precipitation (*p*-value = 5.49×10^{-5}) and nitrogen deposition (*p*-value = 8.1×10^{-2}). The equation resulting from stepwise multiple linear regression (Equation 2) was used to predict annual net nitrogen mineralization for all grassland locations included in the regression and compared to their corresponding measured values (Figure 4.6). The equation predicted a net nitrogen mineralization rate of 12 kg ha^{-1} yr^{-1} (vs. observed value of 16.6 kg ha^{-1} yr^{-1}) at the Colorado site and 22.3 kg ha^{-1} yr^{-1} (vs. observed value of 24.5 kg ha^{-1} yr^{-1}) at the Kansas site. The predictions for the validation sites fall within the acceptable range of measured value plus or minus one standard error.

$$\mathrm{N\_min}_{\mathrm{grassland}} = 0.20 - 0.08 \times \mathrm{Depo} + 0.12 \times \mathrm{Precip} \qquad (2)$$

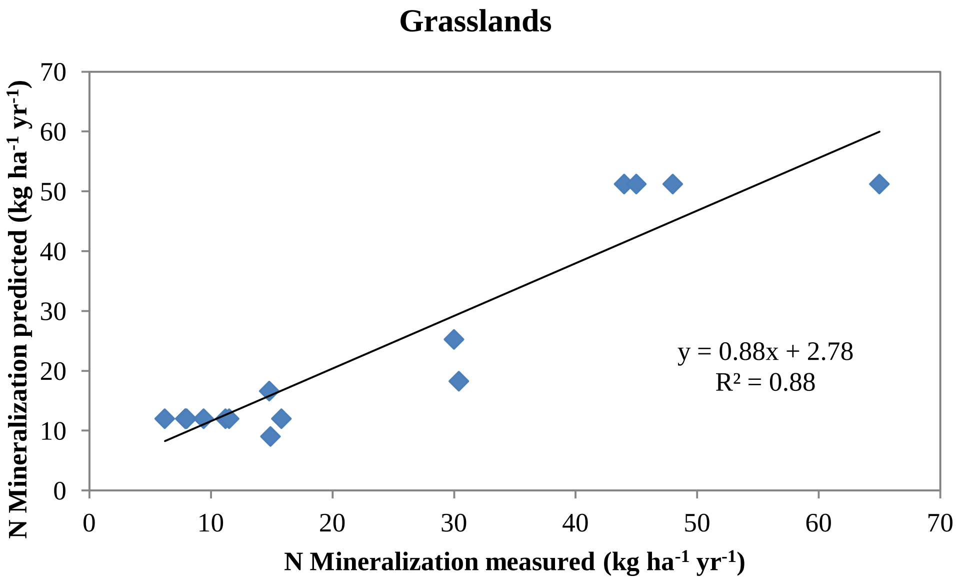

Figure 4.6. Measured and predicted nitrogen mineralization in the per mass grassland category.

4.2.3 Low Elevation Low Temperature Forest Category on Mass per Mass Basis

In the low elevation low temperature forest (mean growing season temperature < 19 °C) category, net nitrogen mineralization regression generated R^2 of 0.71, adjusted R^2 of 0.62, and S.E. of 5.70 (n=14). Significant variables were precipitation (*p*-value = 1.26×10^{-3}), total soil nitrogen (*p*-value = 1.32×10^{-2}), and temperature (*p*-value = 1.65×10^{-2}). The associated equation (Equation 3) was used to predict net nitrogen mineralization for all low elevation low temperature forest locations and compared to their corresponding measurements (Figure 4.7). The equation was used to predict annual nitrogen mineralization for two validation sites. The model predicted a site in Oregon to have a net nitrogen mineralization rate of 29 kg ha^{-1} yr^{-1} (vs. observed value of 25 kg ha^{-1} yr^{-1}) and a site in Michigan to have a net nitrogen mineralization rate of 74.5 kg ha^{-1} yr^{-1} (vs. observed value of 93 kg ha^{-1} yr^{-1}). The prediction for Michigan is not within one standard error of the measured value. The site in Michigan is possibly underpredicted due to a high amount of soil organic matter at the site. Increased soil organic matter has been shown to increase net nitrogen mineralization (Berendse, 1990).

$$N\_min_{lowforest} = -121.45 - 3.65 \times SoilN + 8.34 \times Temp + 0.12 \times Precip \qquad (3)$$

where Temp is average growing season air temperature (°C).

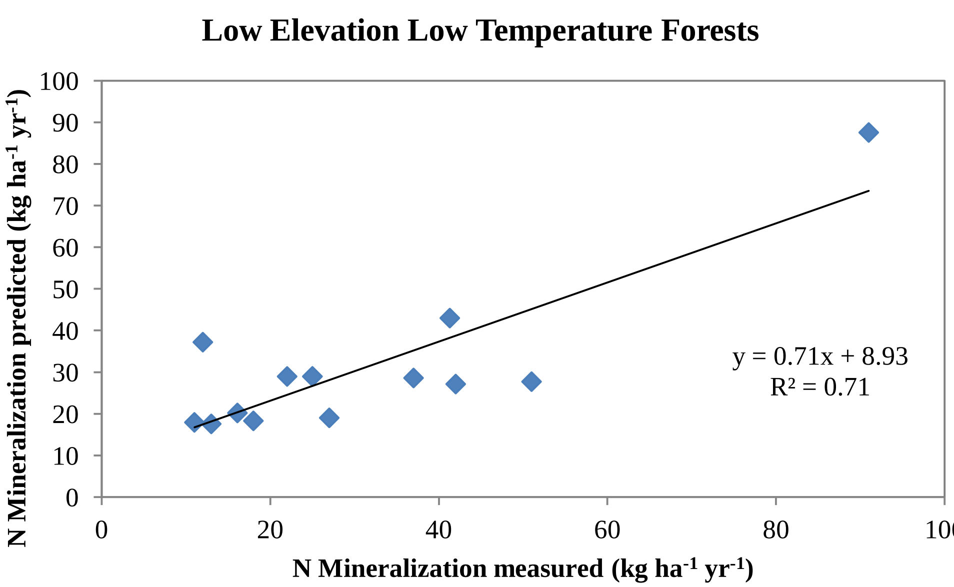

Figure 4.7. Measured and predicted nitrogen mineralization in the per mass low elevation low temperature forest category.

4.2.4 Low Elevation High Temperature Forest Category on Mass per Mass Basis

In the low elevation high temperature forest category (mean growing season temperature ≥ 19 °C), net nitrogen mineralization regression generated R^2 of 0.80, adjusted R^2 of 0.74, and S.E. of 8.90 (n=12). Precipitation (*p*-value = 1.6×10^{-4}), total soil nitrogen (*p*-value = 5.2×10^{-3}), and nitrogen deposition (*p*-value = 9.1×10^{-3}) were significant variables. The equation resulting from regression (Equation 4) was used to predict annual net nitrogen mineralization for all low elevation high temperature forest locations included in regression and was compared to their corresponding measured results (Figure 4.8). Validation sites in California and Florida were predicted to have nitrogen mineralization rates of 19 kg ha^{-1} yr^{-1} (vs. observed value of 31 kg ha^{-1} yr^{-1}) and 50 kg ha^{-1} yr^{-1} (vs. observed value of 43 kg ha^{-1} yr^{-1}), respectively. The prediction for the Florida site is within the acceptable range, while the prediction for California is not. The California site was a regeneration stand and may have had elevated nitrate levels due to harvesting (Frazer et al., 1990). Thus, this site's nitrogen availability was underpredicted because stand harvesting was not taken into account.

$$N\_min_{highforest} = 5.29 + 16.23 \times SoilN - 0.13 \times Depo + 0.17 \times Precip \quad (4)$$

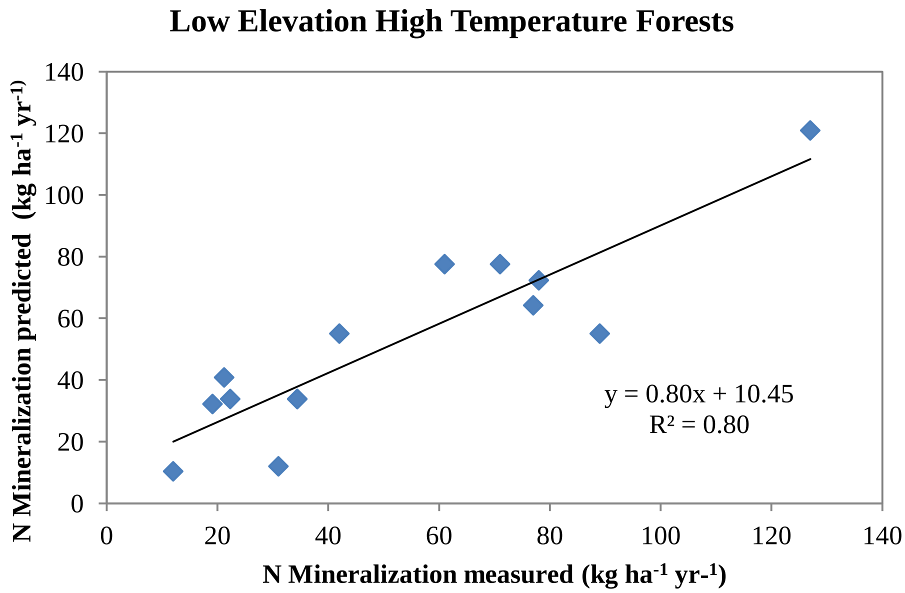

Figure 4.8. Measured and predicted nitrogen mineralization in the per mass high temperature forest category.

Table 4.1. Characteristics, coefficient of determination, and *p*-values for each data category selected for regression based on TKN unit of mass per mass

Category	High elev. forests	Grasslands	Low elev. low temp. forests	Low elev. high temp. forests
Land cover	Forest	Grassland	Forest	Forest
Elevation	≥ 1000 ft	All	< 1000 ft	< 1000 ft
Temperature	All	All	< 19 °C	≥ 19 °C
R^2	0.856	0.880	0.710	0.80
Adjusted R^2	0.820	0.861	0.623	0.736
SoilN *p*-value	$< 1.0 \times 10^{-4}$	-	1.32×10^{-2}	5.20×10^{-3}
N dep *p*-value	1.08×10^{-2}	8.10×10^{-2}	-	9.12×10^{-3}
Temp *p*-value	-	-	1.65×10^{-2}	-
Precip *p*-value	1.79×10^{-2}	$< 1.0 \times 10^{-4}$	1.26×10^{-3}	1.57×10^{-4}

where SoilN is total soil nitrogen (g kg^{-1}), N dep is nitrogen deposition (eqN ha^{-1} yr^{-1}), Temp is average growing season air temperature (°C), and Precip is total growing season precipitation (mm).

Table 4.2. Equations for each data category selected for regression based on TKN unit of mass per mass

Category	n	R^2	Adjusted R^2	Standard error	Equation
High elevation forests	16	0.86	0.82	11.54	$N\_min_{highelev} = -5.61 - 11.34 \times SoilN + 0.15 \times Depo + 0.23 \times Precip$
Grasslands	16	0.88	0.86	4.57	$N\_min_{grassland} = 0.10 - 0.08 \times Depo + 0.12 \times Precip$
Low elevation low temp. forests	14	0.71	0.62	5.70	$N\_min_{lowforest} = -121.45 - 3.65 \times SoilN + 8.34 \times Temp + 0.12 \times Precip$
Low elevation high temp. forests	14	0.80	0.74	8.90	$N\_min_{highforest} = 5.29 + 16.23 \times SoilN - 0.13 \times Depo + 0.17 \times Precip$

where SoilN is total soil nitrogen (g kg^{-1}), Depo is nitrogen deposition (eqN ha^{-1} yr^{-1}), Temp is average growing season air temperature (°C), and Precip is total growing season precipitation (mm).

4.3 Nitrogen Mineralization Equations using Estimated Total Soil Nitrogen Units of Mass per Area (kg ha^{-1})

Total soil nitrogen values provided (g kg^{-1}) were converted to units of mass per area (kg ha^{-1}) in order to best represent nitrogen availability for a region. The total soil nitrogen was estimated using bulk density for each location. Stepwise multiple linear regressions were again performed for each data category and new net nitrogen mineralization equations created. The same variables were found significant in each data category for both mass per mass and mass per area regressions. The equations presented in this section will be useful to determine net nitrogen mineralization when total soil nitrogen is measured and given in a per area basis, as well as providing an estimate over a region. The net nitrogen mineralization maps created in this study were created utilizing these equations with total soil nitrogen on a per area basis. The difference in the equation coefficients and predicted net nitrogen mineralization values in per mass and per area are due to differences in the regression equations. Regression equations differ due to the differences in total soil nirogen values (estimate used for per area soil nitrogen).

4.3.1 High Elevation Forest Category on Mass per Area Basis

In the high elevation forest category, the regression model for net nitrogen mineralization had a R^2 of 0.80, adjusted R^2 of 0.76, and S.E. of 11.54 (n = 16) (Table 4.3). Significant variables were total soil nitrogen (*p*-value = 7.6×10^{-5}), nitrogen deposition (*p*-value = 1.0×10^{-3}), and precipitation (*p*-value = 2.43×10^{-2}). The equation resulting from stepwise multivariable linear regression was used to predict net nitrogen mineralization for high elevation locations included in regression and compared to their corresponding measured values (Figure 4.9). Validation sites in Vermont and North Carolina were predicted to have nitrogen mineralization rates of 20 kg ha^{-1} yr^{-1} (vs. observed value of 15.7 kg ha^{-1} yr^{-1}) and 81 kg ha^{-1} yr^{-1} (vs. observed value of 82 kg ha^{-1} yr^{-1}), respectively. The predictions for the validation sites fall within the acceptable range of measured value plus or minus one standard error. The formula for nitrogen mineralization in the high elevation forest category is presented below (Equation 5).

$$\mathrm{N\_min}_{\mathrm{highelev}} = -0.71 - 0.01 \times \mathrm{SoilN} + 0.25 \times \mathrm{Depo} + 0.16 \times \mathrm{Precip} \qquad (5)$$

where N_min is predicted net nitrogen mineralization (kg ha^{-1} yr^{-1}), SoilN is total soil nitrogen (kg ha^{-1}), Depo is nitrogen deposition (eqN ha^{-1} yr^{-1}), Temp is average growing season air temperature (°C), and Precip is total growing season precipitation (mm).

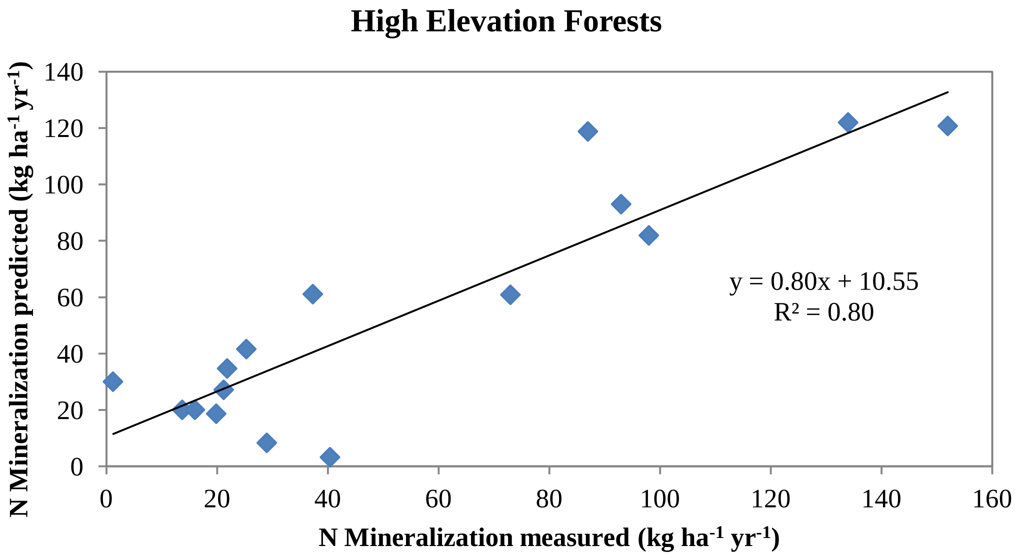

Figure 4.9. Measured and predicted nitrogen mineralization in the per area high elevation forest category.

4.3.2 Grassland Category on Mass per Area Basis

The data from Hibbard et al. (2001) was again excluded from calculations due to possible soil fertilization. The net nitrogen mineralization regression equation for grasslands had a strong correlation (R^2 = 0.88, adjusted R^2 = 0.86, n=16) and S.E. of 4.77. The same two variables were significant as in the mass per mass category: precipitation (*p*-value = 5.49×10^{-5}) and nitrogen deposition (*p*-value = 8.1×10^{-2}). The equations for grasslands mass per mass and mass per area are the same because they have the same significant variables that do not include TKN. The associated equation (Equation 6) was used to predict annual nitrogen mineralization for all grassland locations included in the regression and compared to their corresponding measured values (Figure 4.10). The equation predicted validation sites in Colorado to have a nitrogen mineralization rate of 12 kg ha^{-1} yr^{-1} (vs. observed value of 16.6 kg ha^{-1} yr^{-1}) and Kansas was predicted to be 22.3 kg ha^{-1} yr^{-1} (vs. observed value of 24.5 kg ha^{-1} yr^{-1}). These predictions fall within the acceptable range.

$$\mathrm{N\_min}_{\mathrm{grassland}} = 0.10 - 0.08 \times \mathrm{Depo} + 0.12 \times \mathrm{Precip} \quad (6)$$

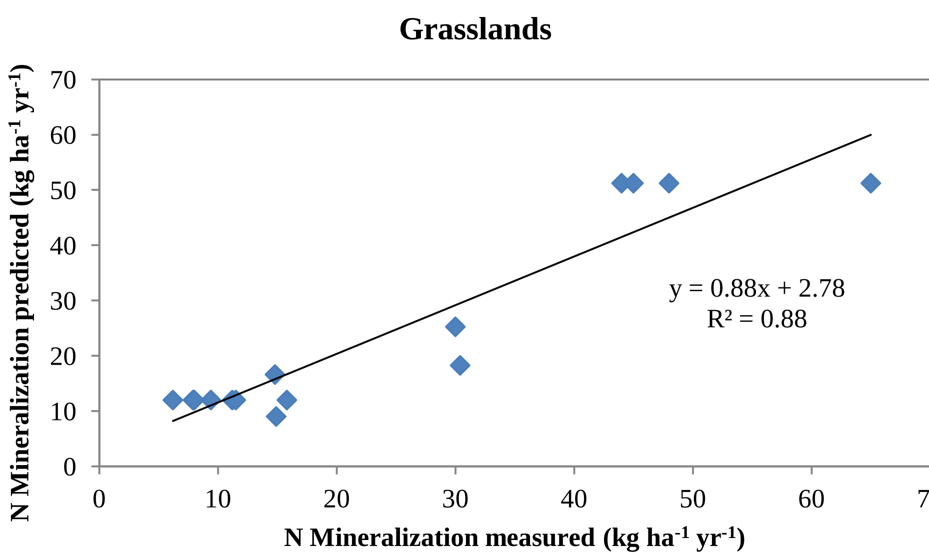

Figure 4.10. Measured and predicted nitrogen mineralization in the per area grassland category.

4.3.3 Low Elevation Low Temperature Forest Category on Mass per Area Basis

In the low elevation low temperature (mean growing season temperature < 19 °C) forest category, nitrogen mineralization regression generated R^2 of 0.71, adjusted R^2 of 0.62, and S.E. of 5.70 (n=14). Significant variables were precipitation (p-value = 9.3×10^{-3}), total soil nitrogen (p-value = 8.1×10^{-3}), and temperature (p-value = 1.14×10^{-2}). The equation generated through regression (Equation 7) was used to predict net nitrogen mineralization for all low elevation low temperature forest locations included in regression and was compared to their corresponding measured results (Figure 4.11). The model predicted that a site in Oregon would have a net nitrogen mineralization rate of 31 kg ha^{-1} yr^{-1} (vs. observed value of 25 kg ha^{-1} yr^{-1}) and a site in Michigan was predicted to be 71 kg ha^{-1} yr^{-1} (vs. observed value of 93 kg ha^{-1} yr^{-1}). These sites do not fall within the measured value plus or minus one standard error. The validation site in Oregon could be overpredicted due to vegetation type because this site is dominated by Douglas-fir trees. Conifers in the Pacific Northwest are generally considered nitrogen poor (Sollins et al., 1980; Fenn et al., 1998). The site in Michigan is again possibly underpredicted due to a high amount of soil organic matter at the site.

$$N\_min_{lowforest} = -127.06 - 0.003 \times SoilN + 8.47 \times Temp + 0.12 \times Precip \qquad (7)$$

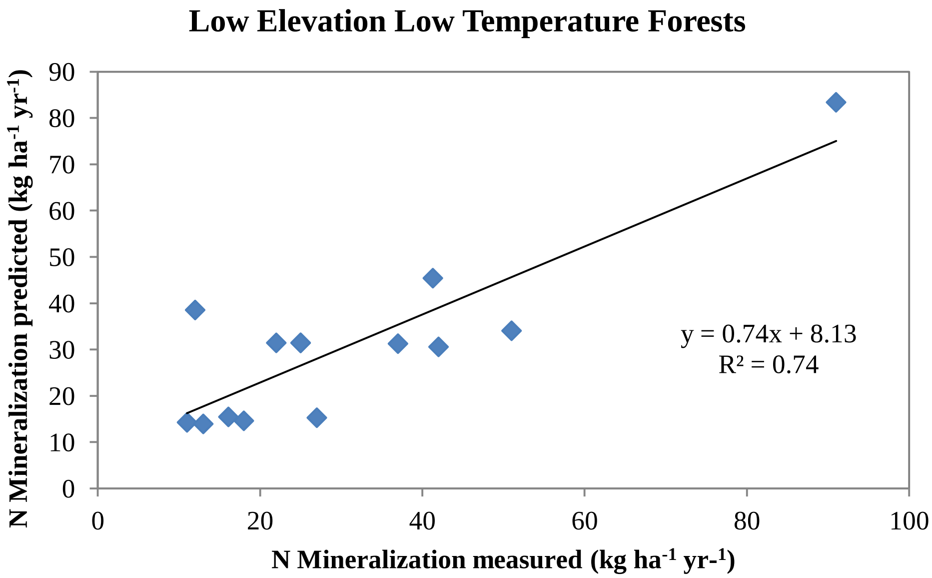

Figure 4.11. Measured and predicted nitrogen mineralization in the per area forest category for low elevation low temperature locations.

4.3.4 Low Elevation High Temperature Forest Category on Mass per Area Basis

In the low elevation high temperature forest category (mean growing season temperature ≥ 19 °C), the net nitrogen mineralization regression R^2 was 0.8, adjusted R^2 was 0.74, and S.E. was 8.9 (n=12). Variables significant in this category were precipitation (*p*-value = 6.16×10^{-5}), total soil nitrogen (*p*-value = 1.96×10^{-3}), and nitrogen deposition (*p*-value = 4.09×10^{-3}). The resulting equation (Equation 8) was used to predict annual net nitrogen mineralization for all low elevation high temperature forest locations included in regression and was compared to their corresponding measured values (Figure 4.12). Validation sites in California and Florida were predicted to have net nitrogen mineralization rates of 24 kg ha^{-1} yr^{-1} (vs. observed value of 31 kg ha^{-1} yr^{-1}) and 50 kg ha^{-1} yr^{-1} (vs. observed value of 43 kg ha^{-1} yr^{-1}), respectively. The predictions for these validation sites fall within the acceptable range of measured value plus or minus one standard error.

$$N\_min_{highforest} = 3.39 + 0.01 \times SoilN - 0.14 \times Depo + 0.17 \times Precip \quad (8)$$

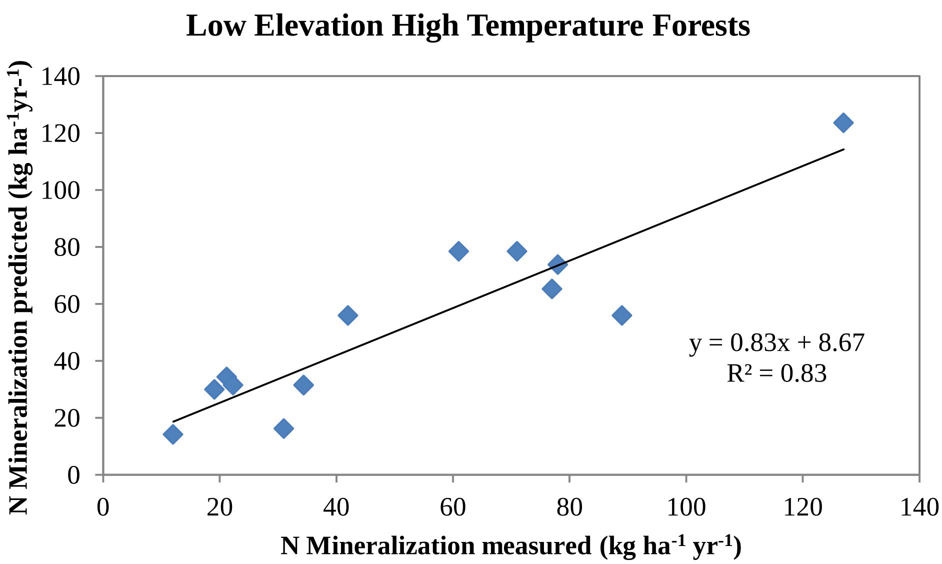

Figure 4.12. Measured and predicted nitrogen mineralization in the low elevation high temperature forest per area category.

Table 4.3. Characteristics, coefficient of determination, and *p*-values for each data category selected for regression based on TKN unit of mass per area

Category	High elev. forests	Grasslands	Low elev. low temp. forests	Low elev. high temp. forests
Land cover	Forest	Grassland	Forest	Forest
Elevation	≥ 1000 ft	All	< 1000 ft	<1000 ft
Temperature	All	All	< 19 °C	≥ 19 °C
R^2	0.804	0.880	0.736	0.831
Adjusted R^2	0.755	0.861	0.656	0.781
SoilN *p*-value	$< 1 \times 10^{-4}$	-	8.10×10^{-3}	1.96×10^{-3}
N dep *p*-value	1.01×10^{-3}	8.10×10^{-2}	-	4.09×10^{-3}
Temp *p*-value	-	-	1.14×10^{-2}	-
Precip *p*-value	2.43×10^{-2}	$< 1 \times 10^{-4}$	9.33×10^{-4}	$< 1 \times 10^{-4}$

where SoilN is total soil nitrogen (kg ha^{-1}), N dep is nitrogen deposition (eqN ha^{-1} yr^{-1}), Temp is average growing season air temperature (°C), and Precip is total growing season precipitation (mm).

Table 4.4. Equations for each data category selected for regression based on TKN unit of mass per area

Category	n	R^2	Adjusted R^2	Standard error	Equation
High elevation forests	16	0.80	0.76	11.54	$N\_min_{highelev} = -0.71 - 0.01 \times SoilN + 0.25 \times Depo + 0.16 \times Precip$
Grasslands	16	0.88	0.86	4.57	$N\_min_{grassland} = 0.10 - 0.08 \times Depo + 0.12 \times Precip$
Low elevation low temp. forests	14	0.74	0.66	5.70	$N\_min_{lowforest} = -127.06 - 0.003 \times SoilN + 8.47 \times Temp + 0.12 \times Precip$
Low elevation high temp. forests	14	0.83	0.78	8.90	$N\_min_{highforest} = 3.39 + 0.01 \times SoilN - 0.14 \times Depo + 0.17 \times Precip$

where SoilN is total soil nitrogen (kg ha^{-1}), Depo is nitrogen deposition (eqN ha^{-1} yr^{-1}), Temp is average growing season air temperature (°C), and Precip is total growing season precipitation (mm).

4.4 Spatial Distribution of Net Nitrogen Mineralization

Predicted net nitrogen mineralization is the highest in the south and eastern portions of the U.S. and the lowest in the west (Figure 4.13). This trend mirrors that of nitrogen deposition and precipitation (Figure 4.14) that increase from west to east. High temperatures (Figure 4.14) correlate with high net nitrogen mineralization (Figure 4.13) in the southern U.S. The highest net nitrogen mineralization values correspond to low elevation eastern forests receiving high precipitation (Figures 4.15 and 4.16). Net nitrogen mineralization is the lowest in the grassland locations (Figure 4.17) and is consistent with low nutrient levels often found in old fields due to past agriculture practices (Pastor et al., 1987). Areas with predicted low nitrogen mineralization are similar to areas with extremely low TKN (Figure 4.14). High elevation forest areas have low predicted net nitrogen mineralization due to low air temperature and slow decomposition rates (Figure 4.18).

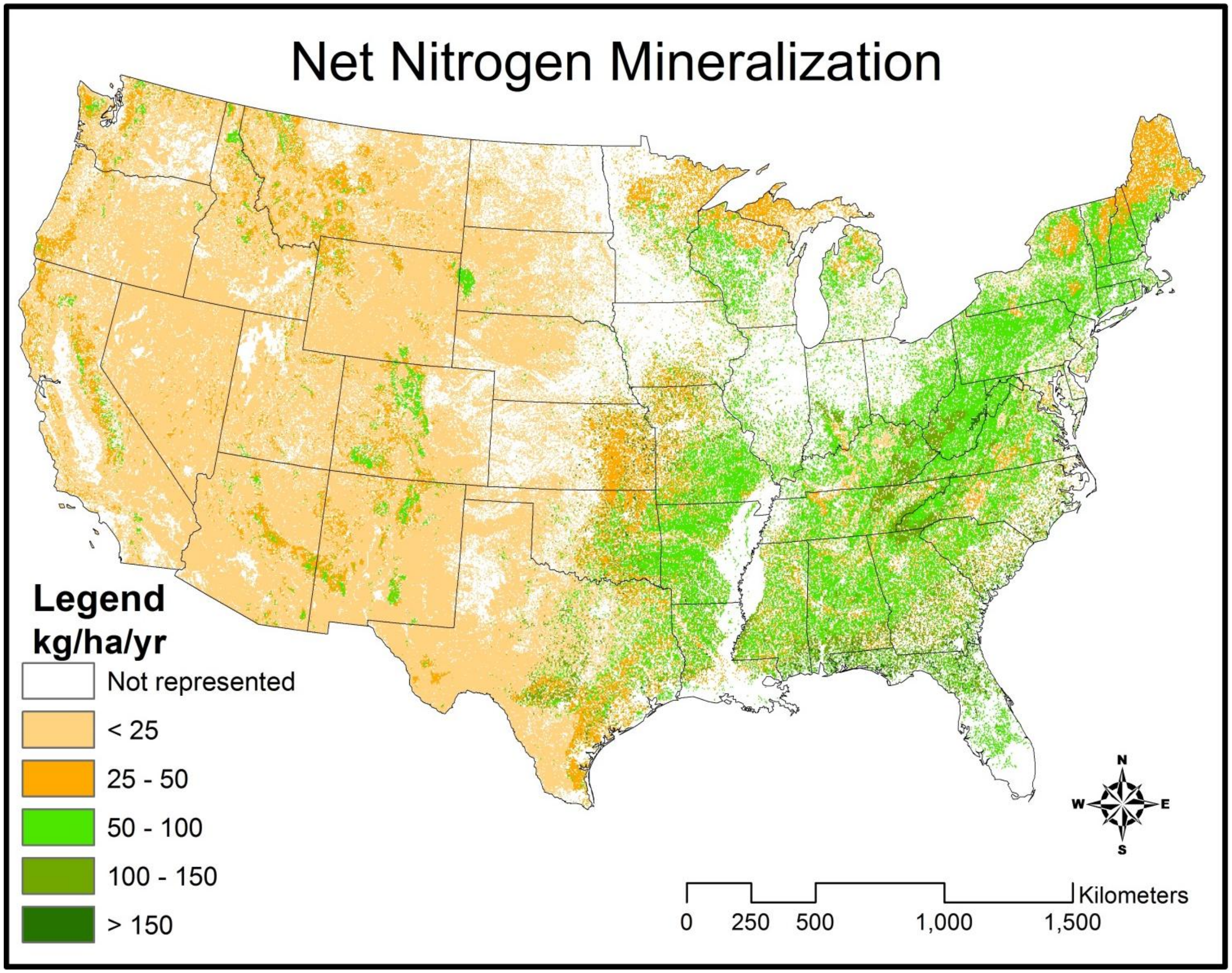

Figure 4.13. Map of net nitrogen mineralization created using developed regression equations. White areas indicate areas not included in this study (i.e., non-forest, non-grassland).

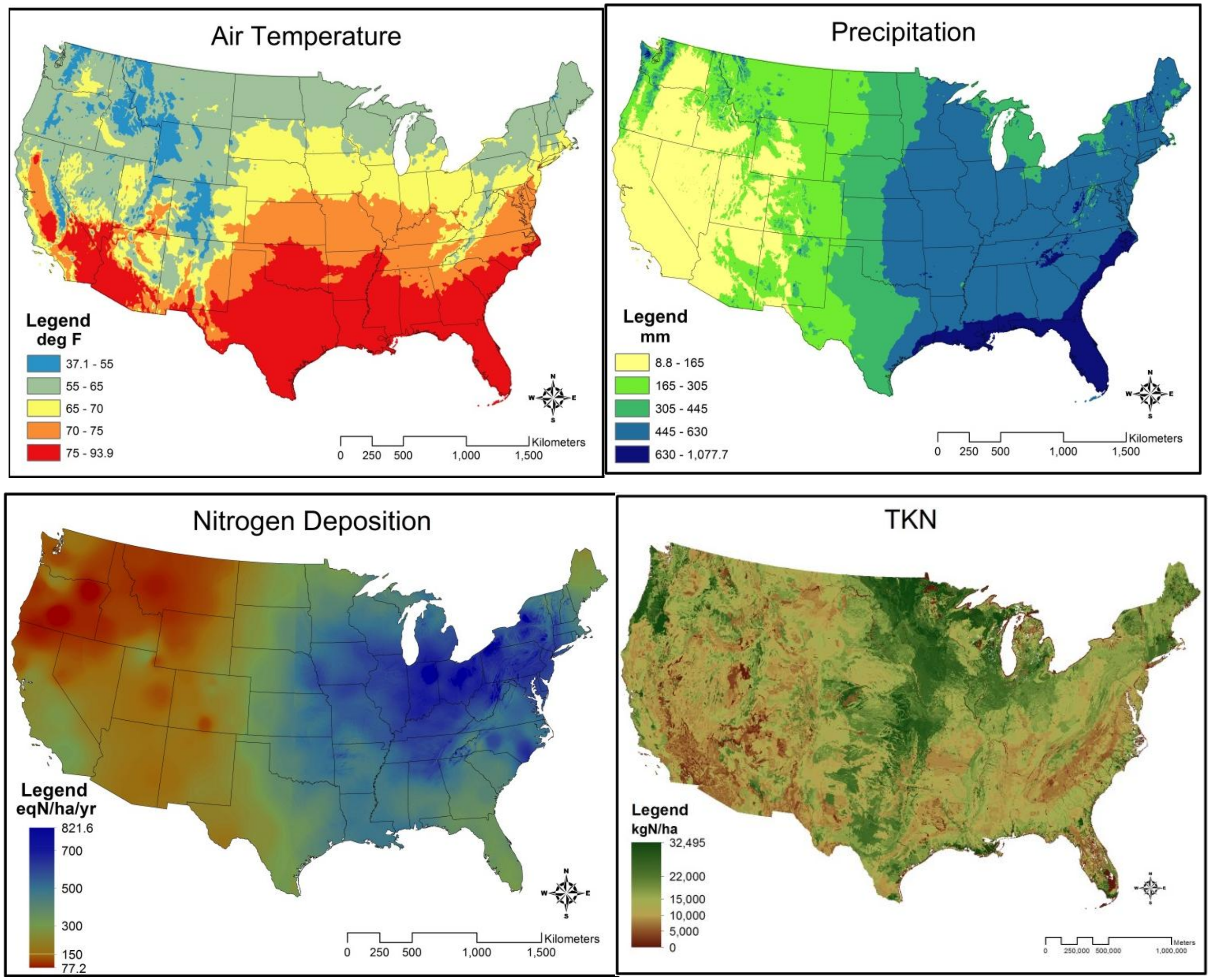

Figure 4.14. Input maps of temperature (upper left), precipitation (upper right), nitrogen deposition (lower left), and total kjeldahl nitrogen (lower right).

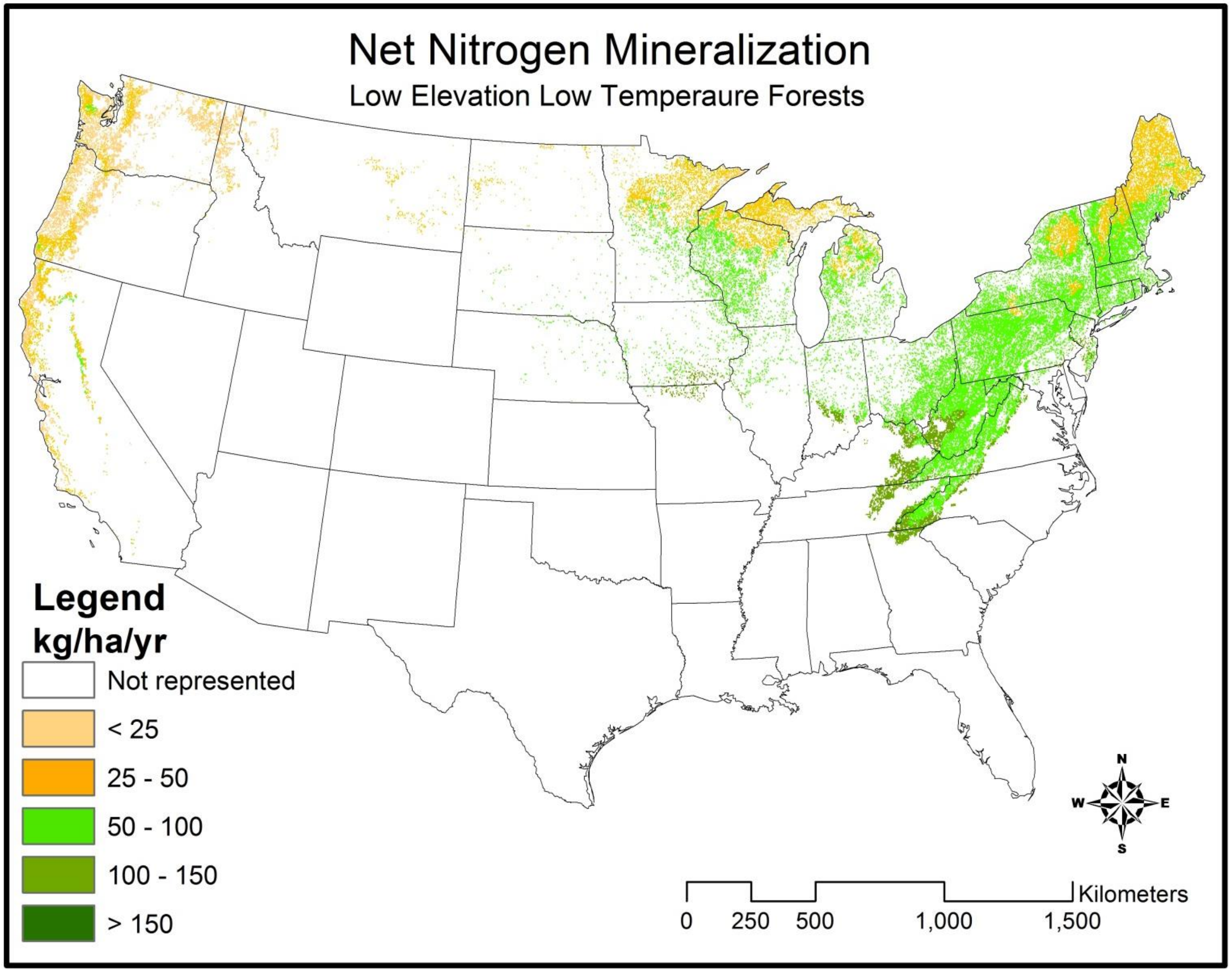

Figure 4.15. Map of net nitrogen mineralization for low elevation low temperature forests.

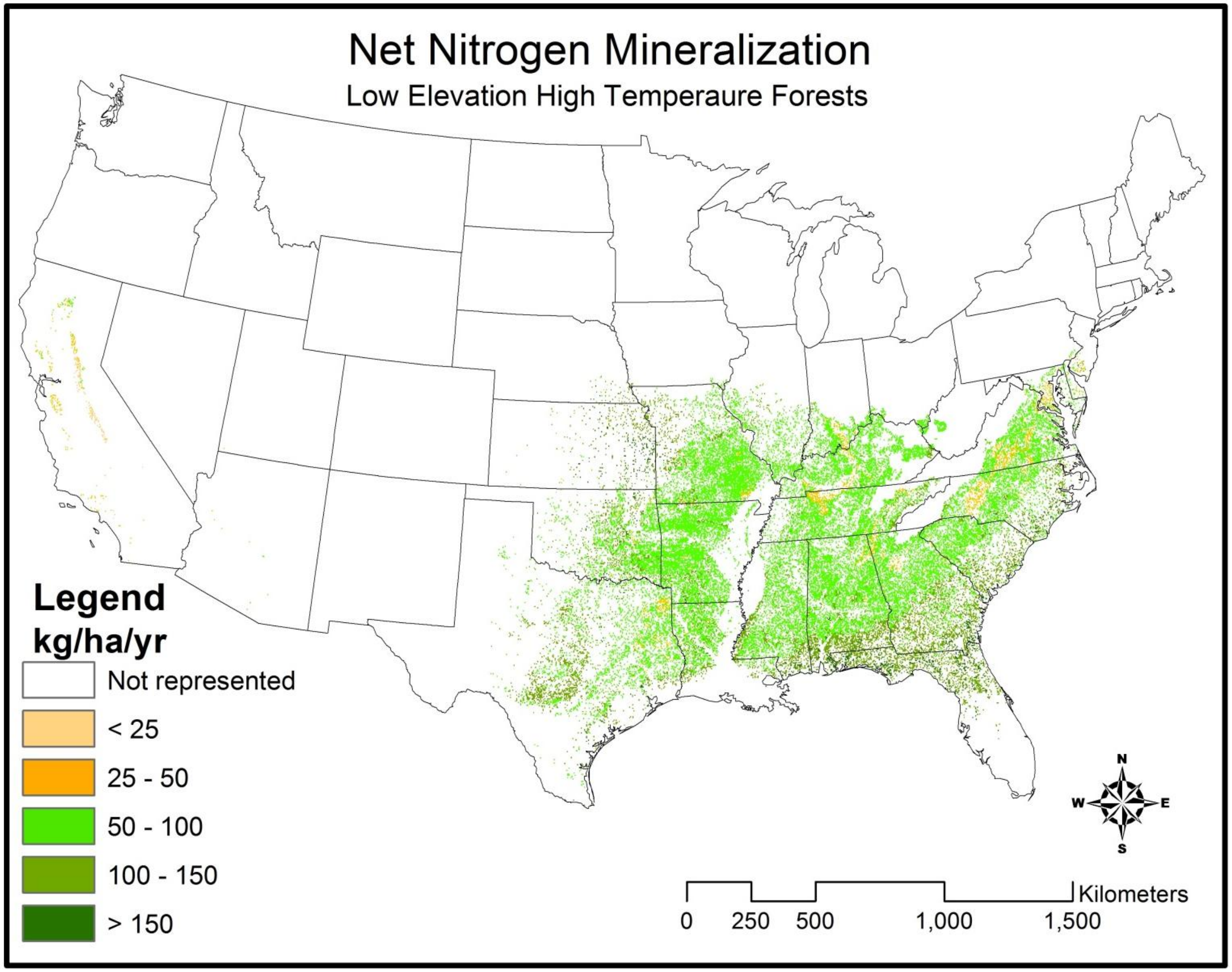

Figure 4.16. Map of net nitrogen mineralization for low elevation high temperature forests.

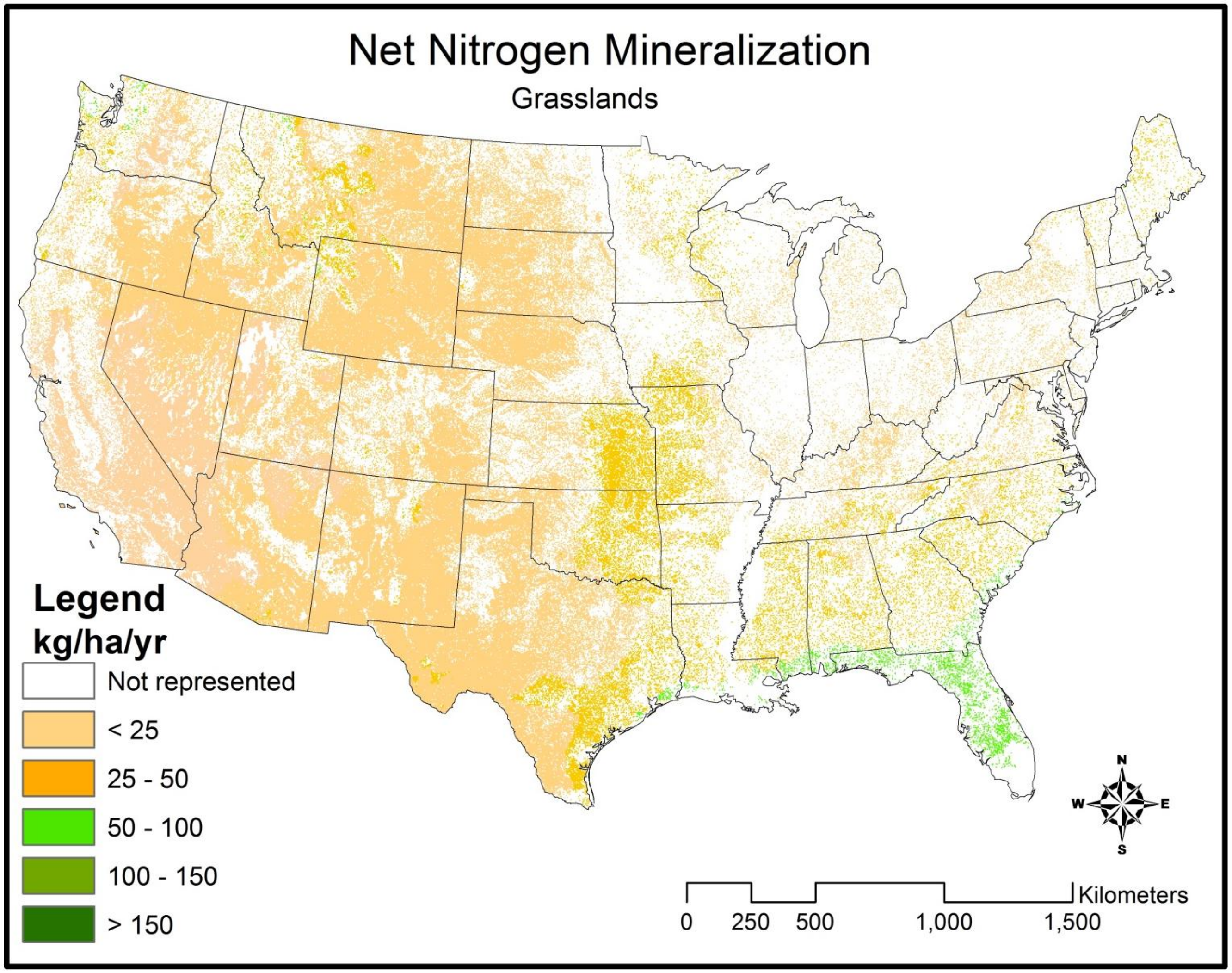

Figure 4.17. Map of net nitrogen mineralization for grassland locations.

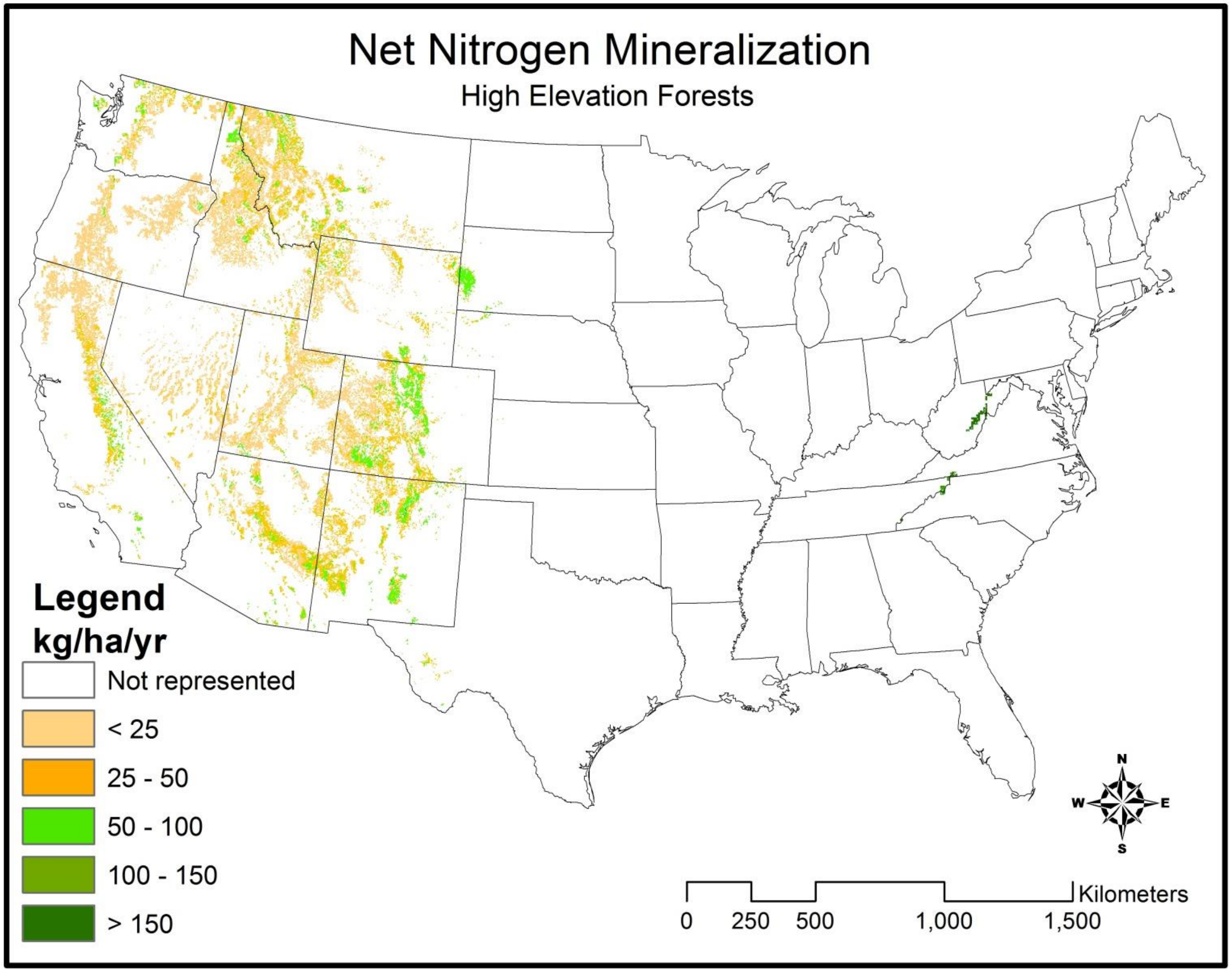

Figure 4.18. Map of net nitrogen mineralization for high elevation forest areas.

4.5 Statistical Analysis Results

Figure 4.19 shows a breakdown of net nitrogen mineralization for each category. Net nitrogen mineralization is categorized by low (< 50 kg ha^{-1} yr^{-1}), moderate (51-100 kg ha^{-1} yr^{-1}), high (101-150 kg ha^{-1} yr^{-1}), and very high (> 151 kg ha^{-1} yr^{-1}). A large majority of grassland and high elevation locations have values from > 50 kg ha^{-1} yr^{-1} (Figure 4.18). The high elevation forest category had 37,370 data points. The mean net nitrogen mineralization for the high elevation category was 22.6 kg ha^{-1} yr^{-1} (standard deviation, $\sigma = 4.86$), median was 22 kg ha^{-1} yr^{-1}, and mode (the value that appeared most often) was 0 kg ha^{-1} yr^{-1}. The grassland category had the majority of data points (222,360) due to a high frequency of shrubland in the western U.S. (Figure 4.21). The mean value for the grassland category was 14.3 kg ha^{-1} yr^{-1} ($\sigma = 2.89$), median was 14 kg ha^{-1} yr^{-1}, and mode was 18 kg ha^{-1} yr^{-1}. Both low and high temperature low elevation forest categories most often had a net nitrogen mineralization rate of 50-100 kg ha^{-1} yr^{-1} (Figure 4.20). Low elevation low temperature forests had 45,624 data points and had a mean of 58 kg ha^{-1} yr^{-1} ($\sigma = 3.46$), median of 57 kg ha^{-1} yr^{-1}, and mode of 49 kg ha^{-1} yr^{-1}. The mean for low elevation high temperature forests was 82.9 kg ha^{-1} yr^{-1} ($\sigma = 7.31$), median was 75 kg ha^{-1} yr^{-1}, and mode was 62 kg ha^{-1} yr^{-1} with 39,920 data points. As a whole, the CONUS (forest and grassland locations) had a mean net nitrogen mineralization rate of 30.8 kg ha^{-1} yr^{-1}, median of 19 kg ha^{-1} yr^{-1}, and mode of 18 kg ha^{-1} yr^{-1} (Figure 4.22). This average value was largely skewed toward grassland locations because of their high frequency (Figure 4.23).

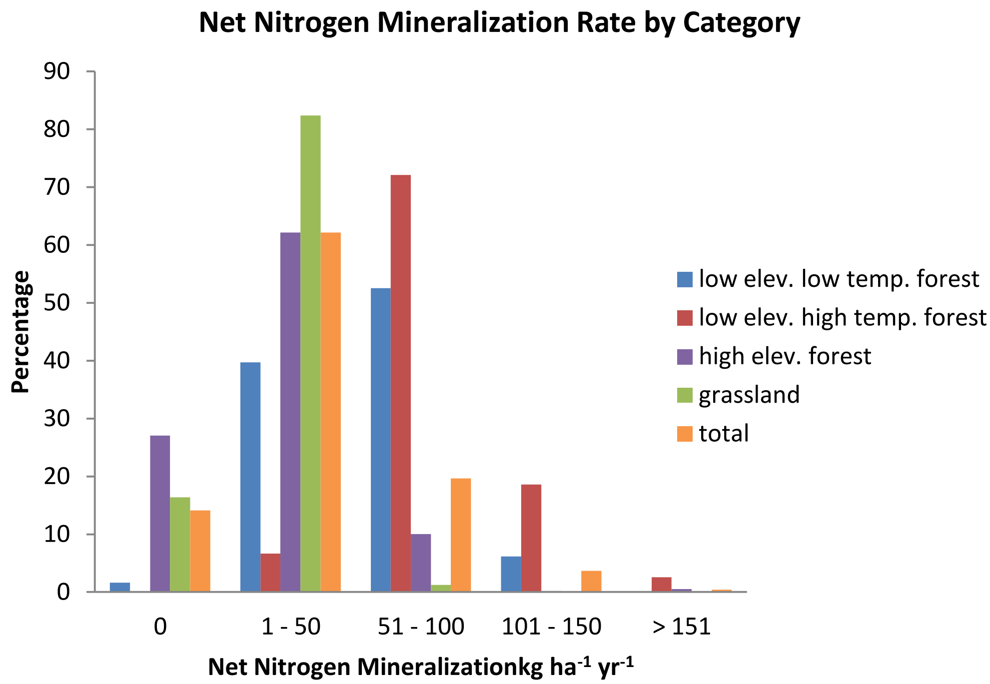

Figure 4.19. Percentage of net nitrogen mineralization in each data category.

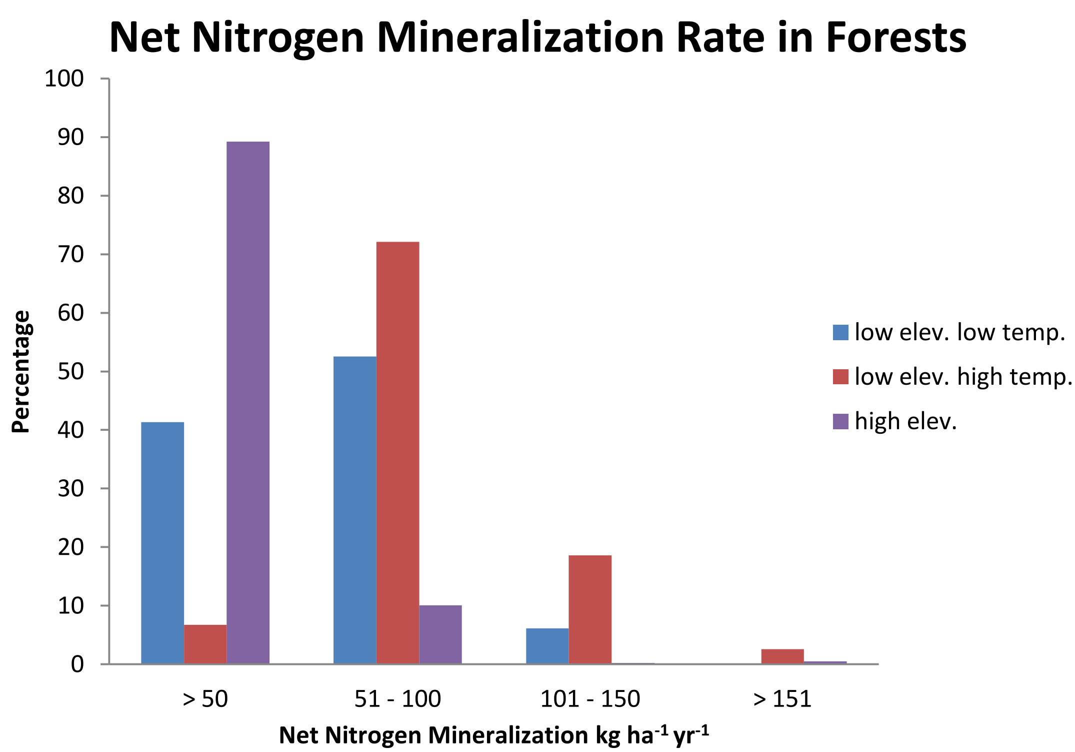

Figure 4.20. Percentage of net nitrogen mineralization for forest areas.

Figure 4.21. Distributions of land cover classes using NLCD.

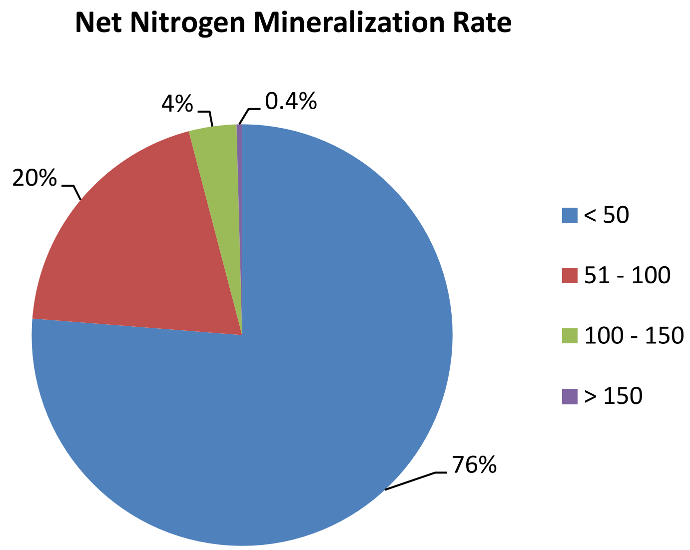

Figure 4.22. Quantities of net nitrogen mineralization (kg ha^{-1} yr^{-1}) over the CONUS.

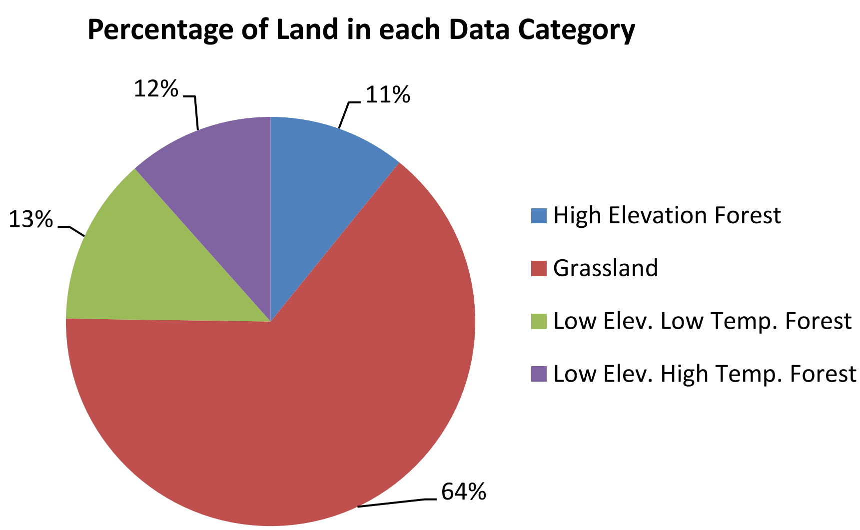

Figure 4.23. Percentage of land represented in this study in high elevation forest, grassland, low elevation low temperature forest, and low elevation high temperature forest categories.

4.6 Discussion

The predicted net nitrogen mineralization values correspond closely with previous modeling studies. In this study and that of Fan et al. (1998), the lowest rates observed for the Great Lakes region are in the Upper Peninsula of Michigan. In both studies, rates are also similar in Wisconsin, Illinois, Indiana, and Ohio. This study also follows that of Burke et al. (1997), with a trend of low to high nitrogen mineralization from the west to east in the Central Grassland region. Bouwman et al. (1997) derived net nitrogen mineralization rates for different ecosystems using C/N ratios. Temperate forests were estimated to have 53.12 kg ha^{-1} yr^{-1}. In my study, multiple variables (air temperature, precipitation, total soil nitrogen, and nitrogen deposition) are used to predict net nitrogen mineralization instead of a single variable. When high elevation, low elevation low temperature, and low elevation high temperature categories from the current study are combined, the mean predicted net nitrogen mineralization rate is 55.29 kg ha^{-1} yr^{-1}. These values are very similar, although the current study focuses only on the CONUS and the study of Bouwman et al. (1997) is a global average. This is likely due to the fact that both C/N ratio and total soil nitrogen represent the nutrient availability of the soil. Grasslands, defined in the Bouwman et al. (1997) study as Mediterranean grazing areas, warm grass/shrub, and cool grass/shrub complexes, have an estimated nitrogen mineralization rate of 85.85 kg ha^{-1} yr^{-1}. This rate is very different from the mean value of 14.3 kg ha^{-1} obtained in this study. This difference is likely due to the extremely different soil types, climate, and vegetation in the U.S. compared to the global average. Grasslands in the U.S. have low total soil nitrogen and receive little precipitation, resulting in low net nitrogen mineralization. A possible reason for high nitrogen mineralization in the Bouwman study is due to their study's definition of grasslands. Mediterranean grazing areas are included in this definition, which would likely have fertilized soil due to animal grazing.

The amount of net nitrogen mineralization needed varies; there is no "perfect" amount that satisfies plant needs. Just among forested ecosystems, nitrogen retention varies widely (Hedin et al., 1995). Areas with larger plants such as forests require a larger amount of nitrogen than areas such as grasslands because they have more mass to retain. The nutrient needs of plants vary both between species and between areas. If a larger quantity of other nutrients such as water and sunlight is available, the plant will require more nitrogen to take advantage of the availability of these nutrients. An area can have too much plant available nitrogen when it is in excess of other nutrients such as phosphorous (Waring and Schlesinger, 1985). Ammonium is a cation that is absorbed in the soil. Therefore, plant available nitrogen in the form of ammonium is resistant to leaching, in which water removes and transports soil and nutrients. However, under favorable conditions such as warm soil temperature, ammonium is converted to nitrate. Soil temperature must be 1.1 °C for the bacteria that convert ammonium to nitrate to be active. A pH of 5.8 to 6 is optimum for nitrification. Because oxygen is required for nitrification, soil needs aeration. Moderate soil moisture is ideal for nitrification; under very dry or saturated conditions, nitrification does not occur. Waterlogged soils contain a majority of ammonium and little nitrate. Nitrate is not absorbed because it is an anion, allowing nitrate to move with the soil water. When nitrate is available in too high quantities, leaching occurs. Leaching occurs more rapidly on sandy soils and in areas of high rainfall. Leaching causes the loss of plant available nitrogen, pollutes stream water, and causes a variety of problems such as algal blooms. Algal blooms are a rapid increase in the population of algae. Often referred to as red tides, algal blooms can be harmful to wildlife when the algae produce toxins or deplete water's oxygen.

4.6.1 Implications

Hydrologic models that rely on observations from eddy flux towers to estimate evaporation (Lu et al., 2003) provide information related to the specific location in terms plant transpiration and productivity rates associated with local soil conditions and may not be representative of nationwide conditions due to differences in soil chemistry. Many models, such as the existing Water Supply Stress Index- Carbon and Biodiversity (WaSSI-CB) model, use empirical relationships among meteorology, water and carbon balance and budget developed from global eddy flux data that may not be representative in the U.S. due to differences in soil nutrition. Eddy flux data are derived from a single location. Nitrogen mineralization can significantly differ even in a small area (Pastor et al., 1984), often varying greatly between individual stands (Fisk et al., 2002). These soil nutrition differences may result in errors caused by under- or over-prediction of ecosystem products, such as net primary productivity. In order for models to accurately predict ecosystem function based on eddy flux data, the representativeness of the eddy flux tower sites to the larger area is vital. If the soil at a tower location is more fertile than the surrounding area, ecosystem function is overpredicted. Likewise, underprediction may occur if soil is less fertile at tower sites. Thus, if there are high amounts of plant available nitrogen at the tower sites and lower amounts surrounding the area, net primary productivity is likely overestimated in models that are based on eddy flux measurements.

The maps of net nitrogen mineralization created in this study provide a starting point for soil nutrient improvements in ecosystem modeling. Outputs from this work could be used in conjunction with Global Climate Models (GCM) to improve representation of CONUS ecosystems.

4.6.2 Difficulties Encountered and Limitations of Study

A challenge that emerged during this study was the difficulty in predicting net nitrogen mineralization for forest ecosystems. Forests differ greatly by region in soil type, input material (i.e., litter and root quality), climate, and previous land use history. Therefore, it is difficult to predict net nitrogen mineralization using a simple equation. The separation of forests by temperature was proven to be the most efficient way to account for differences between forests.

Individual sites were used for validation to test regression equation prediction. However, the equations and maps generated during this study were not meant to be used to predict net nitrogen mineralization at an individual site. Instead, these estimates are meant to indicate nitrogen availability at a larger spatial scale. Other factors influencing nitrogen mineralization exist but are not used in this study due to their limited availability at a continental scale. At a smaller scale (i.e., regional or watershed), other controls of net nitrogen mineralization could include soil pH, soil aeration, specific vegetation type (i.e., species), land use history (e.g., burned forest, natural growth forest), and litter quality. Air temperature was used for this study because data was easily obtainable and proved to have a high statistical correlation to net nitrogen mineralization. However, soil temperature would likely be a better predictor of nitrogen availability.

These maps and equations were used to predict net nitrogen mineralization for forests and grasslands; they may not be accurate for other land types, such as croplands. This study was limited to natural ecosystems. Crop systems were not included because they are fertilized. Extremely low rates of net nitrogen mineralization rates calculated for some locations may indicate a lack of representation for extreme cases (i.e., very high or low temperatures, precipitation, nitrogen deposition, or TKN) in equation development, although effort was made to represent all areas equally well. Also, these equations were developed under steady state conditions; in a longer time scale, they may not be applicable. The model may predict high net nitrogen mineralization, but this will likely balance over a long time scale (Vitousek and Reiners, 1975). Ecosystem disturbances and stresses, such as insect invasions, drought, severe weather, and loss of vegetation reduce ecosystem health (McNulty and Boggs, 2010). The decline of ecosystem health will slow soil processes, including net nitrogen mineralization. Also, a change in climate conditions could alter net nitrogen mineralization; such a change should be considered in future work.

The equations created in this study are limited by accuracy of data (i.e., total soil nitrogen and net nitrogen mineralization data measured in the studies, and the temperature, precipitation, and nitrogen deposition data obtained). The map is limited by the accuracy of extrapolation of the data available (i.e., TKN map, nitrogen deposition map, and temperature and precipitation data). Although the TKN map was created using 1994 soil data, it is a reasonable estimate of TKN. Total soil nitrogen (e.g., TKN) remains fairly static over time, even in nitrogen addition experiments (McNulty and Aber, 1993) because the amount added is small relative to the bulk of organic nitrogen already present in the soil, so this map is a good estimate of net nitrogen mineralization. The EPA's State Implementation Plan (SIP), which limits NO_x emissions, went into effect in 2003. The change in nitrogen emissions may affect nitrogen deposition data utilized in this study. The enforcement of this program may decrease NO_x emissions in areas, resulting in decreased nitrogen deposition. Further studies should examine the impact of NO_x emission reductions on nitrogen mineralization.

The accuracy of this map could be verified with a larger number of field measurements, which are not currently available (i.e., comparing net nitrogen mineralization predictions to measurements). Some data are available that was not included in this study, but not a large number of data points. There is a shortage of net nitrogen mineralization data measured *in situ* with corresponding total soil nitrogen data. To improve study results, a greater number of study sites should be included.

CHAPTER 5

5. SUMMARY AND CONCLUSIONS

In this work, a set of empirical models that can predict net nitrogen mineralization based on total kjeldahl nitrogen and other environmental variables were created. Empirical equations were developed for high elevation forests, low elevation high temperature forests, low elevation low temperature forests, and grasslands using four regionally readily available parameters (total kjeldahl nitrogen, air temperature, precipitation, and nitrogen deposition) or a subset of them as predictor variables. The correlation was very strong ($R^2 > 0.70$) for each category. These empirical models allowed us to scale up site-level measurements to the national scale and develop a map of net nitrogen mineralization for the CONUS using GIS. The map created during this study showcases the extreme variability in net nitrogen mineralization across the U.S. Grasslands and high elevation forests were predicted to have the lowest net nitrogen mineralization, while low elevation forest sites in the east were predicted to have the highest net nitrogen mineralization.

This study suggests different ecosystems have different controls on net nitrogen mineralization. Climate, vegetation type, and topographic characteristics are the three major drivers at the U.S. continental scale. The spatial GIS databases created in this study provide a basis for comparing net nitrogen mineralization at different locations by addressing differences in ecosystem, climate, and soil nitrogen. Creating a national map of net nitrogen mineralization is the first step toward considering nitrogen limitations in large scale ecosystem modeling. Future integrated regional ecosystem models are expected to be improved by including soil fertility information.

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APPENDIX

Appendix. Summary of Data Used for Regression and Validation.

Area	Region	Ecosystem	Forest Type	Soil N g kg^{-1}	Bulk Den. g cm^{-3}	Soil N kgha^{-1}	Temp F	Temp C	Precip mm	Ndep eqN(hayr)$^{-1}$	Ndep kg(hayr)$^{-1}$	Nmin kg(hayr)$^{-1}$
Great Smoky Mtn Nat.Park	Southeast	High elev. forest	Conif.	5.5	1.26	6930	71.26	21.81	430.02	532.77	2.49	87
Great Smoky Mtn Nat.Park	Southeast	High elev. forest	Conif.	5.37	1.26	6766	71.26	21.81	430.02	532.77	2.49	152
New York	Northeast	High elev. forest	Conif.	13.2	0.96	12672	62.68	17.04	569.21	410.40	1.92	25.29
New York	Northeast	High elev. forest	Conif.	15.2	0.96	14592	62.68	17.04	569.21	410.40	1.92	19.85
New York	Northeast	High elev. forest	Decid.	11.5	0.96	11040	62.68	17.04	569.21	410.40	1.92	37.3
New York	Northeast	High elev. forest	Decid.	13.8	0.96	13248	62.68	17.04	569.21	410.40	1.92	21.82
New York	Northeast	High elev. forest	Decid.	16.1	0.96	15456	62.68	17.04	569.21	410.40	1.92	28.99
North Carolina	Southeast	High elev. forest	Conif.	8.97	1.17	10491	58.96	14.98	575.56	463.18	2.16	98
North Carolina	Southeast	High elev. forest	Conif.	6.1	1.17	7137	58.96	14.98	575.56	463.18	2.16	134
Northern California	West	High elev. forest	Conif.	1.797	1.04	1869	73.72	23.18	129.79	117.63	0.55	21.2
Northern California	West	High elev. forest	Conif.	1.698	1.87	3174	73.72	23.18	129.79	84.54	0.39	40.4
Northern California	West	High elev. forest	Conif.	1.565	1.04	1628	73.72	23.18	129.79	117.63	0.55	1.2
Vermont	Northeast	High elev. forest	Conif.	12.2	1.13	13786	64.26	17.92	371.60	502.62	2.35	13.7

Vermont	Northeast	High elev. forest	Conif.	12.2	1.13	13786	64.26	17.92	371.60	502.62	2.35	16
Virginia	Southeast	High elev. forest	Conif.	6.85	1.38	9453	71.5	21.94	459.99	531.09	2.48	93
Virginia	Southeast	High elev. forest	Conif.	8.80	1.38	12144	71.5	21.94	459.99	531.09	2.48	73
North Carolina	Southeast	High elev. forest	Conif.	9.03	1.17	10565	58.96	14.98	575.56	463.18	2.16	82
Vermont	Northeast	High elev. forest	Conif.	12.2	1.13	13786	64.26	17.92	371.60	502.62	2.35	15.7
Arizona	Southwest	Forest	Conif.	1.2	1.04	1246	57.22	14.01	239.01	166.61	0.78	27
Arizona	Southwest	Forest	Conif.	1.5	1.04	1557	57.22	14.01	239.01	166.61	0.78	11
Arizona	Southwest	Forest	Conif.	1.6	1.04	1661	57.22	14.01	239.01	166.61	0.78	13
Arizona	Southwest	Forest	Conif.	1.4	1.04	1453	57.22	14.01	239.01	166.61	0.78	18
Maine	Northeast	Forest	Conif.	10	0.94	9400	65.16	18.42	403.35	279.93	1.31	41.3
Massachusetts	Northeast	Forest	Decid.	17	1.15	19550	65.24	18.47	423.67	514.12	2.40	16.1
Michigan	Midwest	Forest	Decid.	1.7	1.08	1836	61.3	16.28	677.93	459.10	2.14	91
Oregon	West	Forest	Conif.	5.7	0.54	3050	55.54	13.08	519.68	113.89	0.53	51
Oregon	West	Forest	Conif.	3.3	0.54	1766	60.76	15.98	249.17	95.47	0.45	22
Oregon	West	Forest	Conif.	3.3	0.54	1766	60.76	15.98	249.17	95.63	0.45	25
Oregon	West	Forest	Conif.	3.4	0.54	1819	60.76	15.98	249.17	96.81	0.45	37
Oregon	West	Forest	Conif.	3.8	0.54	2033	60.76	15.98	249.17	95.63	0.45	42
Oregon	West	Forest	Conif.	3.3	0.535	1766	60.76	15.98	249.17	95.47	0.45	25
Oregon	West	Forest	Conif.	3.1	0.54	1659	55.54	13.08	519.68	154.56	0.72	12
Oregon	West	Forest	Conif.	3.3	0.54	1766	60.76	15.98	249.17	154.89	0.72	25
Michigan	Midwest	Forest	Decid.	1.6	1.08	1728	62.82	17.12	502.67	430.31	2.01	93

Florida	Southeast	Forest	Decid.	0.6	1.45	870	82.08	27.82	518.92	359.37	1.68	89
Florida	Southeast	Forest	Decid.	0.3	1.50	450	81.86	27.70	907.80	319.16	1.49	127
Florida	Southeast	Forest	Decid.	0.6	1.45	870	82.08	27.82	518.92	359.37	1.68	42
Maryland	Northeast	Forest	Decid.	3.35	1.30	4355	77.92	25.51	560.07	579.61	2.70	71
Maryland	Northeast	Forest	Decid.	3.35	1.30	4355	77.92	25.51	560.07	579.61	2.70	61
NC Piedmont	Southeast	Forest	Decid.	0.7	1.16	812	75.4	24.11	513.33	525.42	2.45	34.4
NC Piedmont	Southeast	Forest	Decid.	0.7	1.16	812	75.4	24.11	513.33	525.42	2.45	34.4
NC Piedmont	Southeast	Forest	Decid.	0.7	1.16	812	75.4	24.11	513.33	525.42	2.45	22.3
NC Piedmont	Southeast	Forest	Decid.	0.6	1.16	696	75.4	24.11	513.33	525.42	2.45	19.1
Northern California	West	Forest	Decid.	1.797	1.04	1869	73.72	23.18	129.79	117.63	0.55	21.2
Sierra Nevada California	West	Forest	Conif.	1.6	1.57	2512	74.44	23.58	44.45	203.11	0.95	31
Sierra Nevada California	West	Forest	Conif.	1.5	1.57	2355	74.44	23.58	44.45	203.11	0.95	12
West Virginia	Southeast	Forest	Decid.	1.31	1.31	6157	67.4	19.67	553.21	776.92	4.70	78
West Virginia	Southeast	Forest	Decid.	1.31	1.31	5502	67.4	19.67	553.21	776.92	4.20	77
Florida	Southeast	Forest	Decid.	0.3	1.50	450	82.08	27.82	518.92	359.37	1.68	43
Sierra Nevada California	West	Forest	Conif.	2	1.57	3140	74.44	23.58	44.45	203.11	0.95	31
Colorado	West	Grassland	-	8.1	1.51	12231	66.46	19.14	246.38	249.26	1.16	6.2
Colorado	West	Grassland	-	14	1.51	21140	66.46	19.14	246.38	249.26	1.16	7.9
Colorado	West	Grassland	-	10.2	1.51	15402	66.46	19.14	246.38	249.26	1.16	7.9
Colorado	West	Grassland	-	11.9	1.51	17969	66.46	19.14	246.38	249.26	1.16	8
Colorado	West	Grassland	-	13.6	1.51	20536	66.46	19.14	246.38	249.26	1.16	9.4

Colorado	West	Grassland	-	8.3	1.51	12533	66.46	19.14	246.38	249.26	1.16	11.2
Colorado	West	Grassland	-	13.6	1.51	20536	66.46	19.14	246.38	249.26	1.16	11.5
Colorado	West	Grassland	-	1.946	0.90	1759	65.44	18.58	229.36	260.62	1.22	14.9
Colorado	West	Grassland	-	1.185	1.17	1386	68.3	20.17	322.33	291.42	1.36	30.4
Minnesota	Midwest	Grassland	-	0.592	1.50	888	65.34	18.52	684.78	452.31	2.11	44
Minnesota	Midwest	Grassland	-	0.535	1.50	803	65.34	18.52	684.78	452.31	2.11	45
Minnesota	Midwest	Grassland	-	0.802	1.50	1203	65.34	18.52	684.78	452.31	2.11	48
Minnesota	Midwest	Grassland	-	1.054	1.50	1581	65.34	18.52	684.78	452.31	2.11	65
Colorado	West	Grassland	-	10.2	1.51	15402	66.46	19.14	246.38	249.26	1.16	15.8
Kansas	Midwest	Grassland	-	3.151	1.05	3299	73.06	22.81	416.81	354.74	1.66	30
Kansas	Midwest	Grassland	-	1.881	0.98	1836	74.34	23.52	447.80	520.95	2.43	14.8
Colorado	West	Grassland	-	14.9	1.51	22499	66.46	19.14	246.38	249.26	1.16	16.6
Kansas	Midwest	Grassland	-	2.697	1.01	2729	73.42	23.01	416.81	393.34	1.84	24.5
Texas	Southwest	Grassland	-	0.7	1.40	980	82.98	28.32	757.17	309.03	1.44	60
Texas	Southwest	Grassland	-	2.0	1.10	2200	82.98	28.32	757.17	309.03	1.44	140
Texas	Southwest	Grassland	-	1.2	1.10	1320	82.98	28.32	757.17	309.03	1.44	160
Texas	Southwest	Grassland	-	1.8	1.10	1980	82.98	28.32	757.17	309.03	1.44	220