Nutrient release and cycling in the soils of a continental lodgepole pine (*Pinus contorta* Doug.) ecosystem, Bootleg Mountain, B.C.

by

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Abstract

Nutrient dynamics in a lodgepole pine forest at Bootleg Mountain, B.C., were investigated through the sampling of soil, snow and groundwater in six one-ha blocks. Nitrogen (NO_3^-, NH_4^+, TIN, TDN, TN), phosphorus (PO_4^{3-}, TDP, TP), and DOC were analyzed in addition to N mineralization and nitrification. Position and dispersion statistics were computed for each variable and correlations (Pearson and Spearman) were computed for each pair of variables. The overall heterogeneities of soil, snow, and groundwater were generally lower between 1-ha blocks than between plots. Productivity in the soil was generally N-limited with low input from snow precipitation. Very little N leached from soil to groundwater. Phosphorus contents were highly variable and were the limiting nutrient in the groundwater. Rates of net and gross N mineralization and nitrification were determined using buried bags and ^{15}N isotope dilutions. Gross rates were greater than net rates and nitrification was low relative to high immobilization rates. The N cycle appears to be tightly regulated, thus further study will be needed to monitor the impact of harvesting on N cycling.

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Dedication

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Chapter 1
Introduction

Anthropogenic perturbations to the global nitrogen (N) and phosphorus (P) cycles now exceed those of any other major biogeochemical cycle on Earth, yet the ability to predict how ecosystems will respond to the rapidly changing N cycle is still poor (Asner et al. 2001). Human influences have greatly changed the environments and substrates associated with N cycle processes (Knowles 2000). For example, in the Rocky Mountains, deforestation and mining have produced acute localized perturbations – short-term fluxes of nutrients, particularly N and P, increase significantly when watersheds are logged (Hauer et al. 1997). Short-term interdisciplinary studies can be used to resolve some of the uncertainties that surround such perturbations, including for example transformations mediated by microbes, such as N fixation, nitrification, N mineralization, and denitrification (Likens and Bormann 1995). By studying the biogeochemistry and the microbiology of specific biogeochemical systems, a better understanding of associated nutrient fluxes in terms of inputs, outputs and associated processes can be achieved (Knowles 2000).

Nitrate and NH_4^+ in forest soils are subject to a variety of processes that link the soil to the groundwater. Logging activities such as clear-cutting and whole-tree harvesting have the potential to affect water and N outflow into the local streams, lakes, and reservoirs (Knight et al. 1991, Likens and Bormann 1995). For example, increasing NO_3^- levels in a soil whose primary productivity is limited by N could result in an increased contribution of the anion to the groundwater regime. Higher levels of NO_3^- in groundwater, and subsequently mountain streams could result in increased productivity and reduced quality

of drinking water. British Columbia is home to many towns that obtain their drinking water from mountain streams and rivers (Myrold 1999, Knowles 2000). Thus, research on the N cycle in watershed soils would assist in determining the factors that will allow management of ecosystems to ensure quality of drinking water.

Towards this end nitrogen dynamics in the soils and groundwater of a site in SE British Columbia have been studied. The results are presenting in this thesis. The research site is located at the Bootleg Mountain at Matthew Creek, British Columbia, which is part of the Purcell Mountains within the Columbia Basin of the East Kootenays. It is a subalpine forest ecosystem, located southwest of Kimberly, B.C. The town of Marysville obtains its drinking water from the Matthew Creek reservoir. The research site is subject to snow accumulations for as long as 8 months; the release of snowmelt during the spring creates potentially large fluxes of nutrients into the soils, groundwater, streamwater and surface waters (Hauer et al. 1997). The site is heavily forested – Lodgepole pine (*Pinus contorta*), Subalpine fir (*Abies lasiocarpa*) and Engelmann spruce (*Picea engelmannii*) (Lea 1989) as well as a variety of herbs and shrubs are the principal species. Thus, determining the N dynamics (particularly of NO_3^- and NH_4^+) in the soils and groundwater at this particular site should provide a scientific basis for predicting the effect of harvesting on the quality of the ambient water regime.

It is necessary to know the current state of a forest ecosystem in order to determine the impact that disturbances such as harvesting may have on NO_3^- and NH_4^+ levels and their subsequent potential fluxes to drinking water (Kroeze et al. 1989). In that context, the main questions that have guided this work are: 1) do N mineralization and nitrification offer a significant source of N (in the forms of NO_3^- or NH_4^+) to the groundwater of a

lodgepole pine (*Pinus contorta* Doug.) forest? 2) What environmental factors regulate the main nutrient fluxes in the soil and groundwater at this site? And 3) are there significant heterogeneity factors (spatial, temporal) that determine rates of nitrification and mineralization of nitrogen?

The approach used to address these specific questions was two-pronged: 1) soil and hydrological (groundwater and snow) factors were characterized within and between forest blocks; and 2) rates of mineralization and nitrification were assessed.

The thesis is divided into six distinct chapters: 1) Introduction (this chapter includes a review of the literature); 2) Site description and project design; 3) Determination of chemical and physical characteristics of soils from continental lodgepole pine forests; 4) Seasonal water and nutrient fluxes in the snow and groundwater of continental lodgepole pine forests; 5) Determination of gross and net N mineralization and nitrification using ^{15}N isotopes; and 6) Conclusions.

1.1 Soil nitrogen cycling in forest soils

Research on soil nutrients is a critical aspect of forest management and sustainability and is linked tightly to drinking water quality. The processes controlling the cycling of N in particular are complex and varied and include: the retention of N from atmospheric deposition (Baron et al. 2000, Dail et al. 2001, Davidson et al. 2003) and the movement of NO_3^-, nitrite (NO_2^-), and ammonium (NH_4^+) among soil horizons (Vanmiegroet and Cole 1984). Such processes affect water quality (Kapoor and Viraraghavan 1997, Clough et al. 2001) and plant nutrition. Furthermore, nitrous oxide (N_2O) emissions from nitrification and denitrification play a role in atmospheric chemistry (ozone depletion, global warming) (Vitousek et al. 1979, Vitousek and Melillo 1979, Zechmeister-

Boltenstern 2001). This section will focus on the movement of nitrogenous ions (NO_3^-, NH_4^+) throughout forest soils and the microbial processes that govern their rates of transformation.

Nitrogen is present in various forms – dinitrogen gas (N_2), organic N (in plants, animals, microbial biomass, and soil organic matter), NH_4^+, NO_2^-, and NO_3^- ions (Myrold 1999) (Fig. 1). The types and rates of transformations of N that are likely to occur are dictated by environmental conditions and the abundance of microorganisms (Knowles 2000), the latter being key catalysts for the transformation of N in soils. The next sections summarize the different parts of the N cycle including the roles of specific microbes.

1.1.1 Nitrogen fixation

After photosynthesis, N fixation – the reduction of atmospheric dinitrogen (N_2) to two molecules of ammonia (NH_3) – has been put forward as the second most important biological process on earth (Zuberer 1999). Nitrogen fixation is mediated solely by free-living prokaryotes (Archaea, Eubacteria, and Bacteria) or prokaryotes in a symbiotic association with other microbes, plants, or animals (Zuberer 1999, Knowles 2000).

Plants require relatively high levels of nitrogenous ions (NO_3^-, NH_4^+) to produce biomass; however, N is often the limiting nutrient for terrestrial plant and microbial growth in soils. Nitrogen for plant and microbial growth can come from the soil, rainfall/atmospheric deposition, or through N fixation (Zuberer 1999). Rates of N fixation can be limited by 1) energetic constraints on the N-fixing organisms; 2) limitation by another nutrient; and/or 3) ecological or physical constraints on the N-fixing organisms (Vitousek and Howarth 1991).

Since N fixation is expensive biologically, it will only occur when there is a ready supply of energy such as light for phototrophs or organic carbon for chemoheterotrophs (Zuberer 1999). The resulting NH_4^+ from N fixation is then used (immobilized) by plants and microbes, or is mineralized and nitrified and eventually denitrified, depending on environmental conditions.

1.1.2 Nitrogen mineralization/immobilization

Nitrogen mineralization in general refers to the production of inorganic N (both NH_4^+ and NO_3^-). Net mineralization is the concurrent production of both NH_4^+ and NO_3^- while gross mineralization (also called ammonification) refers to the transformation of organic N to NH_4^+ (Myrold 1999). Immobilization refers to the conversion of NH_4^+ to organic N through microbial and plant biomass assimilation (Fig. 1).

The production of NH_4^+ from organic N is mediated by enzymes produced by microbes and soil animals. The steps include: 1) the break-down of organic N polymers to monomers by extracellular enzymes; 2) assimilation of monomers and further metabolism; and 3) production and release of NH_4^+ into the soil solution. (Myrold 1999)

Immobilization occurs through two enzymatic pathways: 1) glutamate dehydrogenase working at higher NH_4^+ concentrations and 2) glutamine synthase-glutamate synthetase (GOGAT) which functions at low NH_4^+ concentrations. Both pathways depend on concurrent ATP production in order to proceed (Myrold 1999). Since most microbes are unable to fix N_2 gas, NH_4^+ is mostly assimilated by these pathways (Knowles 2000). Nitrogen immobilized into microbial biomass components is only released after cell death or by the enzymatic processes listed above (Knowles 2000).

Soil N mineralization and immobilization are generally recognized as important processes affecting nutrient availability for plant growth (Subler et al. 1995). In the past, estimates of N mineralization have been limited to laboratory incubations of soil under controlled conditions. In contrast, field methods have allowed for *in situ* measurements in natural ecosystem studies (Binkley and Hart 1989). Such methods include the buried bag method (Eno 1960) for net mineralization and ^{15}N isotope pool dilution for gross mineralization (Kirkham and Bartholomew 1954). Terrestrial systems are in a state of constant turnover and N mineralization and immobilization are often in a steady-state which, under experimental conditions shows no change in NH_4^+ concentrations (Knowles 2000).

Rates of NH_4^+ production and consumption by soil microbes are influenced by a number of factors: 1) if N availability is limiting – consumption or immobilization occurs, or 2) if N is available - production occurs. In general, soil microorganism activity and NH_4^+ production is governed by the C/N ratio (Myrold 1999). Higher levels of carbon will likely result in greater immobilization whereas higher levels of N relative to carbon in soils will increase mineral N availability (Myrold 1999). Other factors that influence the production of NH_4^+ include both abiotic (environmental conditions like carbon content, moisture, temperature, bulk density) and biotic factors (mineralization by soils organisms) (Myrold 1999).

There are various pathways that NH_4^+ can follow after mineralization occurs including uptake by plants, assimilation by microbes or oxidation to NO_3^- by nitrifying bacteria.

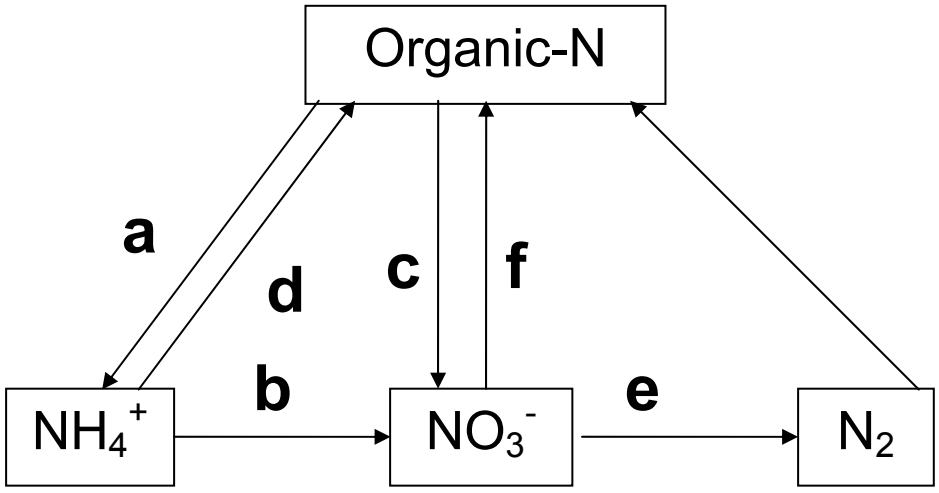

Figure 1. N cycling in forest ecosystems showing important processes and pools. a = gross mineralization; b= gross nitrification; a+c = net mineralization; b+c = net nitrification; d, f immobilization to organic N; e = denitrification to atmospheric N_2 gas (Davidson et al. 1992, Blackburn and Knowles 1993, Myrold 1999).

1.1.3 Nitrification

Nitrification is the oxidation of NH_4^+ to NO_2^- and NO_3^- (Myrold 1999). Gross and net nitrification must be distinguished: 1) gross nitrification refers to the two-step oxidation of NH_4^+ to NO_2^- and NO_3^- (Davidson et al. 1992), whereas 2) net nitrification is the concurrent production of NO_3^- through the two-step oxidation process and directly from organic N sources (Fig. 1). Although nitrification can be either autotrophic or heterotrophic, the former is usually more important in natural ecosystems (Davidson et al. 1992).

The production of NO_3^- is carried out by two groups of soil bacteria that use oxidation reactions to produce energy and fix carbon dioxide (Knowles 2000). Ammonium-oxidizing bacteria such as *Nitrosomonas europaea* convert NH_4^+ to NO_2^- while NO_2^--oxidizing bacteria such as *Nitrobacter winogradskyi* convert NO_2^- to NO_3^- (Myrold 1999).

Ammonium oxidation to NO_2^- is performed by a phylogenetically well-defined group of bacteria (Myrold 1999). *Nitrosomonas, Nitrosolobus,* and *Nitrosospira* have been studied in many types of soils. In the presence of oxygen the reaction also synthesizes ATP via a proton motive force (Knowles 2000). Protons are also released concurrently with NO_2^- production. This release of H^+ may lead to soil acidification in poorly buffered environments (Myrold 1999).

Nitrite oxidation to NO_3^- is performed by NO_2^--oxidizing bacteria such as *Nitrobacter winogradskyi* and *Nitrospira spp.* (Myrold 1999). This reaction is catalyzed by a nitrite oxidoreductase that contains iron and molybdate and is coupled to ATP synthesis (Knowles 2000).

Factors that control nitrification in soils include the presence and abundance of nitrifiers, soil aeration, substrate availability, soil pH, allelochemical inhibitors, and environmental factors such as temperature, water content, salinity, and nutrient availability (Myrold 1999). As NO_3^- is the most important source of N for plants, factors controlling nitrification rates in soil have been studied extensively. In forest soils, very little NO_3^- is actually present because N is efficiently cycled. Also, NO_3^- production via nitrification is nearly equivalent to rates of plant uptake and microbial immobilization (Dail et al. 2001). Since NO_3^- is a mobile anion in soils, elevated NO_3^- levels have the potential to be leached into water systems or become a substrate for denitrification (Vitousek and Howarth 1991, Myrold 1999, Knowles 2000). This can stimulate the growth of algae and macrophytes and lead to eutrophication. Although less likely in forested ecosystems, excess NO_3^- levels may lead to methemoglobinemia or to the production of carcinogenic nitrosamines (Myrold 1999, Knowles 2000).

In forest soils, NO_3^- added or produced tends to be rapidly immobilized. In general, production via nitrification is matched by equal rates of plant uptake and microbial immobilization (Dail et al. 2001). This capacity for NO_3^- immobilization from NO_3^- deposited on soils or via nitrification is influenced by both biotic and abiotic mechanisms (Aber et al. 1989, Berntson and Aber 2000, Dail et al. 2001). It has been documented that there is both a slow and rapid microbial process of NO_3^- immobilization which plays an important role in regulating the mobility of NO_3^- in soils. Once the immobilization capacity is reached, leaching or denitrification of NO_3^- begins (Aber et al. 1989, Berntson and Aber 2000, Dail et al. 2001).

1.1.4 Denitrification

Denitrification refers to the reduction of NO_3^- to gaseous N products, principally N_2 and N_2O (Myrold 1999). In the absence of oxygen, some microorganisms can use NO_3^-, NO_2^-, or N_2O as terminal electron acceptors for respiration (Knowles 2000). The enzymes involved in denitrification are: 1) NO_3^- reductases (Nar or Nap); 2) NO_2^- reductase (Nir); 3) NO reductase (Nor); and 4) N_2O reductase (Nos) (Myrold 1999, Knowles 2000).

A number of environmental factors may control denitrification in the natural environment: availability of oxygen, nitrogen oxide, or a reductant (organic C), and soil and environmental factors such as temperature and pH (Myrold 1999, Knowles 2000). Nitrification is generally the source of the N oxides for dentrification, but they can often come via atmospheric precipitation and fertilizers (Knowles 2000).

1.1.5 Summary

A thorough knowledge of this complex cycle is important in understanding the functioning of ecosystems and predicting the effects of small and large changes to the ecosystem. Nitrogen controls species composition, diversity, dynamics and the functioning of many terrestrial, freshwater, and marine ecosystems (Vitousek et al. 1997).

Generally, N limits net primary production in most terrestrial biomes (Vitousek and Howarth 1991) but human influences have greatly changed environments and the substrates required for N cycle processes (Knowles 2000). Agriculture, combustion of fossil fuels, and other human activities like forestry and fires have substantially altered the global cycle of N (Vitousek et al. 1997).

Much is still unknown about the effects of human influences on the fate of NO_3^- in soils. Davidson et al. (1992) suggested that models predicting the impact of

anthropogenic NO_3^- on forest ecosystems are lacking in their consideration of the existing pathways of microbial NO_3^- production and consumption in minimally impacted forests. Greater rates of N mineralization and nitrification have been reported in forest floors and soils following clear-cutting (Likens et al. 1977, Likens and Bormann 1995, Prescott et al. 2003) and there has been evidence of elevated NO_3^- concentrations in soil and drainage waters (Likens et al. 1977, Likens and Bormann 1995, Clough et al. 2001, Prescott et al. 2003). The soil and groundwater systems are closely linked and losses to the soil system will ultimately have an effect on the nutrient levels in the hydrological regime.

1.2 Forest soil hydrology and chemistry

The groundwater of the Bootleg Mountain area is of interest because it can be used to link processes occurring in the soil to inputs from the snow. Looking at the dynamics and spatial heterogeneity of groundwater levels and chemistry over time allows monitoring of seasonal changes. There are many variables that can be determined to assess water quality and the response of a specific system to environmental variation. Discussions of the water quality variables and a summary of the literature on groundwater quality and dynamics are presented below in order to determine where existing knowledge gaps may exist.

1.2.1 Acidity/pH, conductivity, temperature

The pH values for most natural water systems tend to remain very constant and within a range of pH 6-9. Biological activities may influence pH by increasing and decreasing the concentration of dissolved carbon dioxide or via the production of protons. Some oxygenation reactions like nitrification and sulphur oxidation (but not respiration) often

lead to a decrease in pH, whereas aquatic geochemical processes such as denitrification and sulfate reduction tend to increase pH (Stumm and Morgan 1996). The pH is also a major influence on the survival of organisms. Low or high pH values tend to decrease overall biological activity and may lead to microbial population shifts (e.g. low pH favours fungal growth). The pH of a solution may influence anion or cation speciation in solution (Stumm and Morgan 1996) which can have additional – and often significant – impacts on organisms.

Conductivity is a measurement of the ability of an aqueous solution to carry an electrical current. There are several factors that determine the degree to which water will carry an electrical current including the concentration or number of ions; the mobility of ions and their oxidation state (valence); and the temperature of the water. Conductivity measurements can be used for a number of applications related to water quality which include: 1) determining mineral content, commonly reported as total dissolved solids (TDS); 2) defining variations, in natural water and wastewaters quickly; 3) estimating the sample size necessary for other chemical analyses; and 4) determining amounts of chemical treatment reagents to be added to a water sample to improve its quality (Stumm and Morgan 1996).

Water quality also depends on the temperature, which affects 1) the solubility and, in turn, the toxicity of many other variables; 2) rates of enzymatic reactions; and 3) biological activities. Generally the solubility of solids increases with increasing temperature, while gases tend to be more soluble in cold water. In terms of water quality, temperature is used in determining allowable limits for other variables such as NH_4^+ (Stumm and Morgan 1996).

1.2.2 Organic carbon

Organic matter in water comprises a great variety of organic compounds. Organic matter plays a major role in aquatic systems. It affects biogeochemical processes, nutrient cycling, biological availability, chemical transport and interactions (Stumm and Morgan 1996). Organic matter content is typically measured as total organic carbon (TOC) and dissolved organic carbon (DOC), which are essential components of the carbon cycle. TOC contains particulates and microscopic organisms (heterotrophic bacteria and algae) and DOC refers to organic carbon in solution that will pass through a 0.45 μm filter. Organic material can originate from various sources including the excretion by and decay of organisms including, for example, bacteria, algae and vascular plants (Volk et al. 2002). Allochthonous organic matter enters streams from sources within a watershed, and originates from the degradation of terrestrial vegetation and leaching from soils during runoff events (Volk et al. 2002). DOC can be a mixture of compounds ranging from short-chain to high molecular weight humic compounds. DOC can be found in precipitation – albeit typically in low concentrations from aerosols, it can also be released from plant tissues and decomposing soil organic matter, it can be adsorbed into mineral soil horizons, and eventually it may be exported from terrestrial ecosystems as mineralized carbon dioxide or in streams and rivers (Moore 2003).

Dissolved organic C (and TOC) is often used to estimate the quantity of organic matter present. DOC is affected by factors such as climate (temperature and precipitation), vegetation, and inputs of microbial organic carbon (Stumm and Morgan 1996). The amount of DOC in the groundwater and soil is strongly linked to N and P and it is likely that P dynamics lead to responses in the N and DOC pools (Fahey and Yavitt 1988). It

has been shown that when N is limiting, an ecosystem will generally have high C/N ratios and low N/P ratios (Vitousek and Howarth 1991).

1.2.3 Forms of phosphorus (TP, TDP, PO_4^{3-})

Phosphorus is one of the key elements necessary for growth of plants and animals. Phosphates (PO_4^{3-}) are the ionic forms assimilated by plants and microbes. Phosphates exist in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate. Ortho forms are produced by natural processes such as rock weathering. Organic phosphates are important in nature and their occurrence may result from the breakdown of organic matter. Phosphate may exist in solution, as particles, loose fragments, or in the bodies of aquatic organisms (Stumm and Morgan 1996). The availability of P in forests is sustained by the cycling of the element. It has been found that approximately 50% of the total P in surface soils is in organic forms (Attiwill and Adams 1993).

1.2.4 Current groundwater research

Concerns about high concentrations of mineral N in surface and ground waters have been increasing over the last few years, as high concentrations may alter water quality and contribute to eutrophication of lakes and coastal waters (Myrold 1999, Knowles 2000). Until recently, it was assumed that N was tightly cycling in undisturbed forests within the soil litter, microbial biomass, and plant biomass with little or no N export to surface waters (Creed and Band 1998b). However increasing amounts of atmospheric N deposition from anthropogenic sources have led to research concerning N saturation in forests (Aber et al. 1989). Having an ability to predict the export of N from the land to

adjacent waters is thus essential in establishing and reviewing management practices (Aber et al. 1989), especially in areas where there are disturbances.

There are four main fates of N removal from the surface water flowing through forest ecosystems: 1) plant uptake; 2) microbial immobilization; 3) denitrification; and 4) leaching to the water table (Verchot et al. 1997). Plant uptake and microbial immobilization and result in conservation and cycling of N within the ecosystem through litter fall and microbial death (Verchot et al. 1997). If N leaches to the water table, it can either move on to surface waters, remain as a contaminant, or be recycled in the ecosystem (Verchot et al. 1997). Losses of NO_3^- in drainage water from disturbed forest ecosystems can vary over a wide range. High losses of NO_3^- to stream water or groundwater have been observed in a few sites, while in others only small increases in losses have occurred (Vitousek and Melillo 1979). Losses via denitrification can be significant under certain conditions and vary in response to changes in soil carbon content, water table heights, vegetation and oxygen levels (Groffman et al. 1996).

The fate of N may be influenced by the degree of activity within the soil zone that is the most biologically vigorous, as well as by the natural drainage class, the soil organic matter content, soil type, hydrology, vegetation type, temperature, and rainfall (Simmons et al. 1992, Spalding and Exner 1993). Soil organic matter content and microbial activities tend to be at their highest at the surface and decline sharply with depth (Simmons et al. 1992). Significant nutrient transformations also occur as water moves through watersheds as surface run off and ground water (Peterjohn and Correll 1984). Flushing has also been observed when a water table rises to the soil surface. This promotes the mobilization of nutrients to surface waters that are stored at or near the soil

surface (Williams and Melack 1991, Simmons et al. 1992, Creed and Band 1998a, Creed and Band 1998b, Baron et al. 2000). In wetter areas or during the spring snowmelt period, the water table is closer to the soil surface, and anaerobic conditions may develop (Williams and Melack 1991, Simmons et al. 1992, Baron et al. 2000). Hotspots of microbial activity and denitrification due to the heterogeneity of the system and patchy distribution of organic C at the soil surface are not uncommon (Simmons et al. 1992).

1.3 Snow pack hydrology and chemistry in forest soils

Snow pack studies are useful for obtaining an indication of spring run-off volumes and nutrient chemistry. Fagre (2002) discussed the reasons for performing snow pack studies: 1) snow pack changes following changes in climate (e.g. precipitation could alter nutrient pulses affecting natural resources); 2) atmospheric fluxes of N to a watershed may have adverse effects on aquatic and terrestrial resources; 3) mountain snow packs may accumulate as much as eight months of atmospheric deposition and the release during the spring may create large nutrient fluxes; and 4) ecosystems may be responsive to small changes in atmospheric N depositions.

The deposition of gaseous and particulate nutrients to a surface is often overlooked and underestimated in determinations of total nutrient supply in many ecosystems (Sievering et al. 1996). As most unpolluted terrestrial environments are N limited, primary production is partially controlled by the amount of N made available through soil microbial processes (Vitousek and Matson 1988). It follows that increased deposition of anthropogenically-derived N has the potential to alter the balance of natural ecosystems (Sievering et al. 1996).

Humans have altered the biospheric N cycle and have doubled the rate of N entering the terrestrial N cycle (Vitousek et al. 1997). Rates of 3-5 kg $N \cdot ha^{-1} \cdot year^{-1}$ of atmospheric N deposition may be sufficient to influence previously undisturbed terrestrial and aquatic ecosystems (Baron et al. 2000) by: 1) altering N mineralization and immobilization rates (Sievering et al. 1996); 2) elevating NO_3^- in soils and water, and acidifying surface waters (Williams et al. 1998); and 3) changing foliar N and P concentrations (Williams et al. 1996). At the time of the spring snow melt, large concentrations of NO_3^- occur in the surface waters which are consistent with a release of NO_3^- from the snow pack in the form of an ionic pulse (Williams and Melack 1991, Williams et al. 1996). Microbial N mineralization rates have been found to respond rapidly to increased N availability from the snow melt (Aber et al. 1998) but Williams and Melack (1991) found that mineralization and nitrification processes did not appear to be an important source of NO_3^- during snow pack runoff due to cold temperatures and frozen soils.

Creed and Band (1998b) found that peak concentrations of NO_3^- and DOC occur in the ground and streamwater just prior to the peak spring snow melt. However, the soils remain a sink for NH_4^+ from snow melt water, with less than 1% of the NH_4^+ released from snow exported out of the forest soil ecosystem via the ground water (Williams and Melack 1991). Ammonium could also have been oxidized to NO_3^- which would leave the soil system rapidly (Williams and Melack 1991). Whatever the fate of N from the snow pack melt water, tracing the path of the nutrients through the system is very important for management practices. Knowing the chemistry and amount of snowfall

from year to year can provide a better understanding of the effects of precipitation on soil and water nutrient cycling in forest soils (Ingersoll 2000).

1.4 ^{15}N forest soil field studies

Nitrogen (N_2) in the atmosphere is 99.6337% ^{14}N and 0.3663% ^{15}N. The N in soils is less well mixed than in the atmosphere. Thus, the percentage of N as ^{15}N in soils tends to range from 0.3654 to 0.3673%. Deviations from the atmospheric isotope ratios are measured as δ^{15}N, which is defined as:

$$\frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{standard}}{(^{15}N/^{14}N)_{standard}} \times 1000 \qquad (1.1)$$

where the standard is air. The use of natural abundances of ^{15}N to trace N transformations in more complex systems is constrained by the amount of fractionation that may occur during the transformations between pools (Binkley and Hart 1989). Most ^{15}N tracer studies in forest soil have focused on the efficiency of N-fertilizer applications or on the proportion of applied-N that is taken up by trees (Knowles 1975, Binkley and Hart 1989). However, ^{15}N tracers in field studies can also aid in determining if rates of N mineralization and nitrification are significant in affecting the size of the inorganic N pools in forest soils. Such an application at the Bootleg Mountain research site forms part of this study, as described later.

One can also trace the movement of native-N through the soil-plant system by adding low-levels of ^{15}N, typically less than 50% of the ambient inorganic N pool. In such work, the amount of label recovered in various ecosystem compartments is monitored over a certain time period to determine the ambient rates of N transformations. Application of this method is limited because N movement in soils is quite dynamic and therefore

difficult to trace the changes directly (Vancleve and White 1980, Vitousek and Matson 1985, Binkley and Hart 1989).

The isotope dilution method is a powerful tool for measuring gross rates of microbial transformations of soil N. This method makes it possible to estimate the gross rates of N mineralization and nitrification without the addition of a substrate (Davidson et al. 1991). The method consists of adding small amounts of highly enriched $^{15}NH_4^+$ and $^{15}NO_3^-$. This addition of low levels of ^{15}N into a pool allows the estimation of transformations into and out of a labelled pool (Binkley and Hart 1989). Comparison of the traditional net mineralization and nitrification experiments to the determinations of gross rates of nitrification and mineralization studies (Davidson et al. 1992, Stark and Hart 1997, Verchot et al. 2001) indicate that net rates are poor predictors of gross rates of nitrification, leading to their overestimation.

The main assumptions of the ^{15}N method (Kirkham and Bartholomew 1954) are: 1) microorganisms do not discriminate between ^{15}N and ^{14}N; 2) the rates of processes measured remain constant over the incubation period; and 3) ^{15}N assimilated during the incubation period is not remineralized (Davidson et al. 1991). The isotope pool dilution technique is based on the following steps: 1) addition of ^{15}N enriched mineral N (NH_4^+ or NO_3^-) to the soil; 2) estimation of the amount of ^{15}N enrichment and pool size of the labelled pool at two times; and 3) using a zero order model to derive gross N flux rates (Kirkham and Bartholomew 1954, Berntson and Aber 2000).

1.5 Summary

This brief review has provided a body of information that will be used to link the snow, soil, and groundwater through the measurement of different variables and rates of N

cycling. However, there are still gaps in what we know. This thesis aims to rectify such deficiencies by providing new information on the various environmental factors associated with snow, soil, and groundwater that may be regulating nutrient fluxes at Bootleg Mountain. A specific objective is to determine whether N mineralization and nitrification are significant sources of inorganic N to the groundwater at this site.

Chapter 2
Site description and project design

2.1 Site description

Bootleg Mountain at Matthew Creek, British Columbia, is part of the Purcell Mountains within the Columbia Basin of the East Kootenays (Fig. 2). Subalpine forest characterizes the region, which sits southwest of Kimberly and northwest of Cranbrook and Marysville, B.C. The vegetation of the Bootleg Mountain is characterized by Lodgepole pine (*Pinus contorta*), Subalpine fir (*Abies lasiocarpa*) and Engelmann spruce (*Picea engelmannii*) (Lea 1989) as well as a variety of herbs and shrubs (Table A1).

Bootleg Mountain has an elevation of 2606 m with the study area located at an approximate elevation range of 1690-1728 m with a northeastern slope aspect. This area has a mean daily temperature of 5.7°C, and the total annual precipitation is 383 cm. Snow accumulations are on average 140 cm (Environment-Canada 2004). The area is within the Dry Cool Englemann Spruce-Subalpine Fir (ESSFdk) biogeoclimatic zone (Coupé et al. 1991).

The research site has a stand age of around 121-140 years old. The site has been subdivided into 34-1 ha blocks (Fig. 2), half of which have been approved for harvesting by Tembec, the industrial partner for this study. Harvesting may lead to an influx of NO_3^- and nutrients from terrestrial to aquatic ecosystems (Hauer et al. 1997). This may have an impact on the local watershed that drains into a reservoir that supplies drinking water to the town of Marysville, B.C. Typically, lodgepole pine ecosystems are quite dry and infertile.

Wells et al. (1998) performed a terrain interpretation of the Matthew Creek area and stated that Matthew Creek and its several tributaries drain into the St. Marys River about 12 km upstream of Marysville, near Kimberly, B.C. The study area has been heavily impacted by wild fire and logging, and extensive areas have lost forest cover. Roads into the area have intercepted surface flow, diverting and concentrating slope drainage water via culvert installations. Developments above or in these areas may cause changes in moisture conditions including down slope soil saturation, surface drainage, and reduced forest productivity.

2.2 Project design

An area covering approximately 15 ha was selected on which to perform a series of experiments in 12 blocks (Fig. 3 and 4). The N mineralization and nitrification aspect of this project was limited to 6 blocks (20A, 20, 30A, 30, 28A, 28) (Fig. 3).

Subsurface monitoring was performed in all 12 blocks in order to include a larger sample size for comparison. This site will allow us to investigate factors regulating water and N cycling and outflow before and after whole-tree harvesting. Tembec marked out the blocks in 2001. Using the marked boundaries, the blocks were measured to determine the approximate size in metres and to map out where the wells would be installed. Five wells were installed in each block (Fig. 2 and 4). This pattern was selected in order to allow for characterization of slope effect. A “basin/sub-basin” perspective will characterize each block, such that the dominant flow of water is down slope and the wells are located to capture the changes in water nutrient levels from higher elevations to lower elevations. Also, the six experimental blocks were chosen such that harvesting effects

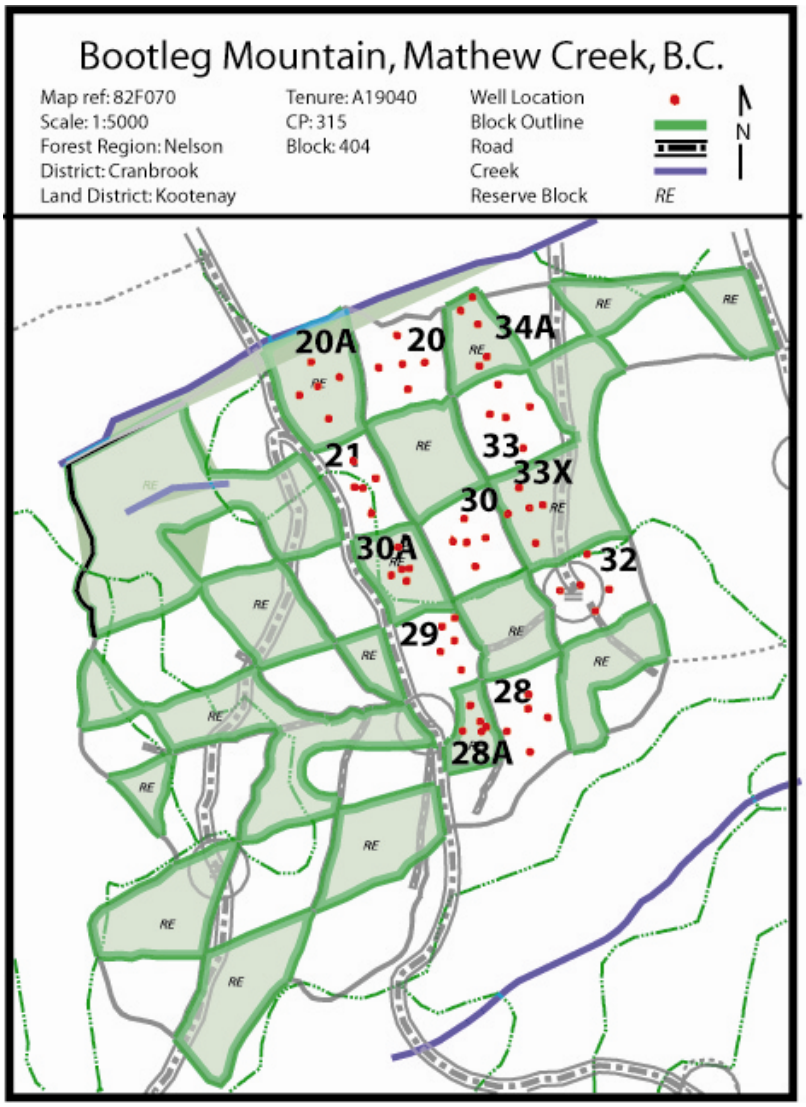

Figure 2. Map of Bootleg Mountain showing hydrologic well locations ●. Experimental blocks are 20A, 20, 30A, 30, 28A and 28. There are also groundwater sampling wells in blocks 34A, 21, 33, 33X, 29, and 32.

would not be enacted on reserve areas. Each well location was located by GPS and the closest tree was flagged (Fig. 2, Table A2).

The 60 wells (five wells per block in 12 blocks) were installed during summer 2002. Soil sampling and pit characterization occurred at each location at the time of hydrological well installation. On a monthly basis, initial subsurface water sampling was performed as the wells were installed, depending on whether or not there was water in the wells. The vegetation, canopy cover, and amount of coarse woody debris were described within a 3-metre radius of the selected site (Table A3). The average dimensions of a PVC well were 200 cm long by 5 cm diameter of which 50 cm was above ground. The portion (150 cm) of the PVC tube below ground was perforated (1 cm diameter, 2.5 cm between holes), and covered with Well Sock®.

In order to be able to relate the soil characterization data from the wells to net and gross N mineralization and nitrification, the blocks were divided into nine regions (Fig. 4). The five regions containing wells were further divided into four quadrants. At the center of the lower right quadrant, a small area (50 cm × 50 cm) was selected to perform the pre- and post-harvest $\delta^{15}N$ isotope dilution, microbial biomass measurements, and buried bag experiments. These areas were marked for future use.

The snow pack study was designed to give an overview of the snow coverage at the maximum seasonal snow accumulation for that year (Fagre 2002). Snow pack studies are useful for obtaining an index of snow water equivalent over an area for use in predicting spring run-off volumes. Measurements were made along five transects running approximately east to west (Fig. 5); down the center of each block at 25 m intervals (Male and Gray 1981) (Table B1). A random number generator was used to determine

the number of metres off-transect (up to 50 m north or south) where each sample was taken. These 51 sites were marked for future sampling.

2.3 Statistical analyses

Statistics (average, ± 1 standard deviation, coefficient of variation, minimums and maximums) were calculated for each variable using Excel (Microsoft-Corporation 2003). Data was checked for normality by graphing standardized residuals. Data not normally distributed were log-transformed. An analysis of variance (ANOVA) was performed to test for the differences among the means for each variable and to assess variation caused by soil depth, well location, and block (Sokal and Rohlf 1981). For the blocks that showed significant differences, a Tukey's test was performed to determine which samples displayed the greatest degree of difference (Sokal and Rohlf 1981). Two-tailed Pearson's and Spearman correlation coefficients were calculated for each pair of variables (Sokal and Rohlf 1981). In general, only the Pearson correlation coefficients are mentioned unless the Spearman coefficients were different. Computations of these statistical tests were performed using SPSS version 12.0 for Windows (SPSS-Inc. 2003).

In order to standardize the data for ease of comparison between the soil, snow, water, and literature, the results of the nutrient analyses were transformed from $\mu g \cdot g^{-1}$ dry weight (dw), $\mu g \cdot L^{-1}$, or $mg \cdot L^{-1}$ to $kg \cdot ha^{-1}$. The volume of the block in kg was first calculated from the width of the layer (~150 cm) and the area of the block (1 ha). For soils, this was then transformed from a wet soil weight volume to a dry soil weight volume. The original value in $\mu g \cdot g^{-1}$ dw, was then multiplied by the volume in kg dw, then divided by the area of the block in hectares. For the transformation of the snow and water data, the equivalence of 1 kg to 1L was used to transform the volume to weight.

The nutrient value in $\mu g \cdot L^{-1}$ was then multiplied by the volume of the block in kg and divided by the area of the block in hectares to get a measurement in $kg \cdot ha^{-1}$.

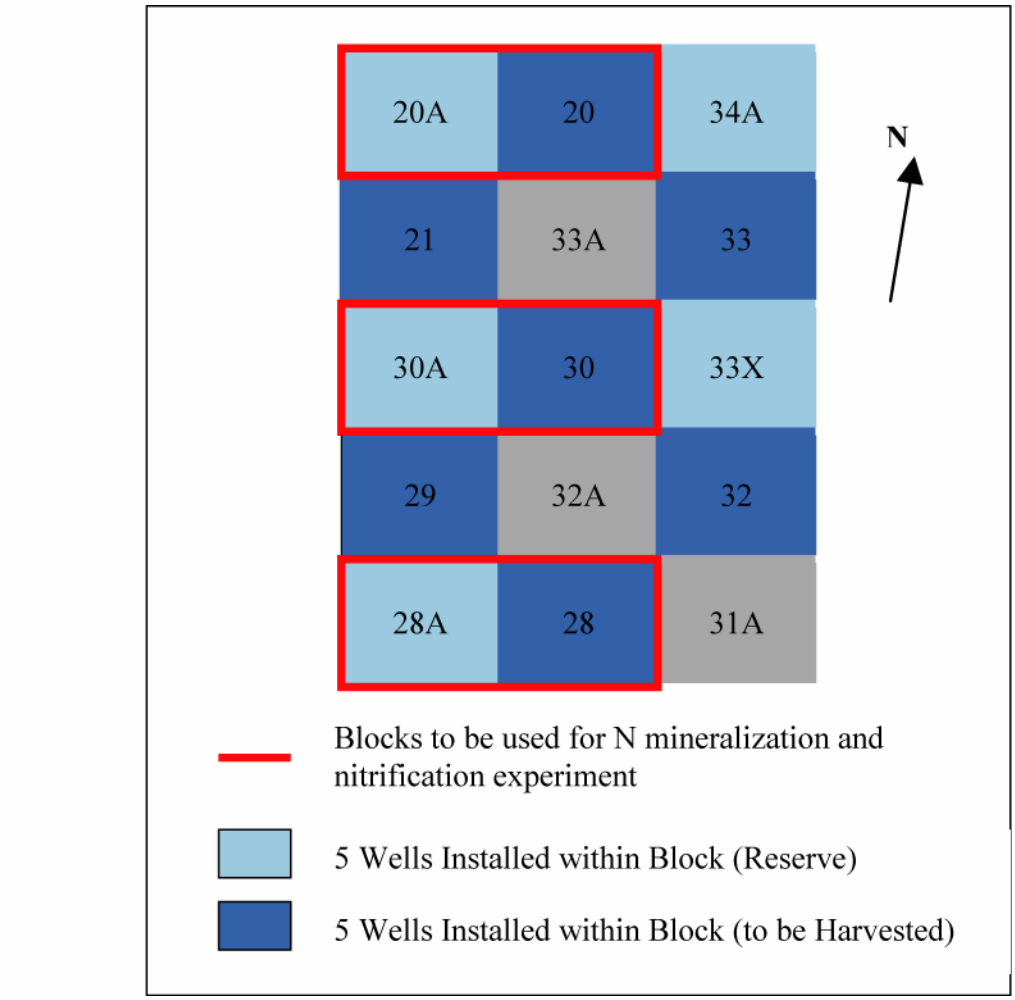

Figure 3. Schematic showing blocks to be harvested versus reserve blocks, blocks in which wells are located, and blocks that will be used for this project.

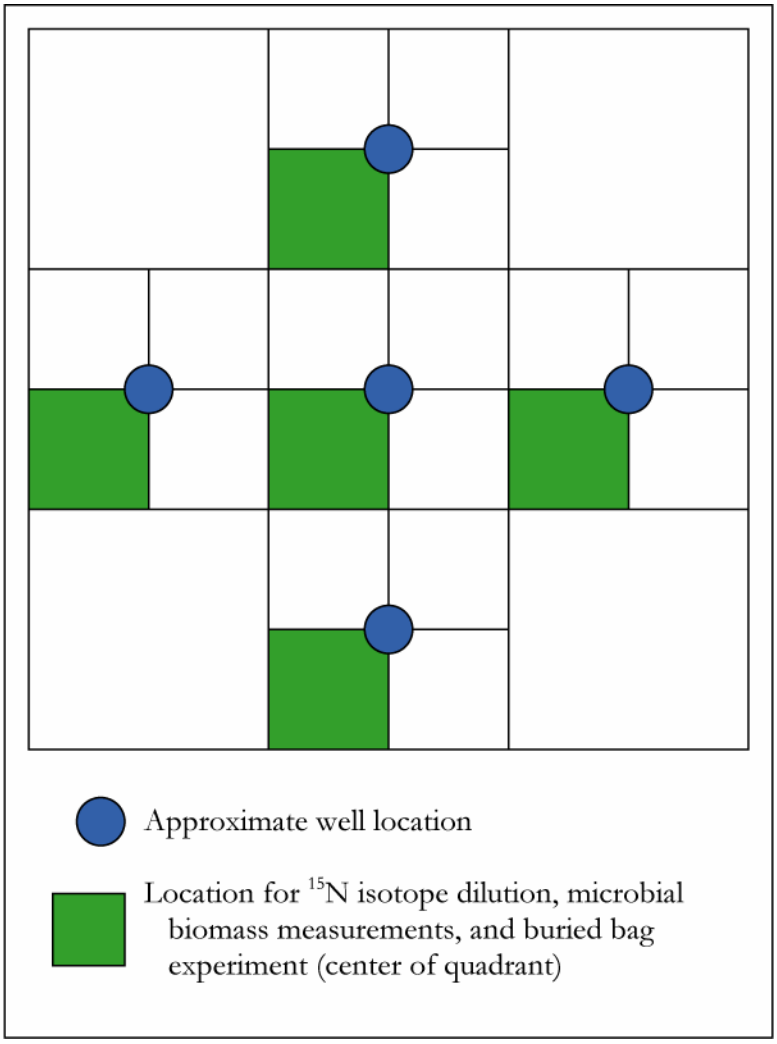

Figure 4. Approximate locations of hydrological wells within a block and the locations for the ^{15}N isotope dilution, microbial biomass measurements, and buried bag experiments occurring at the center of each marked quadrant.

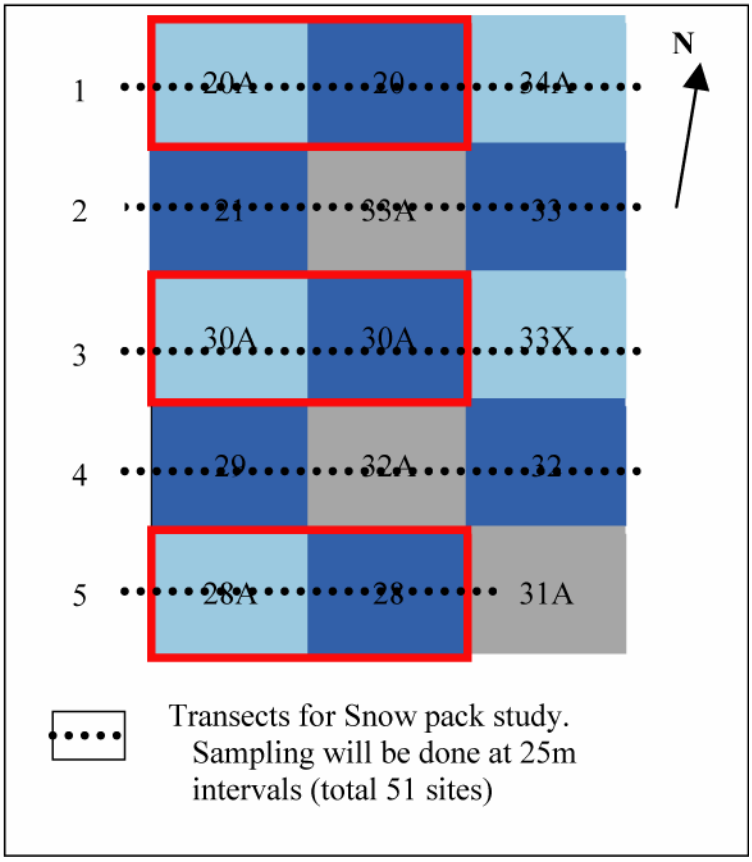

Figure 5. Schematic showing transects for snow pack study.

Chapter 3
Determination of chemical and physical characteristics of soils from a continental lodgepole pine (*Pinus contorta* Doug.) forest

3.1 Introduction

Forest harvesting can have dramatic effects on microclimate, and soil physical (Froehlich 1979) and chemical properties (Schmidt et al. 1996, Startsev et al. 1998) of a site. Better knowledge of nutrient cycles in forests under contrasting forest regimes will help: 1) to develop the best forest management practices; and 2) to determine the effects due to fire, pollution and climate change (Johnson et al. 1997). There has been some research into nutrient cycling on lodgepole pine (*Pinus contorta* Dougl.) forests including the effects of pH on the soil N and P (Fahey and Yavitt 1988), forest biomass and internal cycling of nutrients (Arthur and Fahey 1992), soil hydrology (Nyberg and Fahey 1988), modelling of water and nutrient outflow (Knight et al. 1985), determination of the N cycle (Fahey et al. 1985), and the determination of biotic processes regulating nutrient fluxes (Fahey and Knight 1986). However, further work is needed to enhance understanding of the processes occurring in these soils in alternate locations and under different conditions. Further background of the soil research, N cycling, and a site description were discussed in Section 1.1 and Chapter 2.

An objective of this project was to characterize the soil by determining the physical variables at the site: bulk density, soil layer morphology, and particle size analysis. These analyses provided an understanding of the underlying dynamics at the site, an indication of site heterogeneity, and to gather the background levels of these variables to

see their relation to the water and snow hydrology and the N cycling at Bootleg Mountain.

3.2 Materials and methods

Soil samples were collected during hydrological well installation for the groundwater study (see Chapter 4).

3.2.1 Determination of physical site characteristics of soils

Soil pits were dug to 150 cm, making sure that the horizons were kept separated and disturbance was minimized. Representative samples were taken from the four sides of the pit at 0-10 cm, 10-30 cm, and 30-60 cm and placed in plastic Zip-lock® bags. Each sample was used for archival, soil moisture, and nutrient extractions. Samples were kept in coolers during transport back from the field, and then stored at 4°C until analysis, which occurred within 4-6 hours of sampling (Klute 1986).

Bulk density

Samples for the determination of bulk density were taken using a bulb corer of a known volume. Two depths were taken at adjacent depths (0-10 cm and 10-20 cm). The samples were then taken back to the lab, dried for 24 hours at 105°C and the dry weight was measured for bulk density determinations in $g \cdot cm^{-3}$ (Klute 1986).

Soil layer morphology

Pictures of each pit were drawn and included details of the soil colour, finger texture determination, rooting zones, and the amount and size of rocks as they changed with depth (Fig. A1, Table A3) (Klute 1986).

3.2.2 Determination of soil particle fractions using the standard hydrometer method

Soils from five well locations for each of 12 blocks were collected during the summer of 2002. Samples were taken from the soil pits, from each of the four sides covering ~0-60 cm. Sand, silt, and clay composition was determined by the standard hydrometer method (Gee and Bauder 1986). After air drying, soil samples were sieved (2 mm mesh size) and the fraction greater than 2 mm was weighed to determine the percentage of that fraction. Soil (40.0 g) was weighed into a dispersing cup with 100 mL of sodium hexametaphosphate (HMP) and 200 mL of dH_2O. The solution was then mixed for 5 minutes with an electric mixer (Waring DMC20 Lab mixer, Torrington, CT). Another soil sample (10.0 g) was used for determination of dry weight (convection oven at 105°C for 24h). After shaking, the solution was transferred to the sedimentation cylinder and dH_2O was added to bring the volume up to 1L. Then, the solution was mixed thoroughly for 1 minute with a plunger and the hydrometer (Standard ASTM no.152H, with Bouyoucos scale in $g \cdot L^{-1}$) was immediately inserted carefully. Hydrometer and temperature readings were taken at 30s, 1, 3, 10, 30, 60, 90, 120, and 1440 minutes. Triplicates of each soil were analyzed to see if there was any variation within the sample. Calculations were conducted according to the method in Gee and Bauder (1986).

3.2.3 Assessment of site vegetation

For each site, vegetation types, amount and type of coarse woody debris, amount and size of roots and rocks from each soil layer, and layer depths were recorded within 3 metres of the selected site. This characterization is summarized in Fig. A1 and Table A3. There was a wide variety of herbs and shrubs in addition to Lodgepole pine (*Pinus*

contorta), Subalpine fir (*Abies lasiocarpa*) and Engelmann spruce (*Picea engelmannii*) (Lea 1989).

3.2.4 Determination of initial soil chemistry

From each soil layer, approximately 5 g of soil [dry weight (dw) equivalent] was weighed into 3 – 50 mL centrifuge vials for: 1) ultrapure water extractions (two vials); and 2) 2M KCl extraction (one vial). An additional sample (5 g) was weighed into a tin for determination of soil moisture content (convection oven at 105°C for 24h). Another sample (~15 g) was placed into a vial (20 mL scintillation tube) and immediately frozen for future studies. Ultrapure water (50 mL) was added to each of the 2 centrifuge vials and 2M KCl (50 mL) was added to a third vial. Vials were then agitated (250 rpm, 60 minutes) (Mulvaney 1996). After agitation, all samples were filtered through prerinsed nitrocellulose membrane filters (0.45 μm) (Fisherbrand 09-719-1B, Ottawa, Ont.). For dissolved organic carbon (DOC) analysis, an ultrapure water-extract sample (15 mL) was filtered through a polyvinyl durapore filter (0.45 μm) (Durapore, Fisherbrand HVLPO4700, Ottawa, Ont.). All of the filtrate was immediately stored at -20°C until further chemical analysis. Quality control involved filtering blanks of 2M KCl and ultrapure water.

The ultrapure water-extract samples were analyzed for DOC, TDP, NO_3^--N, NO_2^--N and PO_4^{3-} and the KCl-extracted samples were analyzed for NO_3^--N and NH_4^+-N. DOC was analyzed indirectly by determination of the difference between total carbon (TC) and inorganic carbon (IC) (Shimadzu-Corporation 2001) on a Total Organic Carbon Analyzer (Shimadzu-Corporation, Kyoto, Japan). Blanks, standards (0, 5, 10 ppm), and duplicates were analyzed every 10 samples and the standard curve ranged from 0 – 100 ppm.

Total dissolved P was analyzed by first digesting the water extract sample with potassium persulphate and then analyzing colorimetrically based on an ammonium molybdate and antimony potassium tartrate reaction before reduction with ascorbic acid (Ebina et al. 1983). The blue colour complex was then measured on a Lachat QuikChem FIA+ Ion Chromatograph Auto Analyzer (Zellweger-Analytics 1999). Quality control involved analysis of digested ultrapure water blanks, standards (5 ppb KH_2PO_4), duplicates, and spiked samples (0.1 mL of 1000 ppb KH_2PO_4 + 19.9 mL sample = 5 ppb spike) for every 15 samples.

The analysis of the water-extracted NO_3^--N, NO_2^--N, and PO_4^{3-} was analyzed on an ion chromatograph (Small and Bowman 1998) (Dionex ICS-90, Dionex Corporation, Sunnyvale, CA) equipped with an carbonate-selective AS15 IonPak column (4 × 250 mm, Dionx Corp., Sunnyvale, CA), using a carbonate/bicarbonate eluent (flow rate of 0.5 $mL \cdot min^{-1}$) coupled with a suppressed conductivity detector (Dionex CD25, Dionex Corp., Sunnyvale, CA). Anion standards from 5 to 2000 ppb were used. A blank (ultrapure water), a standard (50 ppb each of KNO_3, $NaNO_2$, KH_2PO_4), a duplicate sample, and a spiked sample (0.5 mL of 500 ppb mixed anions standard + 0.5 mL sample = 50 ppb spike) were run for every 15 samples. Field blanks were treated as samples for quality assurance and quality control.

Nitrate-N and NH_4^+-N were determined in the KCl-extracted soils using an automated colorimetric method (Alpkem Flow System IV CF/FIA analyzer, OI-Analytical, College Station, TX). Nitrate-N was determined by the copperized cadmium reduction method (Norwitz and Keliher 1986, OI-Analytical 2001b) and NH_4^+-N was determined by reaction with phenol and hypochlorite to form an indophenol blue colour (Rhine et al.

1998, OI-Analytical 2001a). Blanks, standards, and duplicates were run every 10 samples.

3.2.5 Statistical analyses

Statistics performed are described in section 2.3.

3.3 Results

Soil from the various sampling blocks were generally homogeneous according to their soil types and bulk densities, but some heterogeneity between sampling blocks was observed for soil moisture, DOC, NO_2^--N, NO_3^--N, NH_4^+-N, total inorganic N, PO_4^{3-} and TDP. For every variable measured there were significant differences between the organic (Org) (~0-10 cm layer containing litter, moss, and organic matter), and the two mineral layers (M1, M2) (~10-30 cm and ~30-60 cm). The soil gravimetric moisture content (GMC) was the highest in the Org layer (1.45 $g \cdot g^{-1}$) and decreased with depth (0.38 $g \cdot g^{-1}$ in M1 and 0.25 $g \cdot g^{-1}$ in M2). Bulk density (BD) increased with depth with averages of 0.26, 0.71, and 0.67 $g \cdot cm^{-3}$ for Org, M1, and M2, respectively. For the chemical variables, it was observed that the amount of the nutrient decreased with depth but had very high heterogeneity as indicated by the high coefficient of variations (Table 1, 2, and A4).

Dissolved organic C was 0.78 $mg \cdot g^{-1}$ dry weight (dw) in the Org layer, 0.12 $mg \cdot g^{-1}$ dw for the M1 layer, and 0.12 $mg \cdot g^{-1}$ dw for the M2 layer. Water-extracted NO_2^- was quite low (0.45, 0.02, and 0.03 $\mu g \cdot g^{-1}$ dw) and often below detection level for many of the soil samples. Water-extracted NO_3^--N and KCl-extracted NO_3^--N levels were vertically heterogeneous, although no significant differences between the layers were observed. Because there was no significant difference between the water-extracted NO_3^--

N and KCl-extracted NO_3^--N data, it can be assumed that both methods of extraction were equivalent. Herein, soil NO_3^--N denotes the results of water-extracted NO_3^--N. The averages for NO_3^--N were 1.18, 0.65, and 0.46 $\mu g \cdot g^{-1}$ dw for the Org, M1, and M2 layers. KCl-extracted NH_4^+-N was 2.93, 0.56, and 0.42 $\mu g \cdot g^{-1}$ dw for the 3 layers. The total inorganic nitrogen (TIN) averages were 3.79, 0.76, and 0.56. TDP levels were 7.65, 0.14, and 0.05 $\mu g \cdot g^{-1}$ dw respectively, for the Org, M1 and M2 layers. PO_4^- was 11.39, 0.41, and 0.32 $\mu g \cdot g^{-1}$ dw for the Org, M1, and M2 layers. Relatively high coefficient of variations for each chemical variable indicates intra-block variation (Table 1, 2, and A4).

Focusing on the six main experimental blocks (20A, 20, 30A, 30, 28A, and 28) the GMC for block 30A was found to be significantly different from most blocks for all three layers (Fig. 6). Bulk densities showed some significant differences between block 30A and the rest of the blocks (Fig. 7). Particle size analysis indicated that the soil type was mostly sandy loams with a few loam sites (Fig. 8). Results obtained from the ANOVA indicated that all blocks were not significantly different from each other.

In general, nutrients were significantly higher in the organic layer than in the mineral layers (Table 1, 2, and A4). For DOC and PO_4^{3-}, no significant differences were observed between blocks (Fig. 9). For TIN, Block 20A was significantly higher than blocks 30 and 28 (Fig. 9). For the initial NO_2^--N, NO_3^--N, and NH_4^+-N levels in soils, there were significantly higher levels of the nutrients in Org layer compared to the two mineral layers (Fig. 10). For NH_4^+-N, block 30A and 28A were significantly higher than the rest of the blocks for data from all layers (Fig. 10).

The results of the Pearson two-tailed correlation calculation (Table 3) showed many correlations between soil variables measured at all three soil layers. As expected, GMC

was positively correlated to all the variables (correlation coefficients ranged from 0.29 to 0.58) at the $p < 0.01$ level and negatively correlated to BD (r = -0.55). BD was also negatively correlated to all the other variables (correlation coefficients ranged from -0.56 to -0.21) which were likely a reflection of the correlation to moisture contents. DOC was highly correlated to PO_4^{3-} (r = 0.82) and TDP (r = 0.82) but weakly correlated to water-extracted NO_3^--N (r = 0.21). DOC was also correlated to water-extracted NO_2^--N (r = 0.46), NH_4^+-N (r = 0.40), and TIN (r = 0.41). As expected, water-extracted NO_3^--N was strongly positively correlated to KCl-extracted NO_3^--N (r = 0.72). This correlation suggests that both methods of extraction were adequate to determine NO_3^--N in the soil.

The relationship between PO_4^{3-} and TDP was also strongly positively correlated (r = 0.96). Phosphate$^-$ and TDP were weakly correlated to NO_3^--N (r = 0.21 for PO_4^{3-} and r = 0.24 for TDP, respectively). Phosphate and TDP were also correlated to NH_4^+-N (r = 0.45 for PO_4^{3-} and r = 0.47 for TDP) and TIN (r = 0.47 for PO_4^{3-} and r = 0.48 for TDP). There was a strong positive correlation between KCl-extracted NH_4^+-N and TIN (r = 0.99) but a weak correlation to NO_3^--N (r = 0.23).

3.4 Discussion

Over short time intervals (1 day), the supply of nutrients and rates of cycling is regulated by the current pool sizes, the mobility of ions (Binkley and Hart 1989), physical site characteristics (particle size, bulk density) (Wilde 1958), and environmental factors (moisture, temperature) (Knight et al. 1985). On longer time scales (weeks and months), these pools are small relative to the fluxes through them (Binkley and Hart 1989). These data from Bootleg Mountain were from a single sampling point in time, so they are used only for background information on the underlying dynamics at the site.

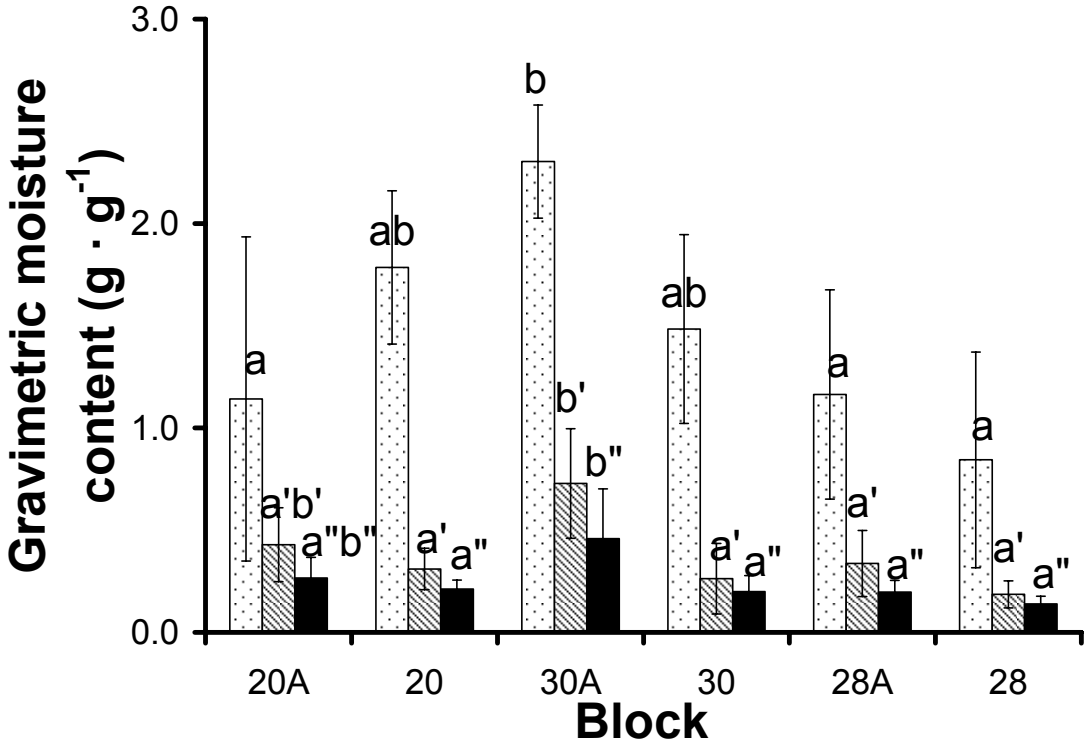

Figure 6. Gravimetric soil moisture contents by depth for 1 hectare field blocks. Blocks with different letters are significantly different for each layer ($p < 0.05$). Each bar represents the average of 5 data points with the error bars equivalent to ± 1 SD. The Organic Layer ⬚ is significantly different from Mineral Layer 1 ▨ and Mineral Layer 2 ■ ($p < 0.05$).

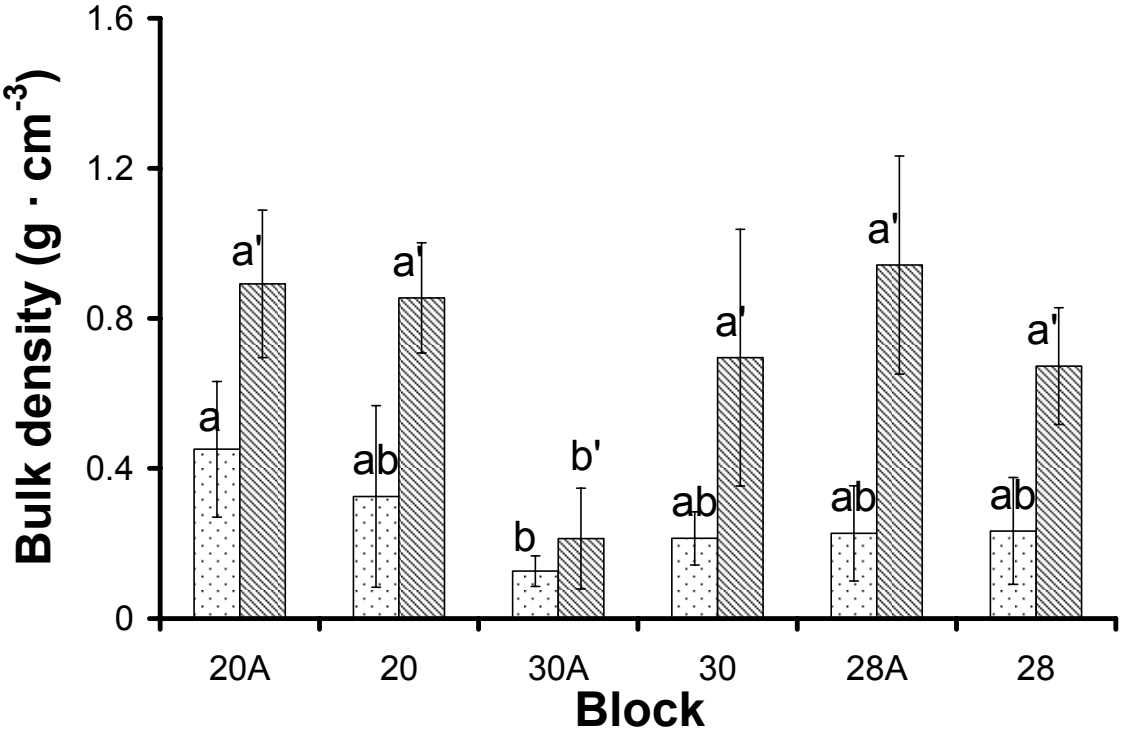

Figure 7. Bulk density by depth for 1 hectare field blocks. Blocks with different letters are significantly different for each layer ($p < 0.05$). Each bar represents the average of 5 data points with the error bars equivalent to ± 1 SD. The Organic Layer ⊡ is significantly different from Mineral Layer 1 ▨ ($p < 0.05$).

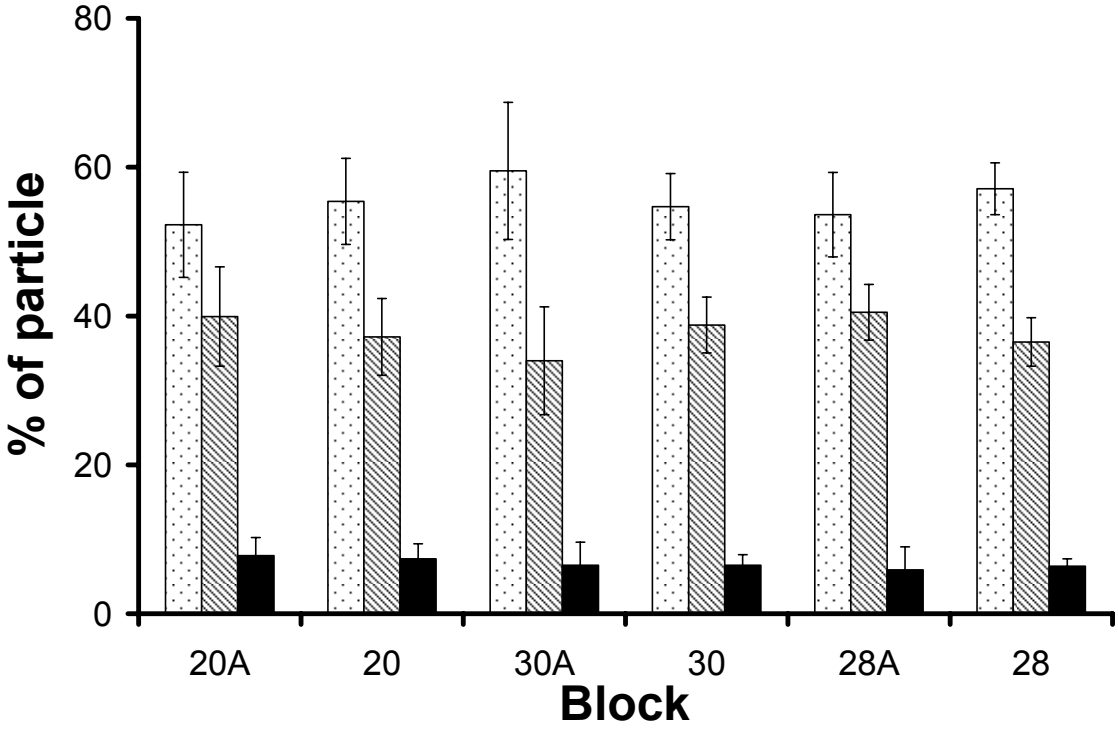

Figure 8. Soil particle size analysis by block. ⬚ % sand, ▨ %silt, ■ %clay. Each bar represents the average of 5 data points with the error bars equivalent to ± 1 SD. These soils range within the textural class of loams to sandy loams on the Canadian Soil Texture Triangle.

Table 1. Basic soil sample characteristics for the variables under study at Bootleg Mountain (three depths per well, five wells per block).

Layer		GMC * ($g \cdot g^{-1}$)	Bulk Density ($g \cdot cm^{-3}$)	DOC ($mg \cdot g\ dw^{-1}$)	PO_4^{3-} ($\mu g \cdot g\ dw^{-1}$) ‡	TDP ($\mu g \cdot g\ dw^{-1}$) ‡
Org *	**mean**	1.45	0.26	0.78	7.65	11.4
	CV (%) †	46.6	65.2	83.7	96.5	88.4
	min	0.18	0.07	0.03	0.72	1.2
	max	2.71	0.69	2.68	35.0	44.6
Min1*	**mean**	0.38	0.71	0.12	0.14	0.41
	CV (%) †	62.8	45.2	77.4	110	96.1
	min	0.01	0.10	0.02	0.01	0.03
	max	1.08	1.36	0.32	0.78	2.28
Min2*	**mean**	0.25	0.67	0.12	0.05	0.32
	CV (%) †	60.6	34.7	137	121	59.0
	min	0.10	0.46	0.02	0.01	0.07
	max	0.84	0.92	0.84	0.24	0.84

*** Org – Organic soil layer; Min1 – Mineral Layer 1; Min2 – Mineral Layer 2; GMC – Gravimetric Moisture Content; L – below detection limit**
† CV (%) – coefficient of variation
‡ Soil was extracted with ultrapure H_2O

Table 2. Basic soil characteristics for forms of inorganic N collected from Bootleg Mountain. (three depths per well, five wells per block).

Layer		NO_2^--N (μg · g dw^{-1}) ‡	NO_3^--N (μg · g dw^{-1}) ‡	NH_4^+-N (μg · g dw^{-1}) §	TIN (μg · g dw^{-1}) §
Org *	**mean**	0.45	1.18	2.93	3.79
	CV (%) †	203	137	119	104
	min	0.00L *	0.09	0.35	0.43
	max	3.81	8.72	16.5	16.6
Min1*	**mean**	0.02	0.65	0.56	0.76
	CV (%) †	184	109	81.3	84.9
	min	0.00L *	0.09	0.08	0.11
	max	0.18	3.15	1.55	2.27
Min2*	**mean**	0.03	0.46	0.42	0.56
	CV (%) †	353	65.0	107	84.1
	min	0.00L *	0.15	0.06	0.08
	max	0.63	1.33	1.83	1.87

*** Org – Organic soil layer; Min1 – Mineral Layer 1; Min2 – Mineral Layer 2; GMC – Gravimetric Moisture Content; L – below detection limit**
† CV (%) – coefficient of variation
‡ Soil was extracted with ultrapure H_2O
§ Soil was extracted with 2M KCl

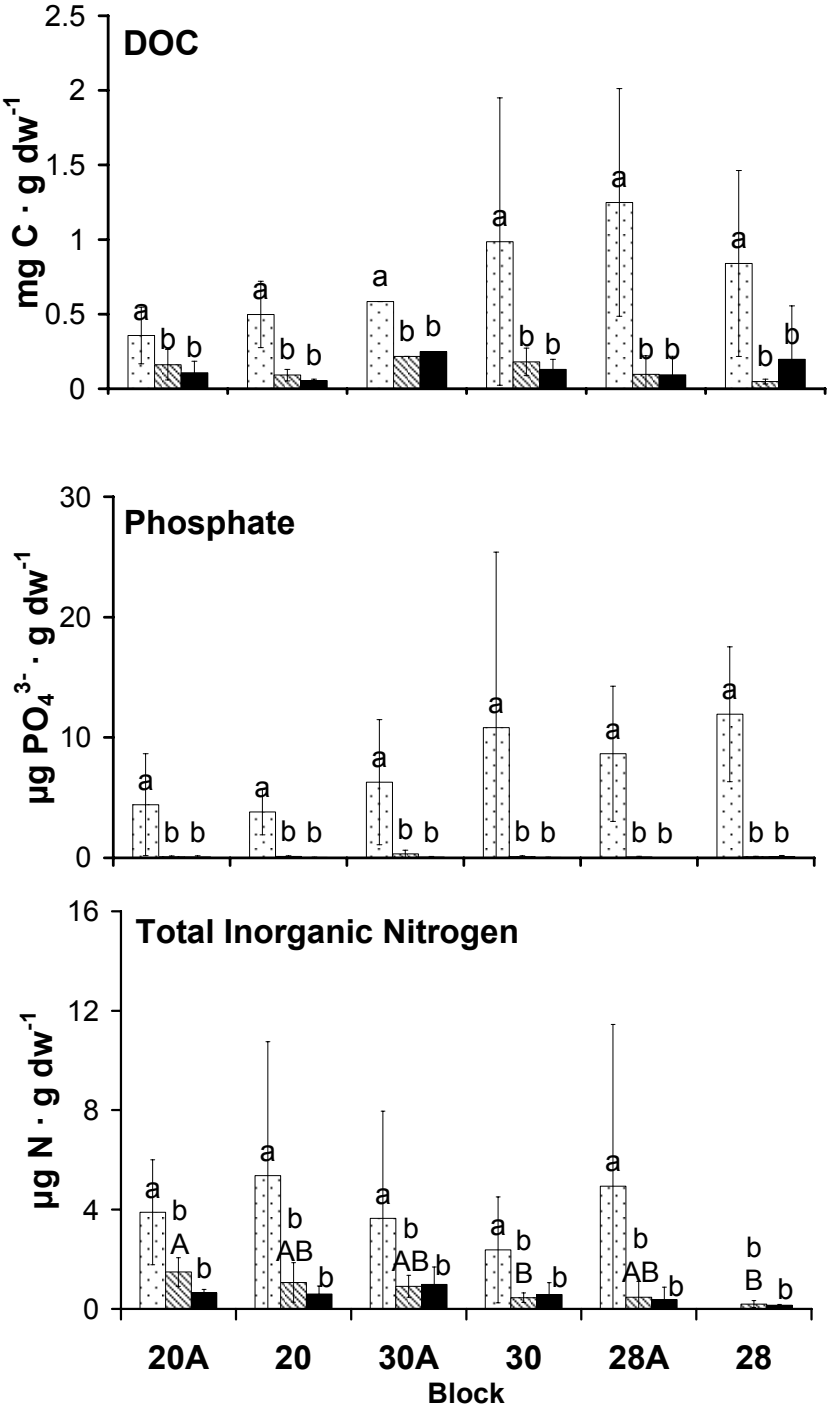

Figure 9. Soil DOC, PO_4^{3-}, and Total Inorganic Nitrogen by layer (⬚ Organic, ▨ Mineral Layer 1, and ■ Mineral Layer 2). Lower case letters show significant differences between layers. Upper case letters show significant differences between the same layers among different blocks ($p < 0.05$). Each bar represents the average of five data points with error bars equivalent to ± 1 SD.

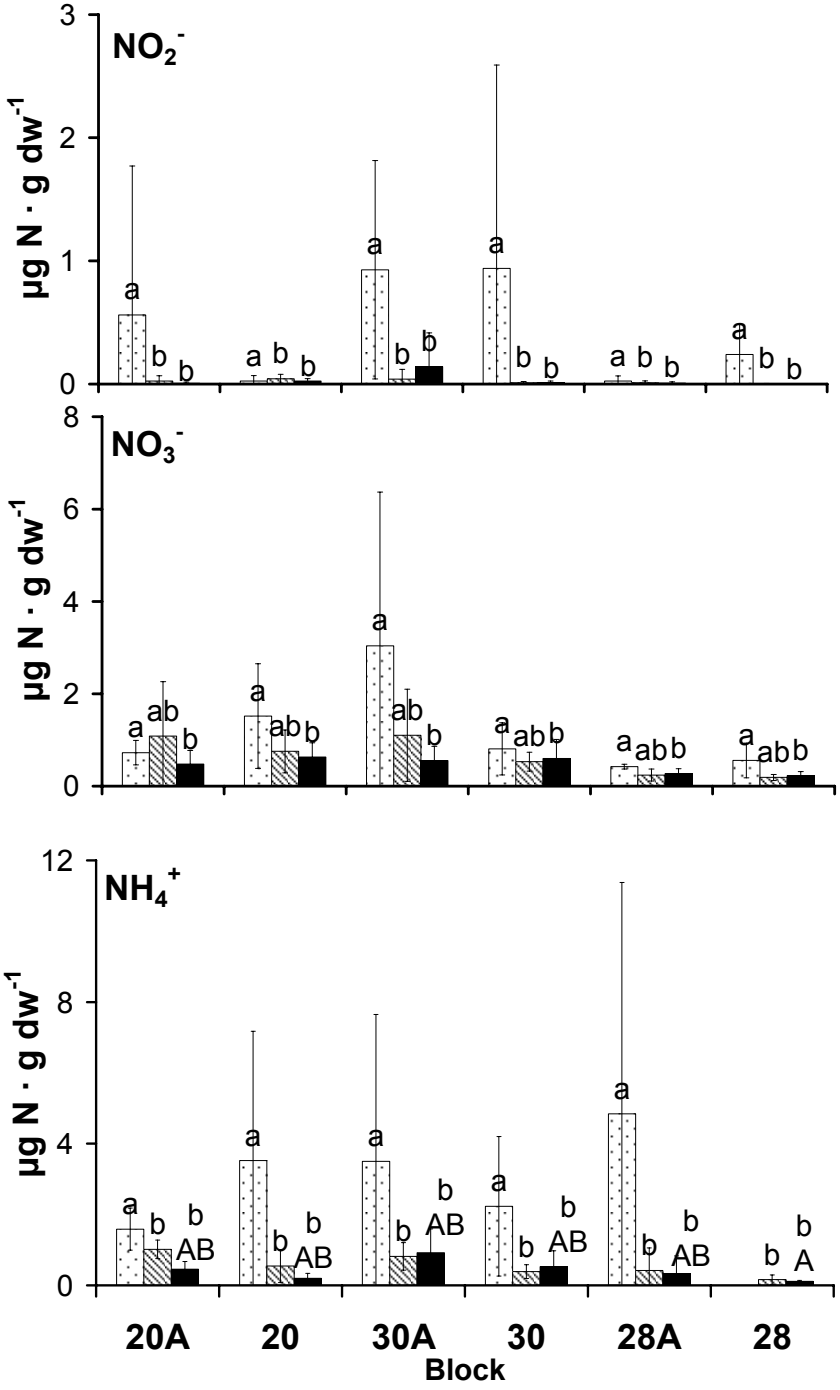

Figure 10. Soil-N from Bootleg Mountain by layer (▫ Organic, ▨ Mineral Layer 1, and ■ Mineral Layer 2). Lower case letters show significant differences between layers. Upper case letters show significant differences among the same layers between different blocks ($p < 0.05$). Each bar represents the average of five data points with the error bars equivalent to ± 1 SD.

Table 3. Pearson correlation coefficients between variables measured in lodegpole pine forest soils.

	GMC	BD	DOC †	NO_2^- †	NO_3^- †	PO_4^{3-} †	TDP †	NH_4^+ ‡
BD	-.55**							
DOC †	.58**	-.56**						
NO_2^- †	.38**	-.22*	.46**					
NO_3^- †	.41**	-.21*	.21*	.29**				
PO_4^{3-} †	.50**	-.46**	.82**	.61**	.21**			
TDP †	.52**	-.47**	.82**	.59**	.24**	.96**		
NH_4^+ ‡	.51**	-.23**	.40**	.43**	.13	.45**	.46**	
TIN ‡	.55**	-.30**	.41**	.46**	.27**	.47**	.48**	.99**

*** Correlation is significant at the 0.05 level (two-tailed)**
**** Correlation is significant at the 0.01 level (two-tailed)**
† Soil was extracted with ultrapure H_2O
‡ Soil was extracted with KCl
GMC – Gravimetric moisture content; BD – Bulk density; DOC – Dissolved organic carbon; TDP – Total dissolved phosphorus; TIN – Total inorganic nitrogen.

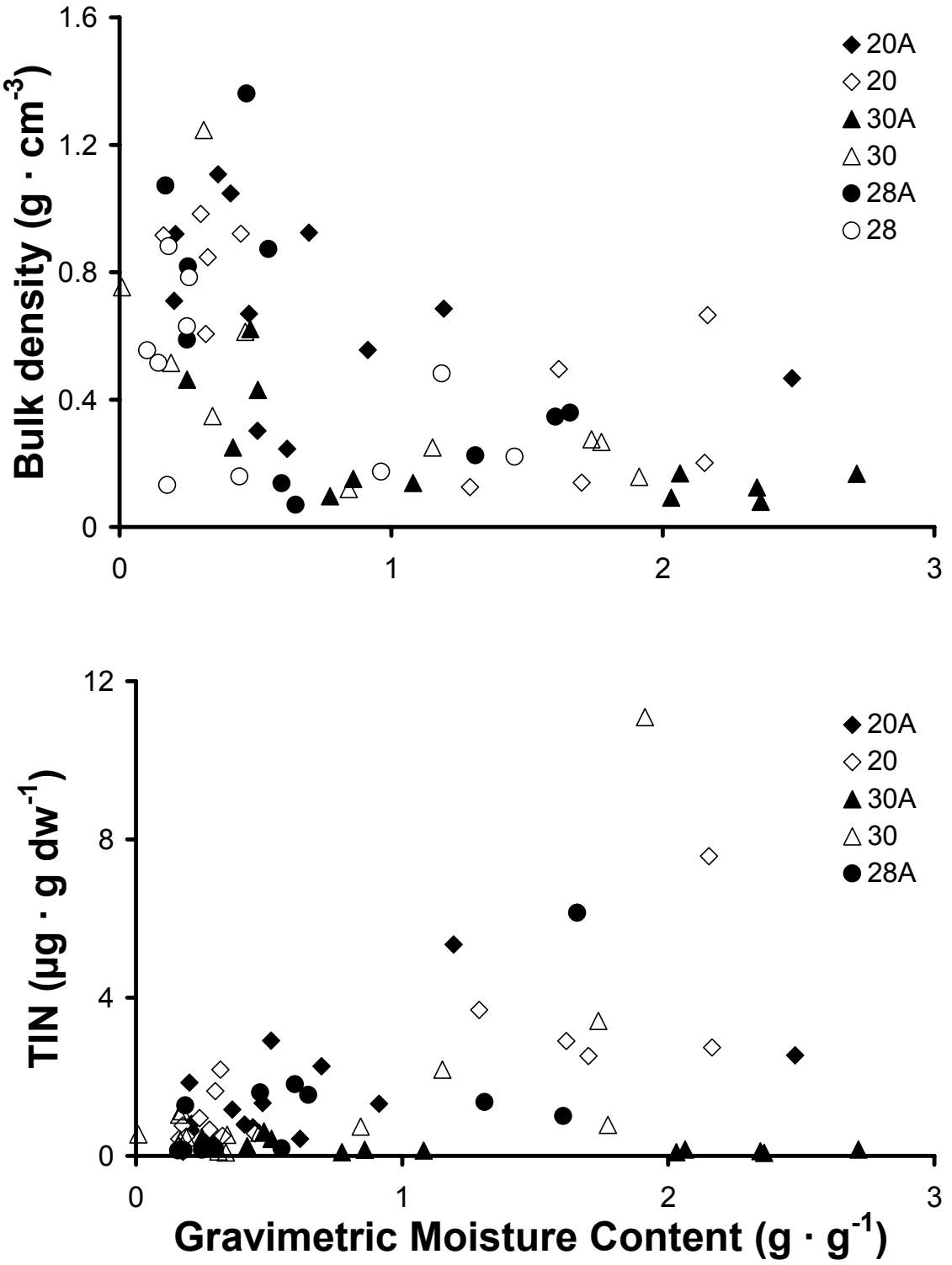

Figure 11. Soil bulk density and total inorganic nitrogen as a function of soil gravimetric moisture from 0-60 cm in a lodgepole pine forest, Bootleg Mountain.

3.4.1 Determination of the soil physical site characteristics

Significant differences in all variables between the soil organic layer (0–10 cm) and the 2 soil mineral layers (10–30 cm and 30–60 cm) were observed. Binkley and Hart (1989) stated that the organic layer typically produces half or more of the N mineralized in forests, and mineralization generally decreases with depth. The study of the lodgepole pine forest at Bootleg Mountain certainly concurs with this general statement.

As expected, soil moisture contents showed a very strong positive relationship with all the variables measured. The fate of N in soils may be influenced by the amount of water available. Up-slope, the water table may be beneath the biologically active zone, and thus aerobic conditions are likely. At deeper depths, even though saturation may occur, it is possible that there will be little or no denitrification occurring because of the lack of available C (Groffman et al. 1996). The Bootleg Mountain data showed that moisture tended to decrease with depth up to 60 cm. On a few occasions, the water table was above 60 cm, which may have affected nutrient cycling and resulted in the large coefficients of variation (CV%) shown for the analyzed variables (Table 1, Table A4). Soil moisture content in the organic and mineral layers of sandy loam soils in a 60-yr-old mixed conifer stand were found to be 1.15–2.28 $g \cdot g^{-1}$ and 0.51–0.60 $g \cdot g^{-1}$ (Schimel and Firestone 1989). Lindo and Visser (2003) also found the soil moisture content of the soils in the conifer stands in northern Alberta to be 1.68 $g \cdot g^{-1}$ which was quite similar to the range found in this study's soils. The soil moisture content in the unburned plots of *Pinus radiata* in the Coastal Mountain Range of Chile ranged between 12 and 21 % in the mineral soils (Litton and Santelices 2003). The soils at Bootleg Mountain were higher but it is likely that the moisture contents from Litton and Santelices (2003) were a

function of the hot dry climate characteristic of the area. A disturbance that removes the trees from the site could result in decreased soil moistures, which will affect all other variables (Litton and Santelices 2003). Knight et al. (1985) also found that the soil profile dries steadily during the summer in the upper 2 m of soil.

The soil moisture content varied significantly across the different blocks, exhibiting the expected spatial heterogeneity. Block 30A especially exhibited the highest water content and the lowest bulk density. Block 30A also had the largest sand content (though not significant). These differences in physical characteristics across the site may have influenced nutrient levels, water quality, and cycling rates (see Chapter 4 and 5).

Bulk density increased significantly with depth between the organic and first mineral layer of the soils. Bulk density in forest soils has been found to vary between 0.2 $g \cdot cm^{-3}$ in organic layers to 1.9 $g \cdot cm^{-3}$ in coarse sandy soils (Wilde 1958); the soils at Bootleg Mountain have been found to be within this range. Highly compacted soil layers may prevent the penetration of roots and were correlated with porosity, degree of aeration, and filtration capacity of soils (Wilde 1958). The negative correlation of bulk density with soil moistures (Fig. 11) in addition to the negative correlations to the nutrient levels were likely primarily a function of soil moisture coupled with a resulting effect from bulk density. Bulk density does not change seasonally and so its effect on rates of cycling and pool sizes is likely constant.

In the lodgepole pine ecosystems of southeastern Wyoming, bulk densities were 1.28 and 1.40 $g \cdot cm^{-3}$ (Fahey et al. 1985), which was higher than the results found at this research site. On a study of a native tallgrass prairie ecosystem, it was also found that the total C and N decreased with increasing bulk density (Brye et al. 2004). These silt loams

were found to have bulk densities of 1.06 and 1.08 g · cm^{-3} for the two sites sampled, which, as expected is higher than the bulk densities determined for the sandy loams at Bootleg Mountain, but still within the range of typical bulk densities. The average soil bulk density for a 20 year old Douglas-fir site were found to be 0.74 g · cm^{-3} (Piatek et al. 2003). This compares well with the data from the Bootleg Mountain study site as it does with the bulk densities in the silt loams of the Boreal Highlands (1.29 to 1.37 g · cm^{-3} in the mineral soil layer) (Moore 2003). Bulk densities may not be affected by disturbances such as wildfires, but lower bulk densities following disturbances have been found to lead to increased rates of superficial water flow and soil erosion (Litton and Santelices 2003).

The ability of forest soils to retain water depends greatly on the amount of silt and clay present; the greater amount of silt and clay, the greater the soil moisture content, all conditions remaining the same (Wilde 1958). This ability to retain water and make it available to trees, plants, and organisms affects the productivity of forest soils. Available water capacity is a function of the rooting depth and texture of soils. Rooting depth may be limited by bedrock, dense hardpan, or seasonal high water table (Wilde 1958). The sandy loams at Bootleg Mountain, with 58.3 % sand, 35.3 % silt, and 6.5% clay contents did not vary much across the site, so it can be assumed that the influence exerted by them would be consistent and based more on the moisture contents, as observed in the correlation matrix.

3.4.2 Relationship of soil DOC to N and P pools

Organic material can originate from various sources which include the excretion and decay of organisms like bacteria, algae and vascular plants (Volk et al. 2002). DOC is affected by factors such as climate (temperature and precipitation), vegetation, and inputs

of microbial organic carbon (Stumm and Morgan 1996). Mcdowell et al. (1998) determined that DOC in the soil solution increased in bioavailability and concentration due to increased energy demand associated with immobilization. They also found that with added N to their site, DOC only undergoes small changes coupled with large increases in dissolved organic nitrogen (DON), resulting in a large decline in the C/N ratio (Mcdowell et al. 1998). The moderate positive relationship between DOC and TIN that was observed at Bootleg Mountain supports this finding. DOC in the soil solution of hardwood and pine plots at the Harvard forest was found to be 10 mg $\cdot$ L^{-1} in the spring and as high as 300 mg $\cdot$ L^{-1} in the summer (Mcdowell et al. 1998). There were never any results as high as 300 mg $\cdot$ L^{-1} in both the soil extraction results and groundwater chemistry results (see Chapter 4), as most of the samples were closer to the 10 mg $\cdot$ L^{-1} range at Bootleg Mountain. When the large coefficients of variation are considered, DOC concentrations do vary across the site, and exhibit a lot of heterogeneity within the blocks but not between the blocks. DOC flux often may not be clearly related to the N status in coniferous forests (Gundersen et al. 1998); however, such a relationship was observed at Bootleg Mountain.

In the sandy soils of a Central European deciduous forest ecosystem, DOC was found to be between 27.9 and 79.9 mg $\cdot$ L^{-1} in the soil leachate of the organic layer and 14.6 mg $\cdot$ L^{-1} in the first 20 cm of the first mineral layer and 3.9 mg $\cdot$ L^{-1} in the second mineral layer up to 60 cm (Solinger et al. 2001). Solinger et al. (2001) also found the same significant ($p < 0.01$) relationship between soil DOC and NO_3^--N ($r = 0.52$) and NH_4^+-N ($r = 0.40$) as determined at Bootleg Mountain. The sharp decrease of DOC over depth is indicative of the ability of the mineral soil to retain DOC through adsorption or

decomposition which was demonstrated to be an effective retention mechanism (Qualls and Haines 1992). In deeper mineral soils with low carbon, DOM may be adsorbed strongly to mineral surfaces, resulting in low DOM concentrations in the soil solution (Kalbitz et al. 2000). DOC concentrations in all the soil studied at the cool-humid Black Forest in Germany decreased with depth, and were lower in the mineral layers of aerobic soils than that of anaerobic soils (Fiedler and Kalbitz 2003). The differences in DOC between the different soil layers is also likely due to differences in microbial activity in the soils (Kaiser et al. 2002).

The very strong relationship between P and DOC found at Bootleg Mountain has been reported in other studies (Datry et al. 2004) and is likely due to the idea that C/P ratios strongly influence P immobilization and mineralization. The amount of P immobilized or mineralized depends on the amount of organic carbon in soils. Also, high levels of P result in eutrophication and increased organic carbon levels in both soils and surface waters (Mullen 1999). A recent study also revealed that the interaction of DOC and PO_4^{3-} increases PO_4^{3-} mobility in soils and may affect the bioavailability of P (Fernandez-Perez et al. 2005).

There were no significant differences in the DOC levels or the C/N ratios across the site. There was greater heterogeneity in the results from blocks 30, 28A, and 28 than in blocks 20A, 20, and 30A.

3.4.3 Availability of N in forest soils

Repeated samplings of the total N pool through a single year should produce essentially the same estimates because the annual fluctuations are very small compared to the total pool. Considering specifically the pool sizes of inorganic N, there is more likely

to be strong seasonal dynamics because the pool size is small relative to annual fluxes (Binkley and Hart 1989). These seasonal fluxes are also exhibited in the changes in the subsurface water nutrient levels over the season (see discussion in Chapter 4). There may be decreased soil inorganic N in the spring due to increased leaching of NO_3^- during the wet winter season (Litton and Santelices 2003).

Attiwill and Adams (1993) determined the total N pools in the litter layer of a 50-year old highly productive eucalyptus forest to be 150 000 kg · ha^{-1}. Also, in a *Pinus patula* stand in South Africa, the total N pool in the litter layer was found to be 1442 kg · ha^{-1} (Dames et al. 2002). As these are total N pools determined by direct combustion of the soils, it is difficult to compare the results from Bootleg Mountain, but since productivity at this site is known to be quite N limited, it is expected that total N pools will be much smaller in the soils at Bootleg Mountain. Piateck et al. (2003) found total N concentrations to be 1600 μg · g^{-1} in the top 20 cm of the soils of a 20 year old Douglas fir forest. These results are also higher than the soils at Bootleg Mountain. Gundersen et al. (1998) found N to be 61 to 291 g N · m^{-2} in the organic layer and 244 to 826 g N · m^{-2} in the mineral layer of the European coniferous forest soils subjected to N deposition in the NITREX project. Again, the results from Bootleg are two to three orders of magnitude lower (0.27 g N · m^{-2} in the organic layer and 0.13 g N · m^{-2} in the first mineral layer), but this discrepancy may be explained by the fact that the NITREX soils were subjected to experimental and natural N deposition much higher than that occurring at Bootleg Mountain.

Many studies have looked at the leachate from soils, rather than an extraction of sampled soils. In order to compare with the findings of this study, the concentration of

the extracts should be considered. Exchangeable inorganic soil N ranged between 15.8 and 23.9 mg · L^{-1} in the unburned soils of *Pinus radiata* forest in the Coastal Mountain Range of Chile (Litton and Santelices 2003). Again, soils from Bootleg Mountain had lower soil N concentration from water-extracted soils (69.1 μg · L^{-1}) and slightly higher KCl-extracted TIN (124 μg · L^{-1}), but still much lower than the results from Litton and Santelices (2003).

Solinger et al. (2001) found NO_3^--N in the leachate from the organic layer of soil from the NITREX project ranged from 1.3 to 10.4 mg · L^{-1}, 7.0 to 10.9 mg · L^{-1} in the top 20 cm of the mineral layer, and 1.1 to 2.3 mg · L^{-1} in the mineral layer up to 60 cm. Ammonium concentrations were much lower than the NO_3^--N concentrations in the organic layer: 1.2 to 2.8 mg · L^{-1} and 0.1 mg · L^{-1} in the mineral layers. This contrasts with the Bootleg findings where NH_4^+-N was dominant in the organic layer but was similar to NO_3^--N in the mineral layers. The results from Bootleg Mountain (0.1 to 1.29 μg · L^{-1}) were still an order of magnitude lower than these results, which was likely due to the inherent lack of available N in these soils. Based on these results, most, if not all of the inorganic N in the soils at Bootleg Mountain is likely immediately immobilized through plant and microbial assimilation (see Chapter 5).

In the rooting zone of soil solutions of lodgepole pine forests in southeastern Wyoming, NO_3^- was at trace levels and NH_4^+ was dominant (0.25 g · m^{-2}) (Fahey et al. 1985), which is very similar to the findings at Bootleg Mountain (0.56 g · m^{-2}). The higher N levels in the organic layer has been suggested to be the result of fungal translocation from the humus to the upper mineral soil layers where a lower C/N ratio enhances N mineralization rates (Fahey et al. 1985). The results from Bootleg Mountain

do not support this idea since similar C/N ratios occurred in all layers. However, the concurrent rates of high immobilization (see Chapter 5) may have influenced this finding as most mineral N would have been immobilized by soil organisms as soon as it was mineralized. Some have hypothesized that decreasing the amount of labile C that is available to microorganisms will in turn decrease microbial N assimilation, which can result in increased N accumulation in soils (Prescott et al. 2003). Such a trend was not observed at Bootleg Mountain. Vitousek and Howarth (1991) stated that when N is limiting, the soils generally have high C/N ratios and low N/P ratios. This was also found in the soils at Bootleg Mountain with a C/N ratio of 207 and an N/P ratio of 0.64.

Soil moisture also plays a role in amounts of N in the soils. Prescott et al. (2003) determined that there is a threshold level at approximately 50% soil moisture content: below 50%, N is uniformly low and above 50%, N could be quite high. This trend also occurred in the soils from Bootleg Mountain (Fig. 11). This relationship could affect NO_3^- availability and leaching if a change in moisture contents or temperature due to harvesting was to occur.

Average NH_4^+-N (145 $\mu g \cdot g^{-1}$) and NO_3^--N (1 $\mu g \cdot g^{-1}$) in boreal conifer stands in northern Alberta (Lindo and Visser 2003) are similar to the findings at Bootleg Mountain in that the bulk of inorganic N in soils is in the form of NH_4^+-N, even though lower concentrations of NH_4^+-N were determined. Nitrate in forest soil is present in very low levels because it is conservatively and efficiently cycled within forest ecosystems (Dail et al. 2001). The variability of the N results is evident in Fig. 10. Higher NO_2^--N and NO_3^--N levels in block 30A are well correlated to higher soil moisture contents which could have resulted in the increased rates of nitrification (see Chapter 5).

3.4.4 Availability of P in forest soils

The cycling of P in some forests is effectively restricted to the litter layer (Attiwill and Adams 1993). Phosphorus availability is largely a function of P cycling via mineralization of organic P. It is also affected by competition between biological and geochemical sinks for PO_4^{3-} anions (Attiwill and Adams 1993). It is likely that P concentrations decrease during long term soil development (Vitousek and Howarth 1991). The N/P ratios in the soils from Bootleg Mountain were 0.41 in the organic layer and 2.1 in the mineral layers. These low N/P ratios in the forest floors agree with the characteristics of N-limitation in soils (Vitousek and Howarth 1991).

In a *Pinus patula* stand in South Africa, the total P pool in the litter layer was found to be 103 $kg \cdot ha^{-1}$ (Dames et al. 2002) and the P pool in the litter layer of the 50 year old eucalyptus forest was 10 $t \cdot ha^{-1}$ (Attiwill and Adams 1993). Both these examples are considerably higher than the results from this study. This difference may be a function of the age of the soils. Much more P weathering and input must have occurred in these considerably older soils than in the younger soils at Bootleg Mountain.

There is increasing evidence that for a number of forests, P is immobilized in the first stages of decomposition to a significantly greater extent than is N (Attiwill and Adams 1993, Dames et al. 2002). It has been shown by Lindo and Visser (2003) that P can be immobilized via laboratory incubations. The low levels of P in the soils from Bootleg Mountain may be an indication of P-limitation and that the bulk of the P is actually present in an unavailable organic form.

Extractable soil P in the mineral soils of unburned plots of a *Pinus radiata* forest in the Coastal Mountain Range of Chile was between 1 and 5 ppm (Litton and Santelices 2003). A lower range of P (0.003 to 2 ppm) was observed in the soil extracts from Bootleg

Mountain. This is likely a function of high immobilization rates and low deposition because the bulk of the P in the soils from Bootleg Mountain is in unavailable organic forms. Low deposition rates of P may also play a role in the low available P in the soils. The largest portion of nutrients is generally found in the organic material on the forest floor which is released into the soil through decomposition and mineralization. Following disturbances such as fires, much of the P in the organic matter is oxidized and left over as ash that is readily incorporated into the mineral soil (Litton and Santelices 2003). The higher values of P in the organic layer have the potential to be released and to increase P levels in the mineral layers. In an undisturbed ecosystem like Bootleg Mountain, the bulk of P should remain in the organic layer unless it is mineralized or decomposed by soil microbial action.

Extractable P in the sandy-textured Marla soils from Little Valley in the eastern Sierra Nevada Mountains was found to be around 10.0 $\mu g \cdot g^{-1}$ in the organic horizon, 7.8 $\mu g \cdot g^{-1}$ in the 5-20 cm depth, and 3.6 to 5.6 $\mu g \cdot g^{-1}$ in the 20-50+ cm depth (Johnson et al. 1997). The results from the organic layer were quite similar to the soils at Bootleg Mountain, except that P in the lower horizons of the soils was quite low.

Phosphate is readily released from organic matter at low C/P ratios and clear-cutting may increase losses to surface waters (Piirainen et al. 2004). Background levels of P in the soils of a boreal forest in Finland were 30.7-38.0 $kg \cdot ha^{-1}$ (Piirainen et al. 2004) in the organic horizon, which was higher than that of Bootleg Mountain, indicating that the bulk of the PO_4^{3-} in the Bootleg Mountain soils may be in an immobilized, organic form.

3.4.5 Summary

The soils at Bootleg Mountain exhibited characteristics that fit with those found in lodgepole pine ecosystems (Fahey et al. 1985, Fahey and Knight 1986, Fahey and Yavitt 1988). The concentrations of inorganic N and P are quite low and forms of inorganic N are probably quickly immobilized into the organic matter as soon as they are mineralized or deposited. Soil moisture contents strongly influence bulk density, nutrient levels and cycling in the soils. DOC can influence both N and P concentrations and aids in the retention of these nutrients in the soils. This was exhibited in the higher nutrient levels found in the organic matter at the research site. Inorganic N pools in the soil are likely not going to change much seasonally relative to the annual fluxes.

A major concern at Bootleg Mountain is the effect of disturbances on this ecosystem. Although they found few significant changes in the mineral soil properties following harvesting, Bock and Van Rees (2002) still suggested that harvesting may accelerate organic matter decomposition and nutrient leaching in the forest floor and mineral soils.

Despite mineralized N being shown to be retained in forest soils; and that N leaching from the soil organic matter is probably related to soil texture and bulk density. Contrary to previous findings at Bootleg Mountain, no correlations of inorganic N to sand, silt, and clay content were found, although a negative correlation to bulk density was determined at Bootleg Mountain. It is unlikely that N saturation is occurring in these soils. Changes in the C/N and C/P ratios influence the cycling of N and P in the soils and higher ratios may result in increased immobilization rates. For all nutrients measured, the concentrations in the organic horizon are significantly higher than the mineral horizons and are indicative of the ability of the organic horizon to retain nutrients.

In terms of spatial heterogeneity, all blocks were similar in their nutrient levels, except for block 30A, which had higher moisture contents and inorganic N and lower bulk densities. Linking these soil data to the snow and groundwater regime is important in management decisions in regards to the quality of drinking water provided from this ecosystem. Also, determining the role that microorganisms play in the nutrient levels and rates of cycling will enhance the ability to predict the changes that may occur following a disturbance. The objective of the soil characterization was to determine the underlying dynamics at Bootleg Mountain. The following chapters will attempt to address the linkages between the soils, snow, and groundwater.

Chapter 4
Seasonal water and nutrient fluxes in the snow and groundwater of a continental lodgepole pine (*Pinus contorta* Doug.) forest

4.1 Introduction

Snowmelt and early spring rain in the lodgepole pine forests are normally the only water sources sufficient to leach soil nutrients (Knight et al. 1985). These conditions lead to the assumption that any significant flow of nutrients out of the ecosystem are going to occur only in the spring because large amounts of nutrients are potentially available for leaching during the spring flush period, especially since root uptake and microbial immobilization during this time is likely reduced (Knight et al. 1985, Fahey and Yavitt 1988). The length of the snowmelt period is dependent on several factors including climate, transpiration during the snowmelt period, and leaf area index. More shading and higher transpiration rates during this period can divert much of the snowmelt water from potential stream flow and retain more water in the soil pores (Fahey and Knight 1986).

The deposition of nutrients such as N is of concern because of the potential for N saturation (Aber et al. 1989, Tietema et al. 1997, Aber et al. 1998, Gundersen et al. 1998). However, very little N has traditionally been deposited in the Rocky Mountains (in the form of snow) (Fahey and Knight 1986). N-fixation has also been found to be negligible in lodgepole pine ecosystems because there are very few symbiotic N-fixing plant species available (Fahey et al. 1985). As most unpolluted terrestrial environments are limited in N, additions of anthropogenically-derived N have the potential to change the balance in undisturbed ecosystems (Sievering et al. 1996).

Following the snowmelt, the water enters the soil and may be either taken up by plants, retained in the soil solution, or continue to flow through to the groundwater and eventually the surface water. Traditionally, assessment of water movement through ecosystems is performed on a watershed basis. Stands (blocks) were originally chosen for study instead of an entire watershed because of the interest in the effects of harvesting trees on soil nutrient quality and water flow. Even in the absence of harvesting, this sampling design is still appropriate for determining potential spatial and temporal effects. The principal problem with the forest stand approach is the estimation of water and nutrient outflow, even from stands that are small and homogeneous (Knight et al. 1985). However, models can be used to calculate the outflow from the system. In this study, water depths were sampled weekly to determine an estimate of the outflow from the system.

In the past, many studies on water and nutrient movement have focused only on outflow from terrestrial ecosystems, with particular considerations to the effects of differing land uses. However, water and nutrient losses from a system are influenced by many factors that can vary spatially and temporally (Knight et al. 1985). Fahey and Knight (1986) divided the annual hydrologic pattern in the Rocky Mountains into three parts: 1) the snow accumulation from October until April; 2) the snow melt period in May and June which contributes to soil saturation, groundwater, and stream flow; and 3) the dry summer where evapotranspiration reduces the soil water content. This sequence occurs at Bootleg Mountain and this study attempts to characterize the interconnections between the snow, soil and groundwater. The snow pack study was performed to obtain an index of snow water equivalent, snow depth, and nutrient analysis for the winter

seasons of 2003 and 2004 at Bootleg Mountain. The objectives of the subsurface water sampling study were to: 1) quantify the volume of water in the wells and relate it to the chemistry of the snow, soil and groundwater; 2) measure the nutrients in the groundwater in the wells at Bootleg over summer 2002 and 2003; 3) quantify the impact of the spring snow melt in terms of nutrients and volume; and 4) to relate the results from the soil study (Chapter 3) to the snow and groundwater. Further discussion of current groundwater and snow research and the site description was presented in Sections 1.2, 1.3 and Chapter 2.

4.2 Materials and methods

4.2.1 Determination of the physical characteristics of the snow pack

The snow survey was performed by taking 51 snow samples at 25 m intervals along five east-west transects down the center of each block (Fig. 5). A random number generator was used to determine the number of metres off-transect (up to 50 m north or south) where each sample was taken (Table B1). The sites were marked in 2003 in order to use the same location in 2004. At each site, a 2 m long, 4 cm diameter PVC tube was inserted into the snow pack. The surrounding snow was then dug out, the depth of the snow pack was measured, and a clean trowel was put under the end of the tube. The snow in the tube was then emptied into a plastic bag (Zip-lock®), ensuring that no snow remained inside the tube. Duplicate vertical snow columns of the entire stratum were taken, but were later combined for chemical analysis. The samples were then weighed and stored at -20°C for further nutrient analysis. The weight was converted to a water equivalent measurement, the product of density and layer thickness. Density was calculated by dividing the weight of the snow by the cylinder volume.

4.2.2 Determination of the snow chemical characteristics

Upon arrival at the lab, snow samples were transferred into covered, acid washed Mason jars and melted at 20°C. Two samples from each sampling site were combined. Conductivity and pH were measured on unfiltered samples using a multiple probe (pH, conductivity, temperature) (Model 63 YSI, Hoskin Scientific, Vancouver, B.C.). Subsamples were filtered as described in section 3.2.4 for analysis of DOC, TDP, TDN, NO_3^-, NO_2^-, NH_4^+, and PO_4^{3-}. An unfiltered subsample (150 mL) was put aside for TP, TN, and TOC analysis. All of the filtrate was immediately stored in the dark at -20°C until nutrient analysis. Filtered and unfiltered blanks of ultrapure water were prepared as a quality control measure.

The snow samples were analyzed for DOC, TDP, TP, NO_3^-, NO_2^-, NH_4^+, and PO_4^{3-}. These variables were analyzed as described in section 3.2.4. TDN and TN were analyzed after digestion with potassium persulphate and NaOH. Then levels were determined colorimetrically by the copperized cadmium reduction method (Norwitz and Keliher 1986, OI-Analytical 2001b) on an automated analyzer (Lachat QuikChem FIA+ Ion Chromatograph Auto Analyzer, Zellweger-Analytics, Millwaukee, WI). A digested ultrapure water blank, a standard (50 ppb KNO_3), a duplicate of a sample, and a spiked sample (0.25 mL 5 ppm KNO_3 + 19.75 mL sample = 50 ppb spike) were also analyzed every 15 samples.

Ion chromatography, as described in section 3.2.4, was used for the analysis of the NO_3^-, NO_2^-, and PO_4^{3-}. Ammonium was analyzed colorimetrically using the Berthelot reaction (Rhine et al. 1998). Ammonia reacts with alkaline phenol, sodium hypochlorite, sodium nitroprusside, and EDTA to form an indophenol blue colour which was measured at 640 nm on a spectrophotometer (Adams 1990). The standard curve ranged from 0 to

100 ppb of NH_4Cl. A blank (ultrapure water), a standard (10 ppb NH_4Cl), a duplicate of a sample, and a spiked sample (0.25 mL of 1000 ppb NH_4Cl +12.25 mL sample = 50 ppb spike) were analyzed for every 10 samples.

4.2.3 Temporal and spatial variation of groundwater levels

Wells made of PVC pipe (5 cm diam.) were installed to an average depth of 150 cm during the summer of 2002 in 12 blocks (Fig. 2-4). Total depth of the hole, length of the well, and the well stick-up were measured at the time of installation. As the pit was dug, the soil horizons were kept separate on a tarpaulin that was laid out beside the pit. The bottom 30 cm of each pit was augered to ensure a tight fit at the bottom of the pit. Representative soil samples were taken during well installation for chemical and physical analyses. As the pit was filled back in, care was taken to ensure that the well was straight and the matching soil material was maintained at the correct depths. Water depths were measured weekly at each of the 60 wells (Fig. 2) using a water level meter (Little Dipper, Heron Instruments, Burlington, Ont.). Discussion of results is limited to the determination of differences between only 30 wells in the six main experimental blocks (20A, 20, 30A, 30, 28A, and 28).

4.2.4 Determination of groundwater chemical characteristics

Field sampling methods

Sampling of the wells were performed on a weekly basis for the month of May in order to capture the potential spring flush of snow melt into the ecosystem (Knight et al. 1991). After that, sampling was performed every other week for June, and every third week for July-September. This gave a total of five sampling sessions in 2002 and eight sampling sessions for 2003. In 2002, the sampling was delayed because of a late snow melt and

concurrent well installation. In 2003, sampling started in the second week of May because of the snow pack and ended early due to a fire hazard in the area. Each sampling session was performed over a period of 2 days. On the first day, water levels were measured, and the wells were pumped free of water. On the second day, the water levels, temperature, pH and conductivity were measured in the well. Water (up to 500 mL) was pumped from the well into pre-rinsed, acid-washed bottles. The samples were kept in coolers for transport from the field to the laboratory where they were refrigerated (4°C) until they were filtered for analysis (within 24 hr after sampling).

Chemical analyses

In the lab, a water subsample (150 mL) was first reserved for TN and TP analysis, leaving no air space and stored at 4°C in the dark until analysis. The rest of the water sample was then filtered and analyzed for DOC, TDP, TDN, NO_3^-, NO_2^-, NH_4^+, and PO_4^{3-} as described in sections 3.2.4 and 4.2.2. All of the filtrate was immediately stored in the dark at -20°C until the analysis of nutrients. Filtered and unfiltered blanks of ultrapure water were also prepared and analyzed for quality control.

4.2.5 Statistical analyses

Data analysis was performed only on wells containing water. Statistics and data analyses performed on data from this section are described in section 2.3.

4.3 Results

4.3.1 Determination of temporal and spatial variability snow pack physical and chemical characteristics

Statistical analyses of the variables measured on snow collected in 2003 and 2004 are summarized in Table 4, 5 and B2. The snow densities (0.45 $g \cdot cm^{-3}$) and snow water equivalents (33.3 cm water) were consistent across the entire site with little variation (CV

of 13.7% and 22.8%, respectively) within each block (Fig. 12). Snow was generally slightly acidic (pH 5.0 – 6.8) with very little variation between the blocks (Fig. 13). The conductivity of melted snow was consistent across all blocks and results varied from 3.3 to 22.2 μS (Fig. 13).

Snow DOC (0.94 – 28.0 mg · L^{-1}) (Fig. 14) and TOC (1.30 – 51.8 mg · L^{-1}) were quite similar showing that the bulk of the organic carbon was dissolved and there was very little particulate matter in the snow samples. Slightly elevated levels of organic carbon in blocks 30A and 28 were observed, but were not significant. The NO_2^- levels were quite low (0.22 – 7.00 μg · L^{-1}) relative to their contribution to total inorganic nitrogen (TIN) and were generally slightly above the detection levels in blocks 20A, 20, and 30A (Fig. 15). Nitrite showed a great deal of variation from block to block and location to location (CV: 105.4%). A range of 0.45 to 118 μg NO_3^- · L^{-1} was measured in the snow and it made up the largest part of the TIN (Fig. 15) unlike that found in the soil (see Chapter 3). Ammonium levels (6.8 – 98.4 μg · L^{-1}) were consistent across all the blocks (except for an elevated amount in block 20 in 2004) and were the second largest contributor to TIN (Fig. 15). Snow TDN (23.0 – 912 μg · L^{-1}) was about 35-65% of the snow TN (103 – 3030 μg · L^{-1}) (Fig. 16). Phosphate ranged between 0.9 and 385 μg · L^{-1}. TDP was about 58-100% of the TP and ranged between 3.8 and 462 μg · L^{-1}. TP ranged between 3.98 and 545 μg · L^{-1} (Fig. 16).

The snow pack study showed very few significant differences between blocks for the physical and chemical variables measured. No difference between the two sampling years (2003 and 2004) was significant except for NO_2^- and TDN. In 2003, pH in the snow of block 20A was significantly higher than the pH in snow in other blocks (Fig. 13).

The 2003 NO_2^- results from blocks 20A, 20, and 30A were significantly higher than NO_2^- in snow in blocks 30, 28A and 28 (Fig. 15). The 2003 NO_3^- in block 20A was significantly higher than NO_3^- in block 30A and 30 (Fig. 15). For TDN in 2003, blocks 20A, 20, and 30A were significantly lower than TDN in block 28A and 28.

Correlations between the variables measured on snow at the study site are reported in Table 6. The non-parametric Spearman correlation coefficients were similar to the Pearson correlation coefficients. Spearman coefficients are only mentioned here if it is different from the Pearson correlation coefficient. Snow water equivalent was moderately negatively correlated to conductivity ($r = -0.41$, $rs = -0.47$) DOC ($r = -0.53$) and TP ($r = -0.39$). The pH was positively correlated to NO_2^- ($r = 0.45$), NO_3^- ($r = 0.54$, $rs = 0.49$) but interestingly, was negatively correlated to TDN ($r = -0.46$). Conductivity was strongly positively correlated to DOC ($r = 0.69$, $rs = 0.82$). DOC was positively correlated to TOC ($r = 0.77$ – not shown) and NO_2^- ($r = 0.34$). There were strong positive correlations of conductivity and DOC to PO_4^{3-} ($r = 0.57$ and $r = 0.59$, respectively), TDP, ($r = 0.63$ and $r = 0.74$), and TP ($r = 0.48$ and $r = 0.72$). Phosphate, TDP, and TP were also strongly positively correlated to TDN, TN, and each other (Table 6). Nitrate was positively strongly correlated with TIN ($r = 0.92$ – not shown) however NH_4^+ only had a moderate correlation ($r = 0.39$) and NO_2^- had no correlation with TIN. Nitrate was also found to be slightly negatively correlated to DOC ($rs = -0.42$). Snow density did not have any significant correlations except for a moderate one to snow water equivalent ($rs = 0.46$).

Table 4. Basic physical and chemical characteristics of snow collected from the blocks at Bootleg Mountain.

Year		Snow Density ($g \cdot cm^{-3}$)	SWE * (cm water)	pH	Cond. * (µS)	DOC * ($mg \cdot L^{-1}$)	TOC * ($mg \cdot L^{-1}$)	PO_4^{3-} ($\mu g \cdot L^{-1}$)	TDP * ($\mu g \cdot L^{-1}$)	TP * ($\mu g \cdot L^{-1}$)
2003	**mean**	0.45	33.3	5.57	8.20	7.67	10.6	49.5	113.4	115.6
	CV (%) †	13.7	22.8	n/a*	51.3	87.9	117.1	105.6	73.5	84.4
	min	0.33	19.6	4.99	3.30	0.94	1.30	0.90L*	3.77	3.98
	max	0.52	47.1	6.84	22.2	28.0	51.8	180.8	320.4	375.06
2004	**mean**	0.45	38.3	5.36	8.8	6.00	9.91	64.1	144.2	129.9
	CV (%) †	22.8	16.7	n/a*	38.4	68.4	84.6	131.5	69.4	103.0
	min	0.10	30.7	4.99	3.80	0.52	22.61	0.90L	30.3	9.75
	max	0.56	51.3	5.97	14.9	15.6	32.3	385.1	462.3	545.4

*** SWE – Snow water equivalent; Cond. – Conductivity; DOC – Dissolved organic carbon; TOC – Total organic carbon; TDP – Total dissolved phosphorus; TP – Total phosphorus; L – below detection limit; n/a – not applicable**
† CV (%) – coefficient of variation

Table 5. Basic N characteristics for snow collected from the blocks at Bootleg Mountain.

Year		NO_2^- ($\mu g \cdot L^{-1}$)	NO_3^- ($\mu g \cdot L^{-1}$)	NH_4^+ ($\mu g \cdot L^{-1}$)	TIN * ($\mu g \cdot L^{-1}$)	TDN * ($\mu g \cdot L^{-1}$)	TN * ($\mu g \cdot L^{-1}$)
2003	**mean**	2.33	33.4	10.8	47.1	280.2	529.48
	CV (%) †	105.4	93.9	46.6	68.6	96.4	77.6
	min	0.22	.45	6.81	13.6	23.0	120.6
	max	7.00	117.8	22.8	136.2	912.3	1938.9
2004	**mean**	0.30 L*	39.4	18.4	56.4	484.2	784.4
	CV (%) †	0.0	82.4	107.1	71.4	43.2	102.5
	min	0.30L *	0.45	6.81	7.56	52.4	102.6
	max	0.30L *	109.8	98.4	157.0	883.8	3027.9

*** TIN – Total inorganic nitrogen; TDN – total dissolved nitrogen; TN – Total nitrogen; L – below detection limit**
† CV (%) – coefficient of variation

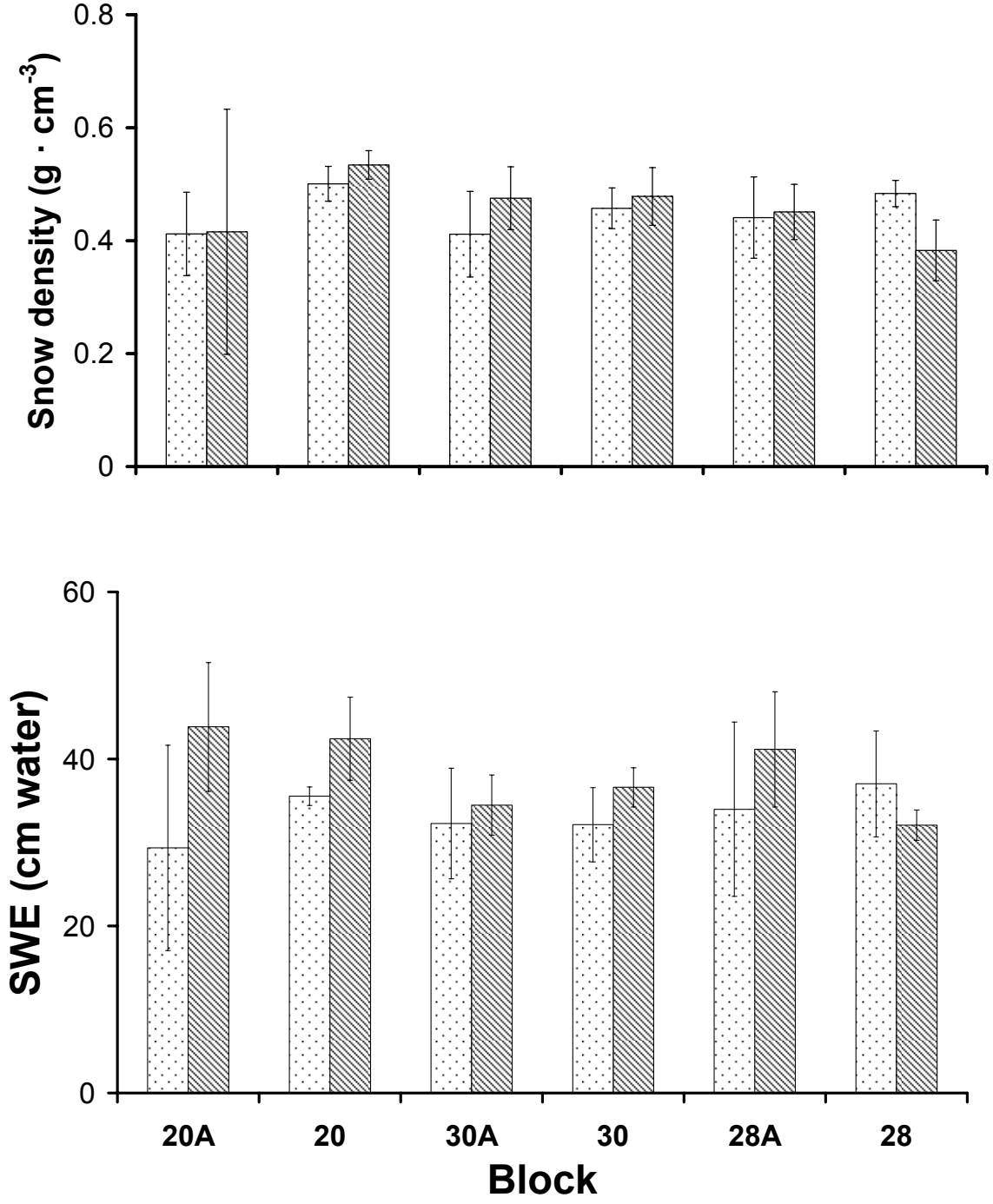

Figure 12. Snow density and snow water equivalent (SWE) in ⬚ 2003 and ▨ 2004. Blocks are not significantly different **(**$p < 0.05$**).** There is no significant difference between years **(**$p < 0.05$**).** Bars show the average (n=4) and the error bars represent ± 1 SD.

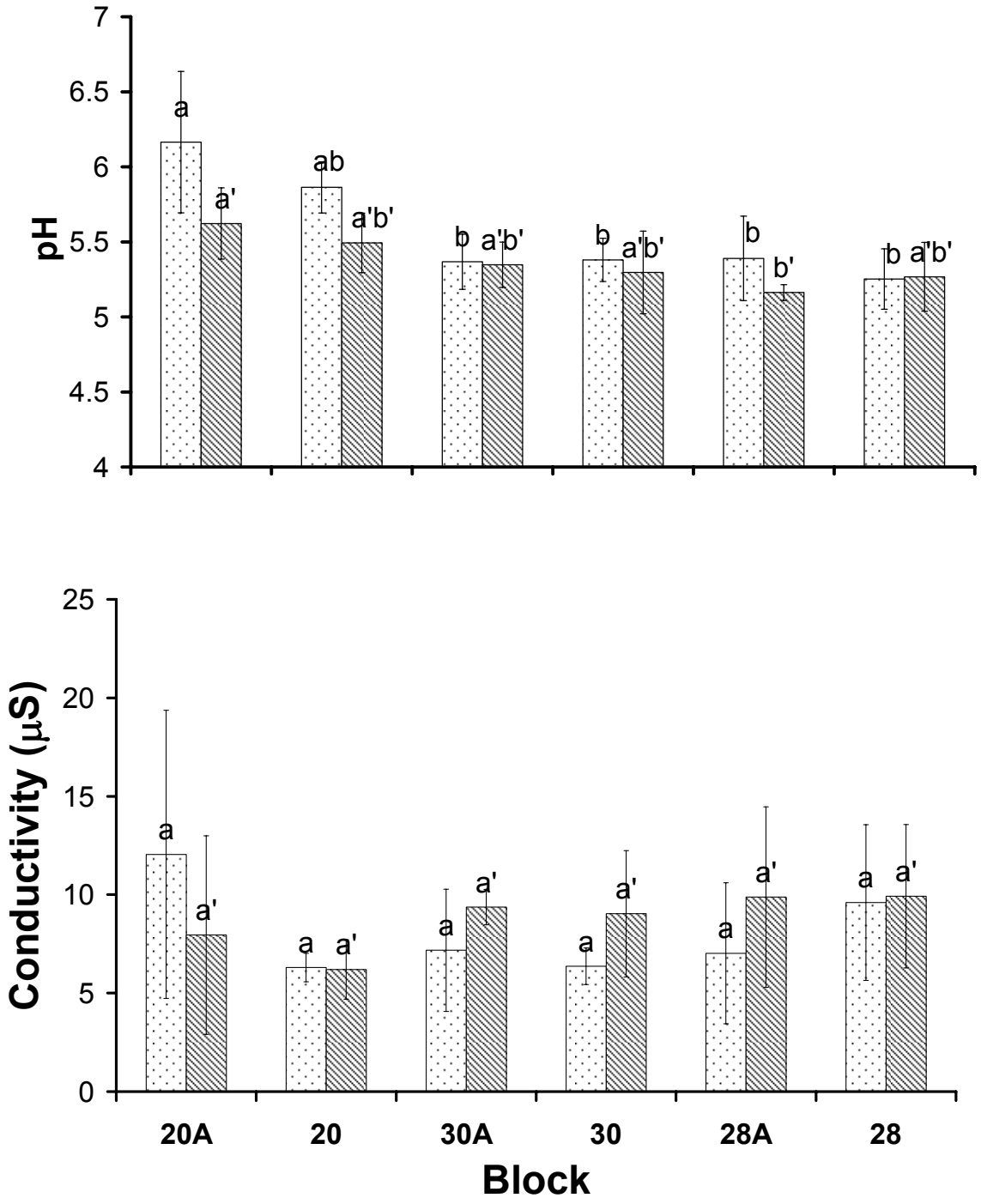

Figure 13. pH and conductivity of snow sampled in ⬚ 2003 and ▨ 2004. Blocks from the same year with different letters are significantly different ($p < 0.05$). There is no significant difference between years ($p < 0.05$). Bars show the average (n=4) and the error bars represent ± 1 SD.

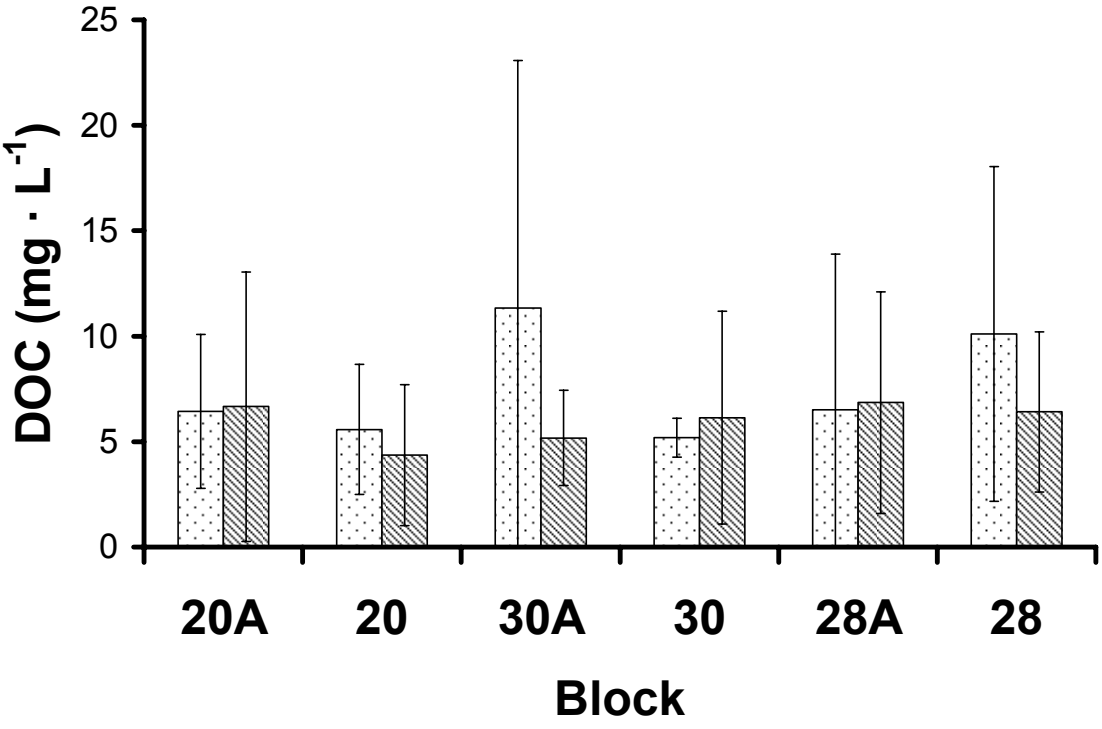

Figure 14. Dissolved organic carbon (DOC) in snow in ⬚ 2003 and ▨ 2004. Blocks are not significantly different ($p < 0.05$). There is no significant difference between years ($p < 0.05$). Bars show the average (n=4) and the error bars represent ± 1 SD.

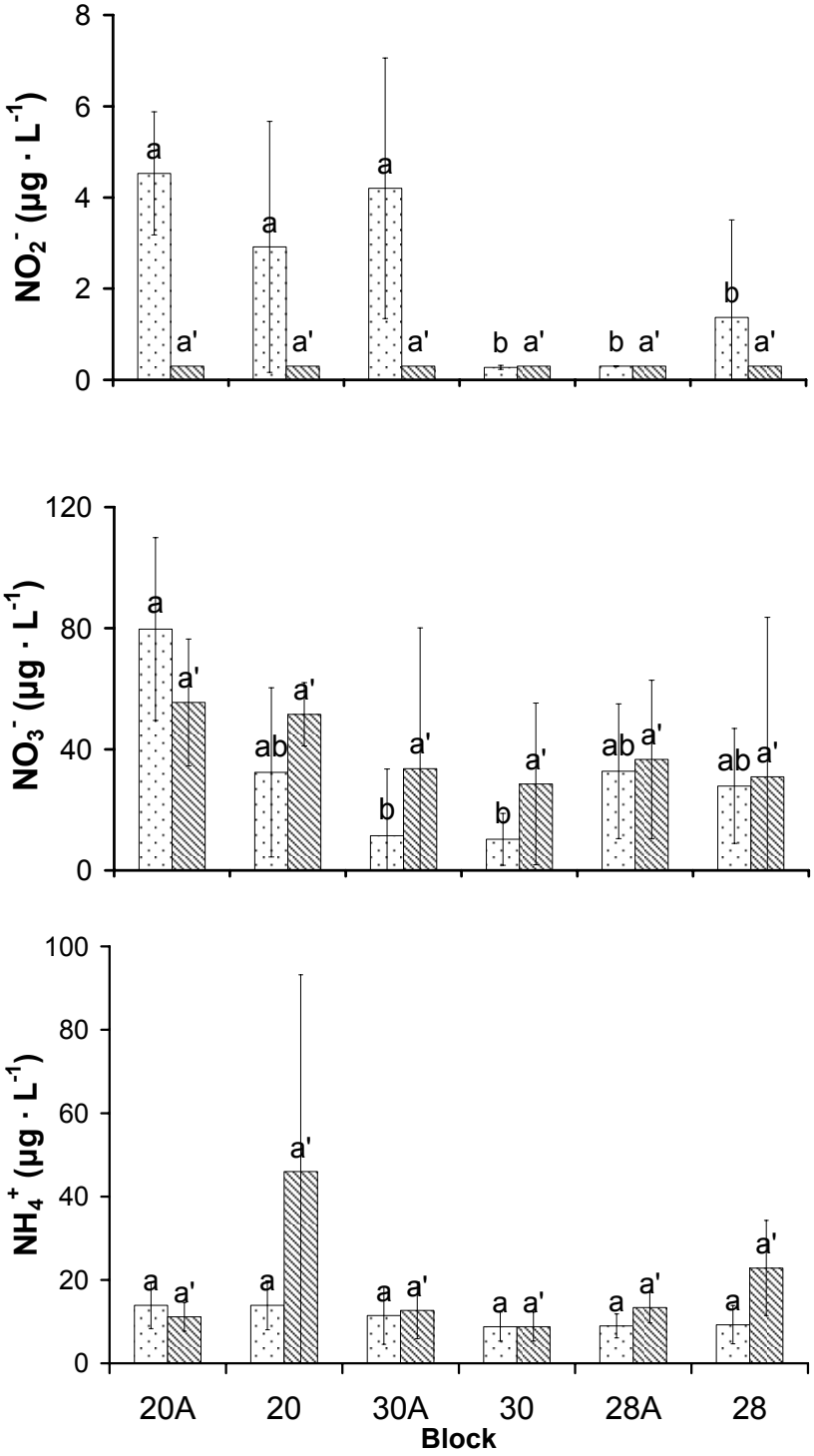

Figure 15. NO_2^-, NO_3^-, and NH_4^+ in snow in ⬚ 2003 and ▨ 2004. Blocks from the same year with different letters are significantly different ($p < 0.05$). There is no significant difference between years except for NO_2^- ($p < 0.05$). Bars show the average ($n = 4$) and the error bars represent ± 1 SD.

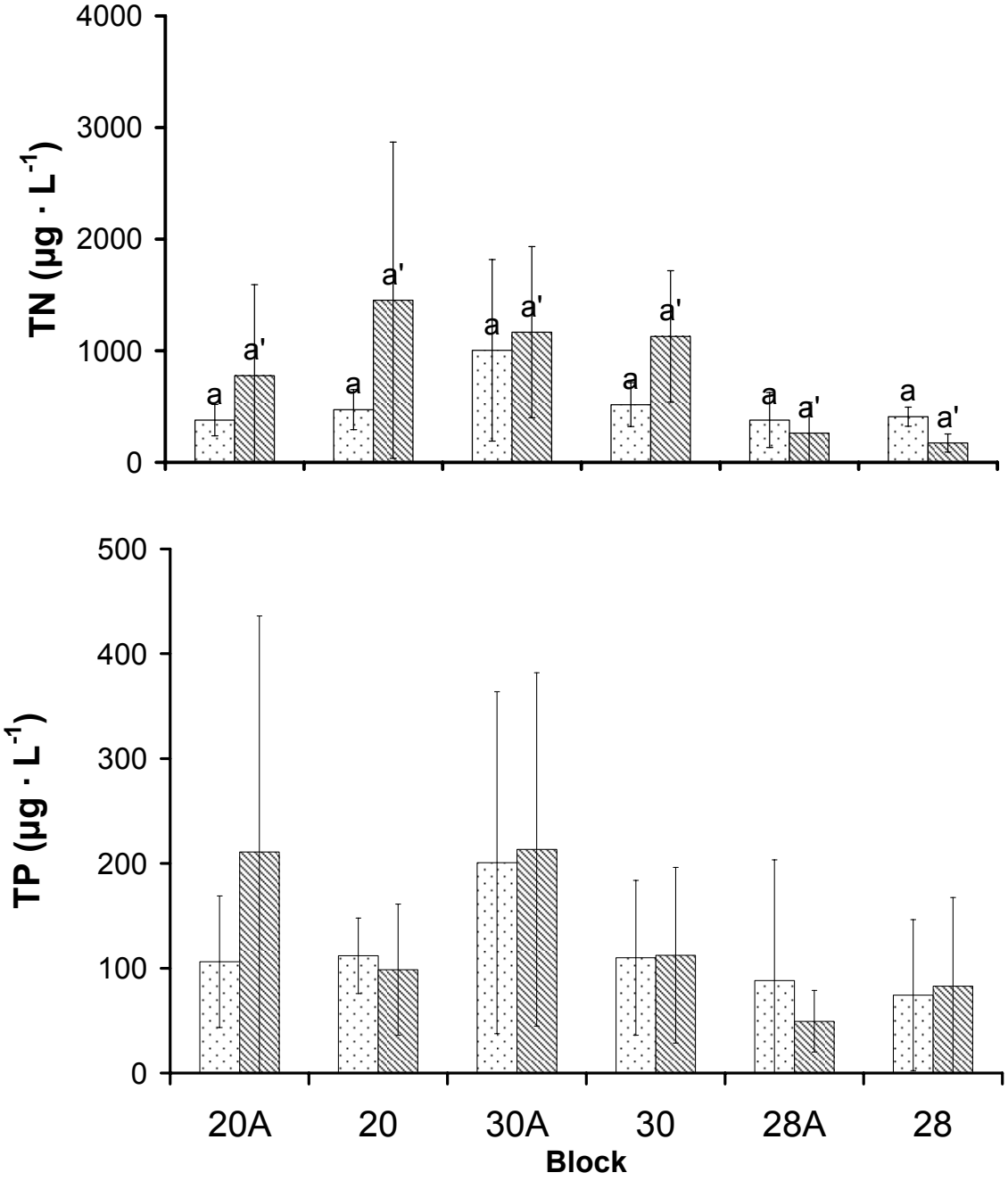

Figure 16. Total nitrogen (TN), and total phosphorus (TP) in snow in ⬚ 2003 and ▨ 2004. For TN, blocks from the same year with different letters are significantly different ($p < 0.05$). For TP, blocks are not significantly different ($p < 0.05$). There is no significant difference between years ($p < 0.05$). Bars show the average (n=4) and the error bars represent ± 1 SD.

Table 6. Correlation coefficients among variables from the snow sampling sessions from 2003 and 2004.

	SD	SWE	pH	Cond	DOC †	NO_2^-	NO_3^-	NH_4^+ †	TDN	TN	PO_4^{3-}	TDP	TP †
SD	—	**.46****	**.17**	**-.17**	**-.09**	**-.02**	**.07**	**.03**	**.11**	**.17**	**.23**	**.05**	**.08**
SWE	.29	—	**.21**	**-.47****	**-.50****	**-.16**	**.35***	**-.06**	**-.17**	**-.28**	**-.27**	**-.39***	**-.40****
pH	.05	.03	—	**-.32***	**-.39***	**.38***	**.49****	**-.03**	**-.43****	**-.04**	**-.11**	**-.28**	**-.04**
Cond.	-.07	-.41**	.08	—	**.82****	**.18**	**-.23**	**.15**	**.48****	**.26**	**.66****	**.73****	**.54****
DOC †	-.03	-.53**	-.21	.69**	—	**.29**	**-.42****	**.24**	**.45****	**.38***	**.75****	**.89****	**.72****
NO_2^-	-.02	-.25	.45**	.21	.34**	—	**.05**	**.22**	**-.42****	**.09**	**.11**	**.11**	**.30**
NO_3^-	.03	.23	.54**	.03	-.39*	.07	—	**-.08**	**-.13**	**-.39****	**-.17**	**-.38***	**-.38***
NH_4^+ †	.07	.00	-.03	.02	-.18	.07	.04	—	**.18**	**.10**	**.23**	**.32**	**.28**
TDN	.07	-.13	-.46**	.39*	.40**	-.47**	-.12	.20	—	**.14**	**.57****	**.57****	**.34***
TN	.21	-.10	-.08	.13	.35*	.01	-.19	.21	.23	—	**.49****	**.53****	**.69****
PO_4^{3-}	.08	-.19	.02	.57**	.58**	.06	.04	.07	.47**	.55**	—	**.87****	**.75****
TDP	.03	-.35*	-.18	.63**	.78**	.07	-.21	.10	.59**	.55**	.88**	—	**.87****
TP †	.11	-.39**	.00	.48**	.78**	.27	-.32*	.23	.37*	.58**	.63**	.81**	—.

*** Correlation is significant at the 0.05 level (two-tailed); ** Correlation is significant at the 0.01 level (two-tailed).**
† data log-transformed for normality for Pearson correlation coefficient determination.
Pearson correlation coefficients calculated on the transformed data are shown in normal font in the bottom part of the table. Spearman non-parametric correlation coefficients calculated on raw data are shown in bold in the top half of the table. SD – Snow Density, SWE – Snow Water Equivalent, Cond. – Conductivity.

4.3.2 Determination of temporal and spatial variability for groundwater table depths and nutrient chemistry

General water sampling results

Water table levels varied within the blocks, between the blocks, and between sampling dates. Initially, changes of groundwater levels over time were analyzed and then were related to groundwater chemistry results. As expected, after the snowmelt, there was a general flush of water and nutrients in the spring followed by a decrease of the water tables, going from 45.3 cm below the surface in June of 2002 to 116.3 cm in July 2002 (Fig. 22). This reduction in the amount of water likely resulted in there being very little amounts of nutrients in the wells. Block 20A by well is a good example of the trend. At well 20A-3 the presence of a stream was noted that greatly contributed to the variability of the water table in that block (Fig. 17). The water table at Block 20, block 30A and block 28 varied little within the block (Fig. 18). There tended to be more variability in the spring (CV: 89.3% in June 2002) than later on in the summer (CV: 34.7% in July 2002) (Fig. 18).

In 2002, water was sampled in the 30 wells on five separate days. During those 5 days, there was a maximum of 150 possible samples. Water depth measurements were made 117 times and water samples were obtained only 48 out of the 150 attempts at sampling the wells because there was not enough water in the wells for sampling or the wells had not yet been installed. In 2003, there were eight separate sampling dates, and water table depth measurements were obtained 238 times out of the possible 240 sampling times. For the entire 2003 season, a total of 150 water samples were obtained from the wells.

Groundwater spatial heterogeneity within research blocks

A component of this study was to evaluate the spatial heterogeneity of the site (Table B4). Some trends were noted when the block to block and well to well variation were compared. Overall averages of all the data from the 13 sampling dates showed that the water table was significantly higher in block 30A (74.6 ± 45.6 cm to the groundwater), than in blocks 20A (99.4 ± 45.6 cm to the groundwater), 28A (109.0 ± 53.7 cm to the groundwater) and 28 (132.5 ± 29.0 cm to the groundwater). Blocks 20 (77.1 ± 40.2 cm to the groundwater) and 30 (88.3 ± 36.1 cm to the groundwater) were also significantly higher than block 28, but were not different from block 30A and 28A. There were no significant differences in the water temperatures between the blocks with an overall average of 16.6 ± 2.1 °C. Block 20A (58.7 ± 70.7 µS) had a significantly higher conductivity than the other blocks whose average conductivities ranged from 24.2 to 30.3 µS. The acidity of the water was consistent across all the blocks (pH 6.2 ± 0.6) with block 28 being just slightly (but not significantly) lower at pH 5.9 ± 0.7. DOC was significantly higher in block 30A (16.6 ± 8.72 mg · L^{-1}) than in block 28A (7.00 ± 11.1 mg · L^{-1}) and 28 (8.04 ± 4.41 mg · L^{-1}). Block 20 (16.2 ± 10.1 mg · L^{-1}) was also significantly higher than 28A but was not different than blocks 20A (9.03 ± 9.24 mg · L^{-1}), 30A (16.6 ± 8.72 mg · L^{-1}), and 30 (13.7 ± 12.2 mg · L^{-1}).

Overall, NO_2^- in groundwater was not significantly different between the blocks, but in 2002, block 28A was significantly higher than in all the other blocks (26.2 ± 31.6 µg · L^{-1}) (Fig. 20). Nitrate in block 28A (260 ± 440 µg · L^{-1}) was significantly higher than in the other blocks, which had an overall average of 72.2 ± 189 µg · L^{-1} for all the blocks. This higher value is attributed mostly to the higher NO_3^- in block 28A in 2003 (299 ± 463 µg · L^{-1}) (Fig. 20). In general (data of 2002 and 2003), NH_4^+ concentration in groundwater

was not significantly different across all blocks, but in 2003, NH_4^+ (8.65 ± 5.27 μg · L^{-1}) was significantly lower in block 28A than the other blocks (Fig. 20). TIN had the same trend as NO_3^-, TDN showed no significant differences, and TN was significantly higher in block 20A (1540 ± 2960 μg · L^{-1}) than block 28A (368 ± 407 μg · L^{-1}) (Fig. 21). The rest of the TN values ranged from 451 to 1350 μg · L^{-1}.

Phosphate showed no significant differences between blocks, but TDP in the up-slope blocks (20A, 30A, 28A, and 20) was significantly lower than TDP in the down-slope blocks (30 and 28). The averages ranged from a low of 12.3 ± 6.21 μg · L^{-1} in block 20A to a maximum of 51.9 ± 16.1 μg · L^{-1} in block 28. Though not significant, TP showed the same general result of lower TP values in up-slope versus down-slope blocks.

Inter-annual variations in groundwater depths and chemistry

There was much variation from date to date, well to well, and block to block when the yearly averages for the water data were analyzed (Table 7 and 8). The water table remained significantly higher in 2003 (90.9 ± 45.1 cm to the subsurface water) than in 2002 (106.4 ± 47.8 cm to water) (Fig. 19). Temperature did not significantly vary from block to block and year to year and the averages were 16.0 ± 2.1°C and 16.8 ± 2.1°C for 2002 and 2003, respectively. The water in the wells was slightly acidic and ranged from pH 5.7 to 7.2 in 2002 and 4.9 to 7.8 in 2003. Although pH was significantly more neutral in 2002 (pH 6.4 ± 0.4) than in 2003 (pH 6.1 ± 0.6) ($p < 0.05$), the small difference is not likely to be important. The conductivity varied greatly within the blocks but there was no significant difference between 2002 (30.3 ± 53.6 μS) and 2003 (31.9 ± 25.4 μS). Dissolved organic C was significantly higher in 2002 with a average of 21.9 ± 14.9 mg · L^{-1} compared to the average of 10.2 ± 6.89 mg · L^{-1} in 2003 (Fig. 21).

Nitrite levels were generally quite low, ranging between 0.001 (below detection limit - BDL) and 64.7 μg · L^{-1} in 2002 and 0.001 (BDL) and 25.9 μg · L^{-1} in 2003 (Fig. 20). There was no significant difference in the NO_2^- between 2002 (5.41 ± 14.2 μg · L^{-1}) and 2003 (4.77 ± 4.64 μg · L^{-1}). Nitrite made up the smallest portion of TIN. Nitrate also had a lot of variation, but was not significantly different between years, with a average of 16.6 ± 14.3 μg · L^{-1} in 2002 compared to 89.7 ± 213 μg · L^{-1} in 2003. Nitrate (Fig. 20) represented the largest portion of TIN in the groundwater, unlike that of the soils (see Chapter 3). The averages of NH_4^+ were 13.9 ± 8.9 and 30.7 ± 84.5 μg · L^{-1} in 2002 and 2003 and were not significantly different between years (Fig. 20). Although the average of TDN (532 ± 340 μg · L^{-1}) was higher than the average of TN (380 ± 495 μg · L^{-1}) in 2003 (Fig. 21), in general TDN represented 62 – 99% of the TN, when comparing the averages of TDN (1680 ± 1720 μg · L^{-1}) and TN (2210 ± 2400 μg · L^{-1}) for 2002. For both TDN and TN, the averages for 2002 were significantly higher than 2003. Phosphate ranged between 0.90 (BDL) and 16.3 μg · L^{-1} in 2002 and between 0.90 (BDL) and 175 μg · L^{-1} in 2003. There was no significant difference between PO_4^{3-} in 2002 (2.51 ± 3.20 μg · L^{-1}) and 2003 (3.58 ± 16.5 μg · L^{-1}). TDP was about 0.1 – 42% of the TP. TDP in 2002 was found to be marginally significantly higher in 2002 (30.0 ± 25.5 μg · L^{-1}) than in 2003 (28.1 ± 27.9 μg · L^{-1}). TP was significantly higher in 2002 (660 ± 109 μg · L^{-1}) than in 2003 (170 ± 363 μg · L^{-1}) (Fig. 21).

Seasonal variation of groundwater depths and chemistry

An analysis of the results by sampling date (Table B3), indicate significantly less water in the wells in late July, August and September than in May, June, and early July (Fig. 22). Water temperature varied between 13 and 19°C in 2002/2003 (Fig. 23). The water

was slightly more acidic in the spring than it was in late summer with the lowest pH values generally occurring after the spring snow melt was complete (Fig. 23). Nitrite increased significantly in August and September of 2002, but stayed fairly consistent in 2003, with a slight increase in August (Fig. 24). Nitrate showed no significant trends due to the large variation in the data set, but a general decrease over the summer season was observed (Fig. 24). Ammonium also showed no significant trends but did decrease over the summer (Fig. 24). Dissolved organic C was significantly higher in June of 2002 than in August of 2002, and showed a slight decrease (not significant) in levels over the summer of 2003 (Fig. 25). Total organic C (9.8 ± 93.0 mg $\cdot L^{-1}$, data not shown) was fairly close in value to DOC (10.2 ± 67.6 mg $\cdot L^{-1}$), so it is assumed that the bulk of organic carbon in the water is dissolved and TOC results will therefore not be discussed any further. Total dissolved N and TN levels decreased significantly from June to September 2002 but remained fairly consistent in 2003 (Fig. 25). Total P showed the same trend (Fig. 25). The ratios of TDN/TN and TDP/TP were also fairly consistent over the season with TDN/TN being slightly higher in June 2003 (larger inorganic N portion) than any other date. Total dissolved N was $53 \pm 34\%$ of the TN and TDP was $42 \pm 63\%$ of the TP (data not shown). This is a large amount of variation and may be related to the spatial and temporal heterogeneity observed at the site.

Determination of correlations between water quality variables

From the correlation matrices for all the data from both sampling years, variables were poorly correlated and tended to be weak in most cases (Table 9). The Pearson and Spearman correlation coefficients were similar in most cases, thus the Spearman

coefficient will only be mentioned here if it is different from the Pearson correlation coefficient.

Some strong correlations were observed between the variables measured in this study. As expected, DOC was strongly positively correlated to TOC for both the Pearson (r = 0.69) and Spearman (rs = 0.87) tests (data not shown). Dissolved organic C was also correlated to TDN (r = 0.31, rs = 0.42) and TN (rs = 0.42).

Nitrate and TIN were strongly positively correlated (r = 0.86 – not shown). Nitrate was also correlated to TDP (rs = 0.36). Ammonium was only correlated to TIN (r = 0.43 – not shown), according to the Pearson correlation coefficient. However, NH_4^+ was positively correlated to TIN (rs = 0.54 – not shown), TDP (rs = 0.40), and TP (rs = 0.35) based on Spearman coefficients. Nitrite was found to be negatively correlated to TN (r = -0.40). In addition to the correlations mentioned already, TIN was also found to be positively correlated to TDP (rs = 0.30 – not shown).

Total dissolved nitrogen (TDN) was also positively correlated to TN (r = 0.47) and TP (r = 0.52). The Spearman correlation coefficient was positive between TDN and TN (rs = 0.46), PO_4^{3-} (rs = 0.31), TDP (rs = 0.41) and TP (rs = 0.42). Total N was also positively related to TP (r = 0.58, rs = 0.48) in addition to the previously mentioned relationships.

Phosphate was strongly positively correlated to TDP (r = 0.36, rs = 0.47) and TDN (Spearman – listed above). As expected, TDP and TP were correlated (r = 0.40).

An unexpected result was that depths to the groundwater were slightly negatively correlated with NO_3^- (r = -0.26), TDN (r = -0.19), TDP (r = -0.28), and TP (r = -0.18). The same connections were exhibited when the 2002 and 2003 data was considered separately (data not shown). The Spearman correlation coefficient was similar but had an

Table 7. Basic subsurface water sample characteristics for the variables under study at Bootleg Mountain (30 wells) in 2002 (n=5) and 2003 (n = 8).

Year		Depth to Water (cm)	Temp * (°C)	Cond. * (µS)	pH	DOC * (mg · L^{-1})	PO_4^{3-} (µg · L^{-1})	TDP * (µg · L^{-1})	TP * (µg · L^{-1})
2003	**mean**	106.4	16.0	30.3	6.41	21.9	2.51	30.0	660.1
	CV (%) †	44.9	13.1	176.8	n/a*	68.3	127.12	78.4	165.4
	min	165.0	12.0	0.30	5.67	0.01 L *	0.90 L *	2.57 L *	7.60
	max	1.8	20.7	287.4	7.20	64.0	16.3	121.7	5549.6
2004	**mean**	90.9	16.8	31.9	6.08	10.2	3.58	28.1	170.2
	CV (%) †	49.6	12.3	79.6	n/a*	67.6	459.4	99.1	213.0
	min	165.0	11.7	13.3	4.92	0.01 L *	0.90 L *	2.57 L *	3.33
	max	0.5	22.0	189.7	7.76	40.7	174.7	193.3	3698.5

*** Temp. - Temperature; Cond. – Conductivity; DOC – Dissolved organic carbon; TDP – Total dissolved phosphorus; TP – Total phosphorus; L – below detection limit; n/a – not applicable**
† CV (%) – coefficient of variation.

Table 8. Basic subsurface water sample characteristics for N at Bootleg Mountain (30 wells) in 2002 (n=5) and 2003 (n = 8).

Year		NO_2^- ($\mu g \cdot L^{-1}$	NO_3^- ($\mu g \cdot L^{-1}$)	NH_4^+ ($\mu g \cdot L^{-1)}$	TIN * ($\mu g \cdot L^{-1}$)	TDN * ($\mu g \cdot L^{-1}$)	TN * ($\mu g \cdot L^{-1}$)
2003	**mean**	5.41	16.6	13.9	28.1	1683.7	2208.8
	CV (%) †	262.7	85.6	64.0	67.9	102.1	108.8
	min	0.30 L *	0.45 L *	6.81 L *	6.81 L *	0.45 L *	153.2
	max	64.7	68.2	32.5	78.2	10506.6	12702.6
2004	**mean**	4.77	89.7	30.7	126.9	531.6	380.09
	CV (%) †	97.1	237.7	275.0	176.9	63.9	130.1
	min	0.30 L *	0.45 L *	6.81 L *	6.381 L *	0.45 L *	5.45
	max	25.9	1353.3	800.6	1363.1	1454.7	4329.4

*** TIN – Total inorganic nitrogen; TDN – total dissolved nitrogen; TN – Total nitrogen; L – below detection limit.**
† CV (%) – coefficient of variation.

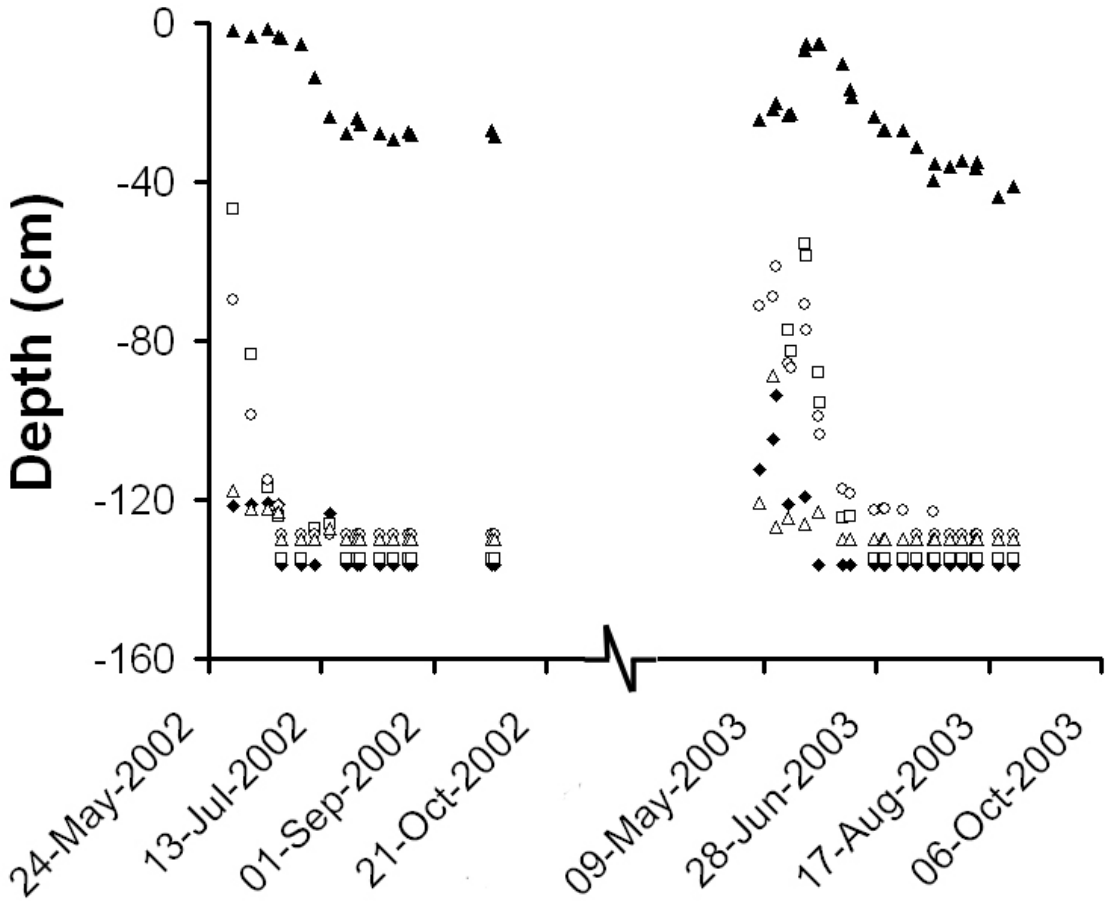

Figure 17. Water tables for block 20A. This graph shows the general water table trends over the two sampling seasons. ♦ is well 20A-1, □ 20A-2, ▲20A-3, ○ 20A-4, and Δ 20A-5.

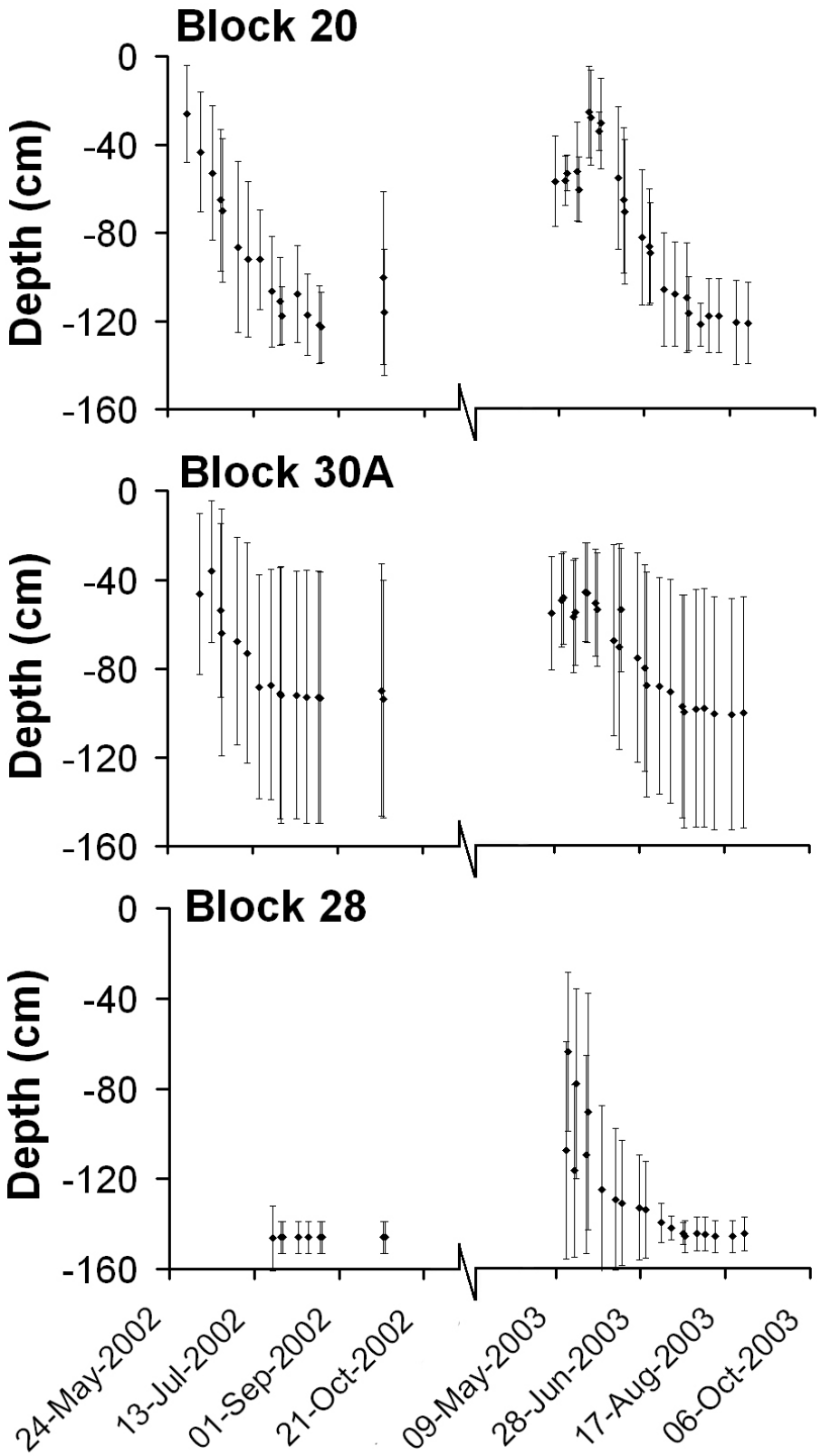

Figure 18. Seasonal water tables for block 20, 30A, and 28. Data shown are average ± 1 SD for five wells at each sampling date.

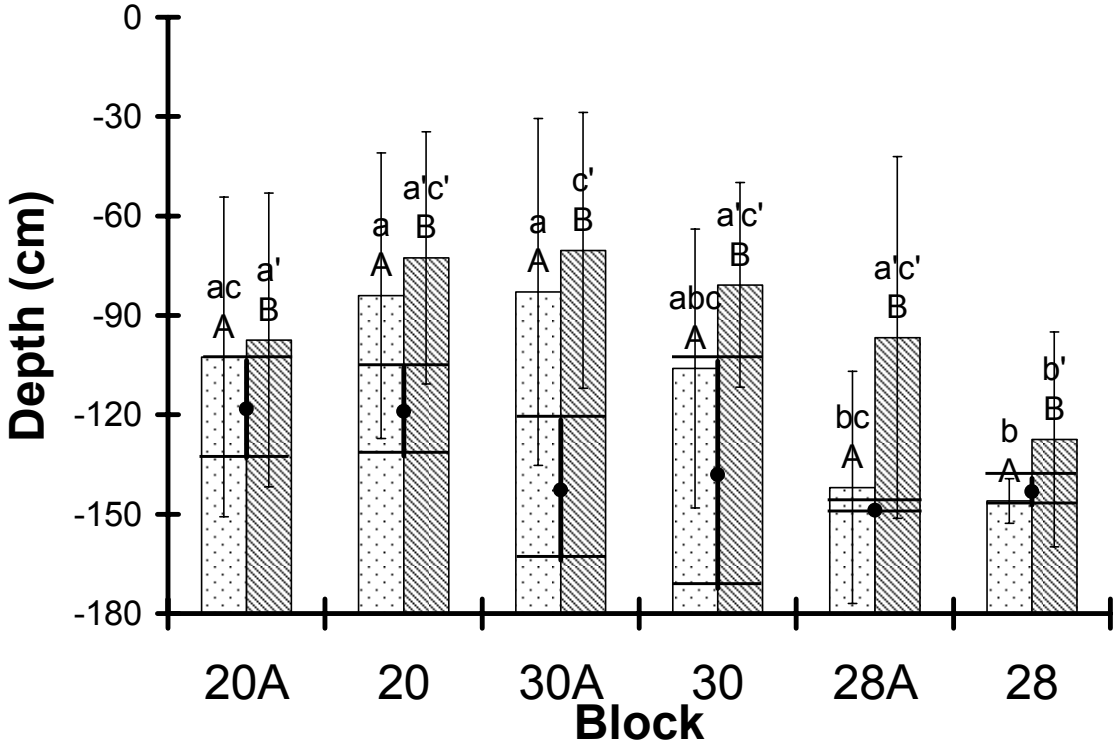

Figure 19. Water tables in blocks in ⬚ 2002 and ▨ 2003. Lower case letters indicate significant differences between blocks within the same year ($p < 0.05$). Upper case letters indicate significant differences between years ($p < 0.05$). ● represents the average ± 1 SD well depth of each block.

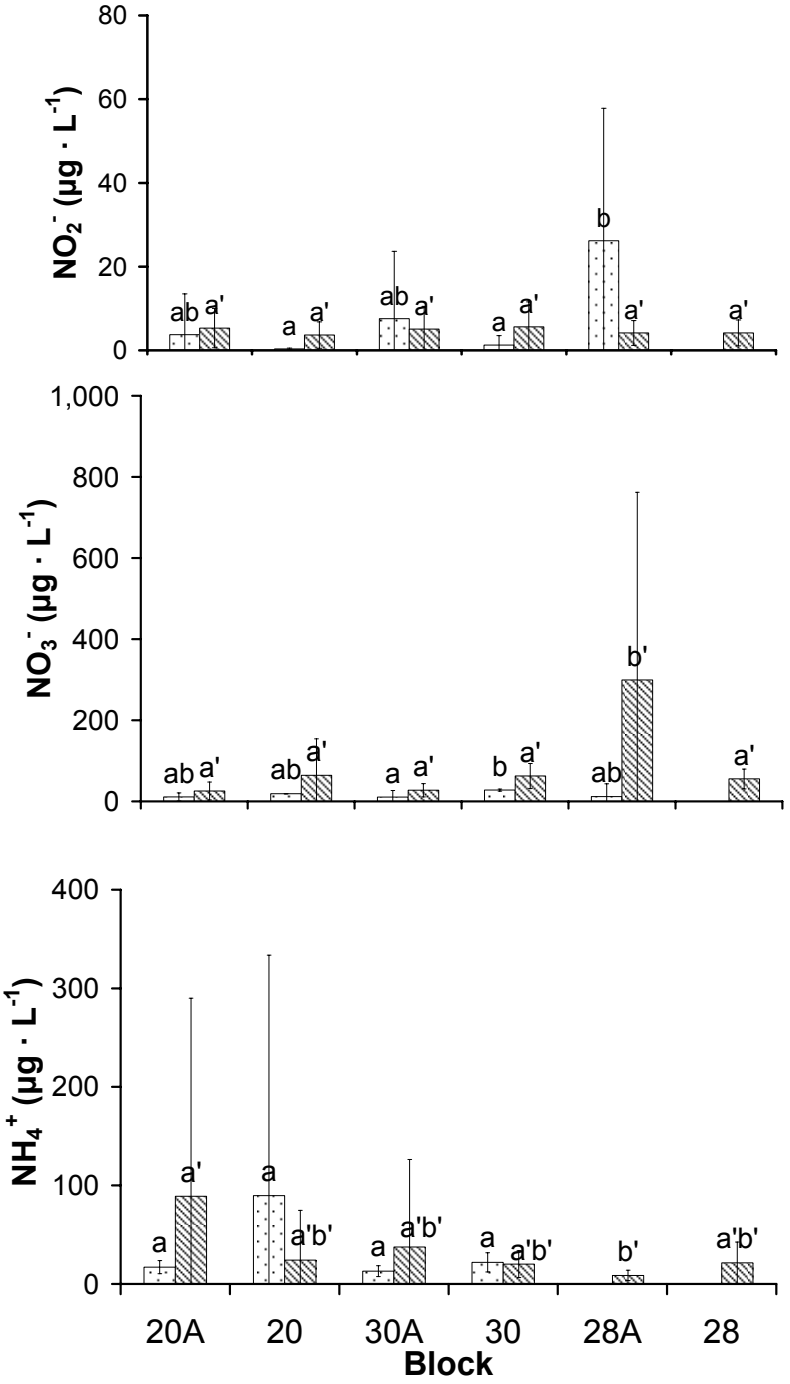

Figure 20. NO_2^-, NO_3^-, and NH_4^+ concentration in groundwater in ⬚ 2002 and ▨ 2003. Lower case letters indicate significant differences between blocks within the same year ($p < 0.05$). Bars show the average and ± 1 SD.

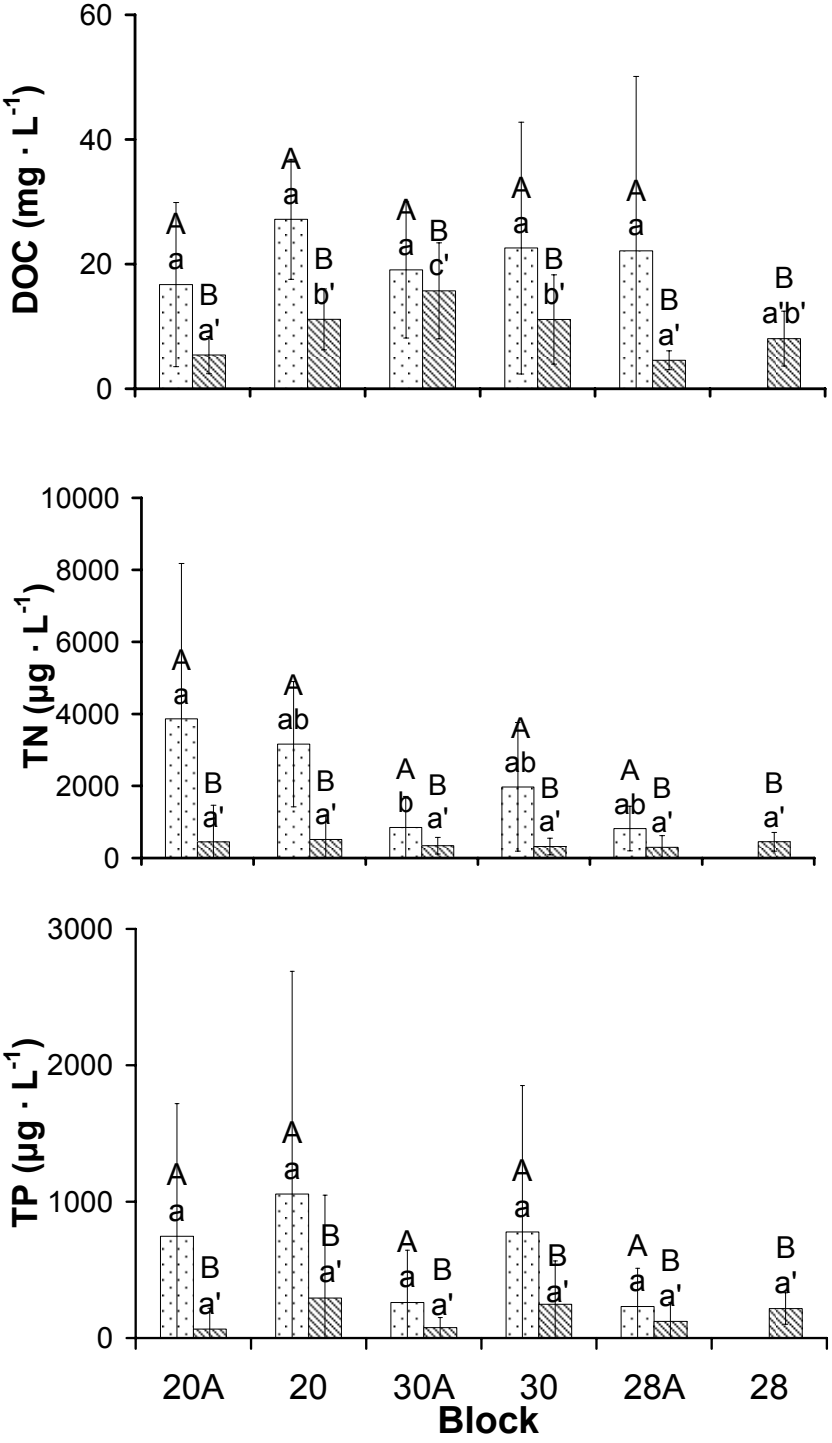

Figure 21. DOC, TN, and TP concentrations in groundwater in ⊡ 2002 and ▨ 2003. Lower case letters indicate significant differences between blocks within the same year ($p < 0.05$). Upper case letters indicate significant differences between years ($p < 0.05$). Bars show the average and ± 1 SD.

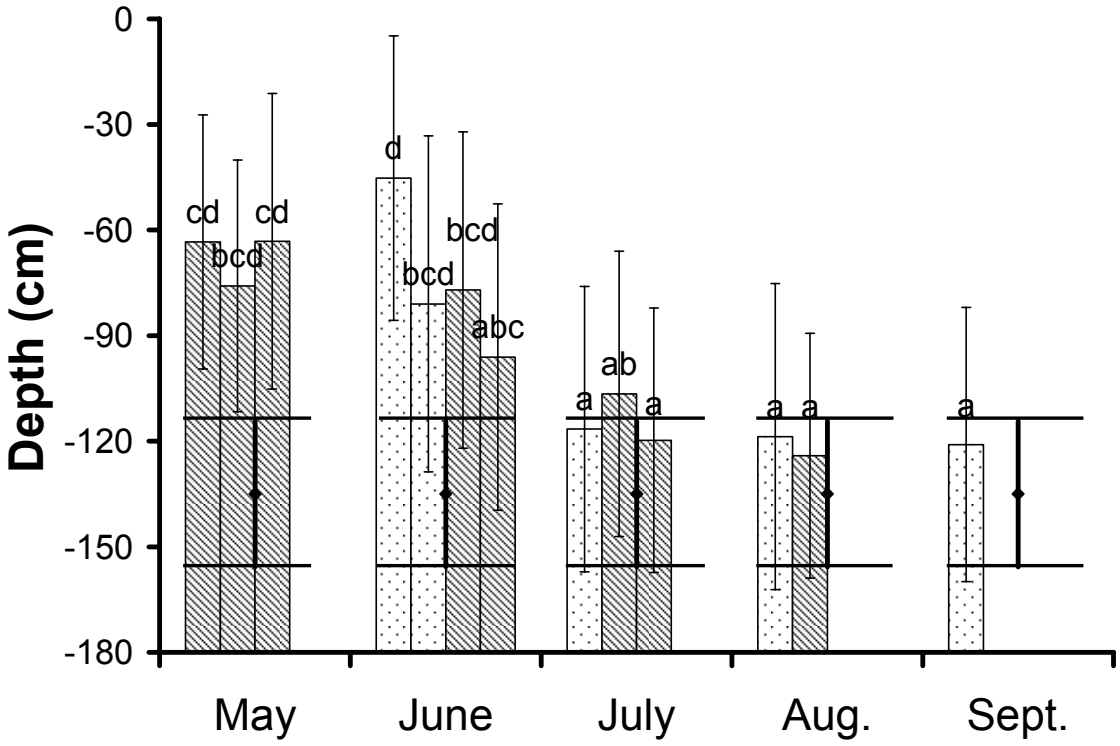

Figure 22. Seasonal variations of water table by sampling date for ⬚ 2002 and ▨ 2003. Lower case letters indicate significant differences between sampling dates ($p < 0.05$). ● represents the average ± SD well depth of all 30 wells. Bars show the average and ± 1 SD.

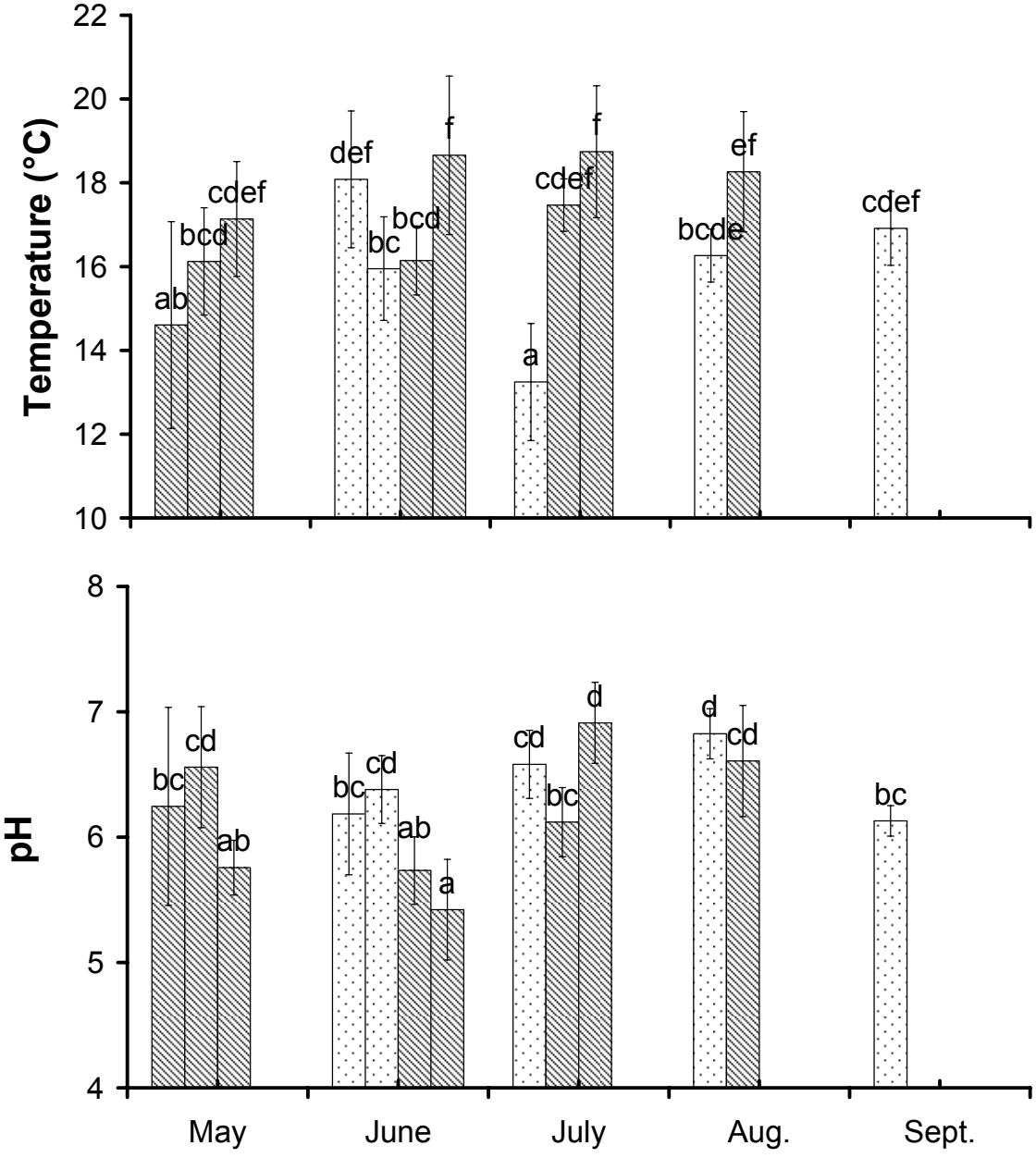

Figure 23. Seasonal variations in groundwater temperature and pH by sampling date for ⬚ 2002 and ▨ 2003. Lower case letters indicate significant differences between sampling dates ($p < 0.05$). Bars show the average and ± 1 SD.

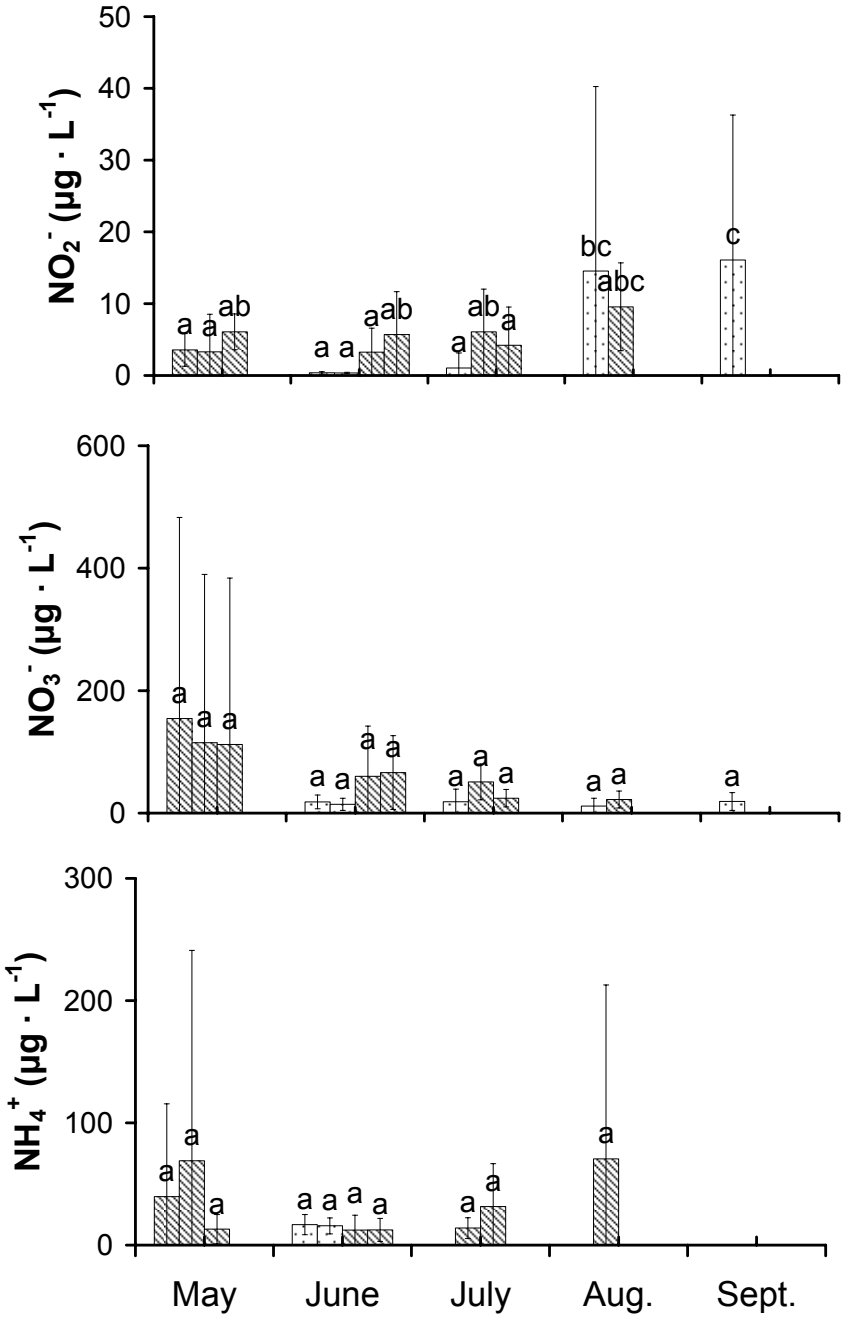

Figure 24. Seasonal variations of NO_2^-, NO_3^-, and NH_4^+ in groundwater by sampling date for ⊡ 2002 and ▨ 2003. Lower case letters indicate significant differences between sampling dates ($p < 0.05$). Bars show the average and ± 1 SD.

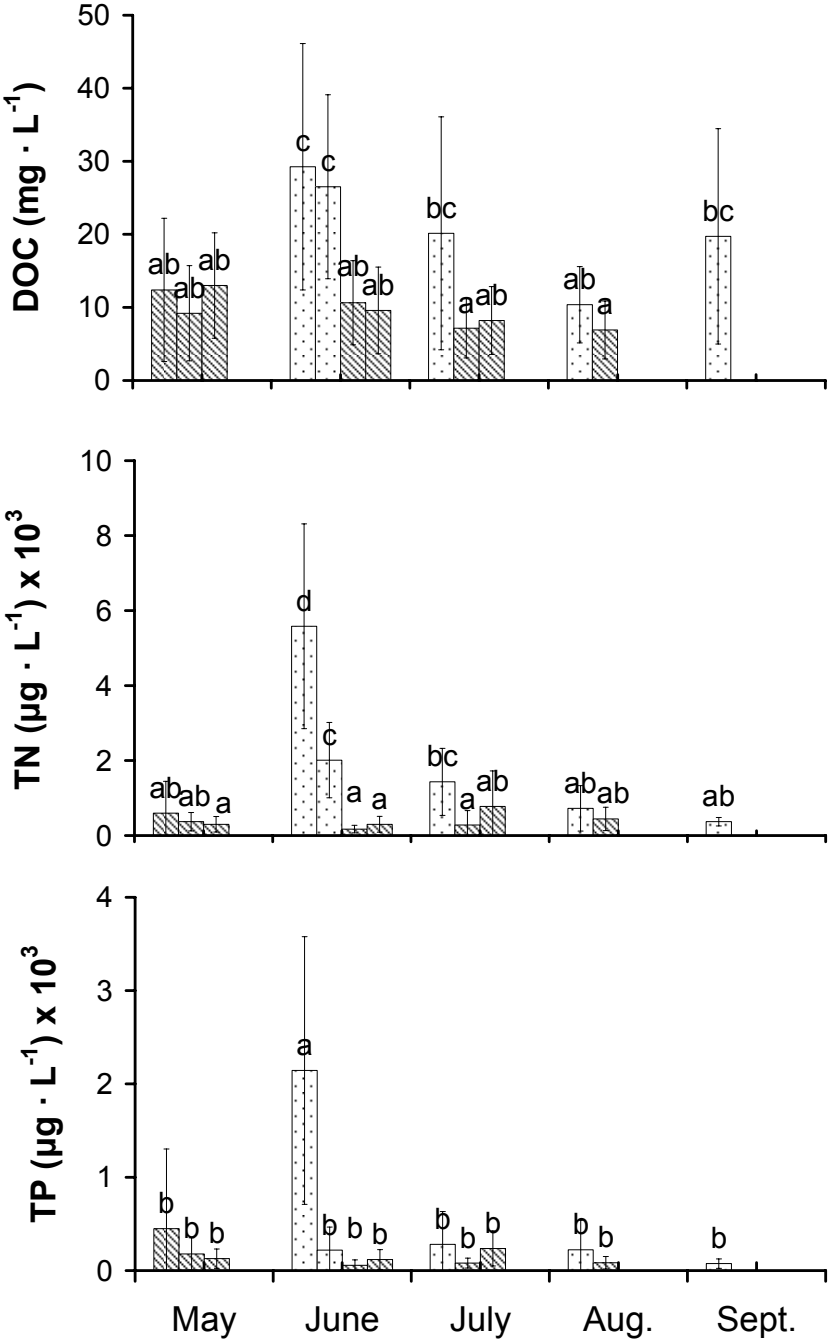

Figure 25. Seasonal variations of DOC, TN, and TP in groundwater by sampling date for ⬚ 2002 and ▨ 2003. Lower case letters indicate significant differences between sampling dates ($p < 0.05$). Bars show the average and ± 1 SD.

Table 9. Correlation coefficients among water quality variables from 2002 and 2003 (n= 390) ‡

	GWD	Temp	Cond †	pH	DOC †	NO_2^- †	NO_3^- †	NH_4^+ †	TDN †	TN †	PO_4^{3-} †	TDP †	TP †
GWD	—	**-.11**	**-.01**	**-.04**	**.25****	**.13**	**-.18***	**.06**	**-.19***	**-.14***	**.01**	**-.20***	**-.22****
Temp	-.07	—	**.29****	**-.19****	**-.06**	**.18***	**.03**	**.07**	**.15***	**.02**	**.06**	**.08**	**.12**
Cond †	-.04	.23**	—	**.14**	**.02**	**.18**	**-.05**	**-.04**	**-.09**	**-.02**	**-.01**	**-.05**	**-.06**
pH	-.03	-.27**	.01	—	**-.10**	**-.25****	**-.21****	**.16***	**-.06**	**.25****	**.14**	**-.06**	**.04**
DOC †	.18*	-.04	-.24**	-.18*	—	**-.13**	**-.18***	**.12**	**.42****	**.42****	**.20****	**.28****	**.15***
NO_2^- †	.05	.15*	.28**	-.28**	-.06	—	**.17***	**-.09**	**-.16***	**-.41****	**-.07**	**-.03**	**-.09**
NO_3^- †	-.26**	-.02	.22**	-.10	-.14	.14	—	**.29****	**.15**	**-.16***	**.06**	**.36****	**.24****
NH_4^+ †	.03	.06	.01	.17*	-.14	-.19*	.03	—	**.26****	**.22****	**.16***	**.40****	**.35****
TDN †	-.19*	.26**	-.17*	-.22**	.31**	-.05	.00	-.02	—	**.46****	**.31****	**.41****	**.42****
TN †	-.13	.02	-.22**	.20**	.26**	-.40**	-.06	.27**	.47**	—	**.15***	**.19***	**.48****
PO_4^{3-} †	-.14	.04	.06	.12	.09	-.20**	.02	.06	.18*	.20**	—	**.47****	**.18***
TDP †	-.28**	.05	-.07	-.05	.20*	-.08	.17*	.28**	.23**	.28**	.36**	—	**.40****
TP †	-.19*	.11	-.02	.03	.12	-.10	.14	.25**	.52**	.58**	.18*	.40**	—

*** Correlation is significant at the 0.05 level (two-tailed); ** Correlation is significant at the 0.01 level (two-tailed).**
† data log-transformed for normality for Pearson correlation coefficient determination.
‡ n=390 is the maximum number of elements. Because of variability of available water in the wells at different sampling dates, n ranged from 138 to 197.
Pearson correlation coefficients calculated on the transformed data are shown in normal font in the bottom part of the table. Spearman non-parametric correlation coefficients calculated on raw data are shown in bold in the top half of the table. GWD – Depth to groundwater; Temp – Temperature; Cond.=Conductivity.

additional negative correlation of depth to TN (rs = -0.14). This may not be meaningful but the relationship may be found to be important in terms of the large variation found at this site.

4.4 Discussion

4.4.1 Relationship between snow and groundwater physical characteristics

The spring snowmelt period is an annual occurrence at Bootleg Mountain. Snow and groundwater samples at this time of year generally vary according to sampling date and air temperature. There is a potential for a flushing mechanism to occur as the water table rises close the soil surface which allows for mobilization of nutrients stored at or near the soil surface in the organic layer (Creed and Band 1998b).

Snow water equivalents (SWE) determined from the sampling sessions in March 2003 and 2004 were quite similar to the values (14-35 cm water) found in lodgepole pine forests in Wyoming by Knight et al. (1985). They concluded that nutrient outflow and retention in that forest was more likely dependent on leaf area index and root area than on biomass accumulation or ephemeral spring flushes of snowmelt water (Knight et al. 1985). The lack of correlation of SWE to the nutrients analyzed at Bootleg Mountain suggest also that biomass accumulation or spring fluxes of snowmelt water had little contribution to nutrient outflow at Bootleg Mountain (Table 6). Spatial heterogeneity was not a factor, although deeper snow depths were observed along the edges of blocks that were close to the road.

The pH of the root-zone solutions in the lodgepole pine (*Pinus contorta* ssp. *latifolia*) forest ecosystems in southeastern Wyoming was around 6.0 and did not change significantly as the snowmelt proceeded (Fahey and Yavitt 1988). At Bootleg Mountain, the pH in the snow was slightly more acidic than that of the groundwater, but the pH of

the groundwater remained relatively constant after the snowmelt and over the entire summer season. Spatially and annually, pH did not vary significantly across the site. This is expected as pH levels can be tightly linked to biological processes (oxidation and reduction reactions) in the soil and water. However, the pH of the irrigation solutions percolating through Norway spruce forests in Germany were found to have negligible effects on the mobilization of C, even though increasing pH did increase the release of organic C from mineral soils (Munch et al. 2002). Thus, the high buffering capacity of the soil is likely the main reason for the tight range of pH determined during the course of the study at Bootleg Mountain.

The negative correlation between groundwater conductivity and DOC at Bootleg Mountain indicated that increasing ionic strength could reduce the availability and mobility of DOC which was similar to the laboratory findings of Kalbitz et al. (2000) but not to the findings of Solinger et al. (2001). At Bootleg Mountain, snow conductivity and DOC were positively correlated which is likely related to the low organic matter content of the snow. However, groundwater NO_3^--N was positively correlated to conductivity in the groundwater at Bootleg Mountain as was also found in a deciduous stand in the Steigerwald region of northern Bavaria, Germany (Solinger et al. 2001). At Bootleg Mountain, conductivity in the snow showed no significant difference across the site; but groundwater was much more variable. Groundwater conductivity did not vary significantly between 2002 and 2003, but it did increase slightly over the summer. Such an increase in conductivity may be the outcome of a seasonal increase in temperature and organic C matter in the groundwater (Stumm and Morgan 1996).

Specific studies on the dynamics of water table depths in mountain areas are lacking. Discussions of the seasonal and spatial changes in water table depths are linked to nutrient dynamics in the following sections.

4.4.2 Temporal and spatial variability of snow and groundwater DOC and the relationship to nutrient chemistry

Some studies have found seasonal changes in the concentration of DOC and DON in forest floor leachates to be directly related to litterfall inputs (Solinger et al. 2001). The release of DOC from the forest floor has been shown to be positively correlated to temperature from laboratory experiments. Seasonal changes in the release of DOC from forest soils are assumed to be connected with increasing microbial activity during warmer conditions in the summer (Currie et al. 1996, Kaiser et al. 2001).

DOC concentrations in the soil have been found to be higher in summer than in winter in the soils of a central European deciduous forest (Kalbitz et al. 2000). This could lead to the conclusion that DOC release is attributed to biological controls. In contrast, the studies of Solinger et al. (2001) in deciduous stands of northern Bavaria and Michalzik et al. (2001) in spruce forests of Norway and Germany reported no correlation of temperature and DOC concentration. Similar results were found at Bootleg Mountain. This could be evidence of other processes occurring in the interactions between the canopy, snow, soil, and groundwater.

Lignin decomposition has been shown to be an important process for DOC mobilization, especially at low N contents (Ander et al. 1990). Solinger et al. (2001) also concluded that concentrations of DOC in the soil are not hydrologically controlled and are mainly driven by water fluxes on annual and biweekly time scales. Such an annual flush of DOC was observed following the spring snowmelt in two headwater catchments

in Colorado (Boyer et al. 1995). At Bootleg Mountain, DOC did not vary much in 2003, but in 2002, significantly higher values were observed in June following the snowmelt. Further study at Bootleg Mountain would be necessary to conclude that a spring flush does contribute DOC to the groundwater. DOC concentrations in the groundwater were generally higher than that of the snow, so it is possible that the main source of DOC was from particulate organic matter in the soils rather than from the snow. Similar seasonal fluxes of DOC and groundwater levels were observed at two spruce forest sites in Birkenes, Norway and Waldstein, Germany (Michalzik et al. 2003). Dissolved organic matter concentrations and chemical composition were also found by Kaiser et al. (2002) to vary throughout the year in a forested area of NE-Bavaria, Germany.

Concentrations of DOC in precipitation over a northern boreal landscape in Thompson, Manitoba were determined to be 8 mg · L^{-1} which appeared to be quite high due to possible increased deposition of ash by local forest fires (Moore 2003). At Bootleg Mountain, the snow precipitation had similar DOC concentrations to that reported by Moore (2003). Subsoil leakage of DOC from the mineral soils, ranging from 7.1 to 27.7 mg · L^{-1} in a northern boreal landscape in Manitoba (Moore 2003), was also very similar to the findings at Bootleg Mountain. In the groundwater of a storm water infiltration basin in Lyon, France, Datry et al. (2004) observed a positive link between DOC and P as was observed with DOC and TDP at Bootleg Mountain.

Dissolved organic C concentrations in deep soil horizons as well as DOC output with the mineral subsoil leachate are usually low (Michalzik et al. 2003, Schwesig et al. 2003). Thus, a substantial portion of DOC may be mineralized or adsorbed in the subsoil. Groffman et al. (1996) determined a range of DOC values between 2.3 and 6.5 mg · L^{-1} in

the groundwater of a riparian forest on Rhode Island, which again is lower than that at Bootleg Mountain. Similar values of DOC (25-30 mg · L^{-1}) to that found at Bootleg Mountain were found in a forested area of NE-Bavaria, Germany (Kaiser et al. 2001). The major source of DOC in seepage waters is from the organic forest floor layers (Kaiser et al. 2001). Dissolved organic carbon in snow and groundwater at Bootleg Mountain was spatially homogeneous although high coefficients of variation were observed at each well and within each block.

4.4.3 Variations in temporal and spatial availability of snow and groundwater N pools

Inorganic N in the groundwater at Bootleg Mountain did not change very much over the summer season. However, when groundwater table depths are taken into consideration, the significant decrease in the water table is correlated to NO_3^- and as the level of water in the groundwater well declined, N concentration decreased. In the lodgepole pine ecosystems of Wyoming, Knight et al. (1991) also noted that the N outflow from the rooting zone was affected by both the concentration of NO_3^- and the volume of water flux and seasonal effects were not obvious by only considering one variable. In the soils from *Pinus radiata* forests in the Coastal Mountain Range of Chile, N contents in soils decreased at the end of the growing season (Litton and Santelices 2003). In order to explain this observation, these authors postulated that a large input of detritus could lead to a strong immobilization of N in soil organic matter.

Pulses of NO_3^- from the snowpack during snowmelt did not pass through the soil and concentrations of NO_3^- remained low during the melt in the Little Valley of the Sierra Nevada Mountains (Johnson et al. 1997). At the same location, Johnson et al. (1997) observed peaks of NO_3^- in stream waters only during years of low snowfall. However,

during years of high snowfall, no pulse of NO_3^- was observed (Johnson et al. 1997). Nitrogen saturation may be occurring in Little Valley because higher NO_3^- released during snowmelt may become uncoupled to biological demand (N mineralization and vegetative uptake) and end up being leached to stream water (Aber et al. 1989, Tietema et al. 1997, Aber et al. 1998, Gundersen et al. 1998). Creed and Band (1998b) found that peak concentrations of NO_3^- in the groundwater occurred during the peak of hydrologic activity in the spring. At Bootleg Mountain, the opposite was observed with the negative correlation between NO_3^- and depth to groundwater. However, consideration of the fact that both groundwater flow volume and NO_3^- decreased over the season, lends support to the finding that NO_3^- is more prevalent in the groundwater when there is more saturation of the soils.

Little seasonal or spatial variation of inorganic N and P concentrations was observed in the root-zone solutions of lodgepole pine (*Pinus contorta* ssp. *latifolia*) forest ecosystems in southeastern Wyoming, probably due to the fact that these are limiting nutrients and are in high biotic demand in the soils (Fahey and Yavitt 1988). Losses of N and P from the soils were strongly linked to the mobility of DOC in these soils from Wyoming. Based on this finding, correlation of DOC, N, and P could be expected at Bootleg Mountain. The groundwater from Bootleg Mountain did indicate strong correlation of DOC to TDN, TN, PO_4^{3-} and TDP. This relationship between N, P, and DOC in the groundwater is likely centered around P dynamics lending evidence to rapid mineralization of organic P leading to responses in the N and DOC pools due the P being the limiting nutrient within the groundwater (Fahey and Yavitt 1988). This connection of

DOC and N (particularly NO_3^-) was also found at the soil-stream interface of Smith Creek, Michigan (Hedin et al. 1998).

The NH_4^+ and NO_3^- in the snow pack in Wyoming was 0.08 mg · L^{-1} and 0.13 mg · L^{-1}, respectively (Fahey et al. 1985), was higher than what was at Bootleg Mountain. Inputs of N via precipitation at this site are quite low due to the relatively unpolluted local atmosphere. However, following the intense fires of summer 2003 in the area near Bootleg Mountain, N in the snows of 2004 was slightly higher than in the previous year. These fires may be a factor in the amount of N being deposited annually on the research site.

Hydrologic N balances (N inputs via precipitation versus N loss through leaching and denitrification) tend to yield N inputs in excess of outputs (Likens et al. 1977, Vitousek and Howarth 1991, Likens and Bormann 1995). Soils were found to be a sink for NH_4^+ from snowpack melt water in a study by Williams and Melack (1991) where less than 1% of NH_4^+ from the snow ended up in the surface water of an alpine basin in the Sierra Nevadas. Average concentrations of NH_4^+ in the snow and groundwater measured at Bootleg Mountain were similar. However, in contrast to the findings of Williams and Melack (1991), NH_4^+ was higher at Bootleg Mountain in the groundwater than in the snow in the spring of 2003. These elevated values could be related to increased mineralization rates of organic N flushed through the soil into the groundwater (Williams and Melack 1991). Alternatively, the reason for higher NH_4^+ in the groundwater than in the snow is that more NH_4^+ could be adsorbed to runoff sediment entering the groundwater (Ettema et al. 1999). This is evidenced by the high particulate matter in the groundwater in the spring.

Nutrient outflow in the different lodgepole pine stands in Wyoming varied greatly (Knight et al. 1985). Nitrogen also appeared to be retained in the soil even at high levels of water outflow. Knight et al. (1985) found that snow and subsoil solutions did not differ significantly in total N and P concentrations, and found that the bulk of the N in the soils was in organic forms (rather than predominantly inorganic NO_3^- and NH_4^+ in the snow). In contrast, most of the N was in organic form in all locations (soil, snow, and ground water) at Bootleg Mountain. This difference is probably linked to the observations of rapid immobilization of N in the soils (see Chapter 5). At the same location in Wyoming, Fahey et al. (1985) found that inorganic N in the forest floor leachate was <0.05 mg $N \cdot L^{-1}$, which is very similar to what was measured at Bootleg Mountain.

Groundwater NO_3^- at a riparian site in New England ranged from 0.1 to 0.6 mg $\cdot L^{-1}$ was comparable to what was found at Bootleg Mountain. At the same site, the water table rose significantly in the spring and fell into the lower B and C horizons during the growing season (Addy et al. 1999). Gundersen et al. (1998) suggested that once an appreciable amount of NO_3^- appears in the soil solution, it has the potential to be leached down the profile during times where there is a lot of water flow. However, soils with low concentrations of NO_3^- such as that at Bootleg currently would not pose any problems to stream water quality (Binkley et al. 1999) if no disturbances were to occur.

High concentrations of NO_3^- in soil water still have the possibility of leading to stream water impacts. The spring saturation of soils at Bootleg Mountain could potentially allow denitrification to occur in the soils at the interface between the soil and groundwater. However, denitrification in the groundwater of these soils is unlikely because the water

table is below the biologically active zone and aerobic conditions exist with little C availability (Groffman et al. 1996). The amount of water in the soils at Bootleg Mountain is likely the main control of the microbial activities in soils and thus the rates of cycling (Paul et al. 2003).

The high organic N contents in the groundwater at Bootleg Mountain (determined from the difference between TIN and TN) were quite similar to the value of 2.3 mg $N \cdot L^{-1}$ of dissolved organic N in the deciduous stand of the Stiegerwald region of Germany (Solinger et al. 2001). At Bootleg Mountain, not much temporal variation of TN in groundwater was noted except for some high values in June 2002, possibly due to the spring snowmelt flush. Again, spatial heterogeneity was not a major factor in inorganic N concentrations across the research site at Bootleg Mountain, but high coefficients of variation indicate much variability at each well location.

4.4.4 Variations in temporal and spatial availability of snow and groundwater P pools

A wide range P concentration in the groundwater has been reported in the literature with a general lack of determination of P pools in groundwater systems. Binkley et al. (1999) summarized the impacts of N and P fertilization on water quality. Examples that Binkley et al. (1999) discussed included: 1) the stream water of a slash pine in Florida where background phosphate concentrations were <0.1 mg $\cdot L^{-1}$; 2) the second growth Douglas-fir stand in Washington State with PO_4^{3-} concentrations of 0.9 mg $\cdot L^{-1}$; and 3) the second growth Douglas-fir stand in Central Oregon with a PO_4^{3-} pool of 0.006 mg $\cdot L^{-1}$. Binkley et al. (1999) also determined that the average P concentration of streams draining from all the forested areas from Europe, South America, and North America summarized in the article is 0.02 mg $\cdot L^{-1}$. These results are within the range of the PO_4^{3-},

TDP, and TP values at Bootleg Mountain. At the Rhode River drainage basin in Maryland, riparian forest groundwater concentrations of TP ranged from 7 to 18 $\mu g \cdot L^{-1}$ (Peterjohn and Correll 1984) which was close to PO_4^{3-} levels at Bootleg, but quite a bit lower than the TP findings from Bootleg Mountain.

Phosphate is strongly retained by mineral soils and can form highly insoluble Al- and Fe-phosphate complexes that do not allow for significant phosphate leaching, even after a disturbance such as logging (Piirainen et al. 2004, Fernandez-Perez et al. 2005). Phosphate may be playing a key role between N and DOC dynamics. Interaction of PO_4^{3-} with DOC has been found to increase the mobility of PO_4^{3-} which may affect the soil bioavailability of P (Fernandez-Perez et al. 2005). Kalbitz et al. (2000) also suggested that much is still unknown about the relationships between DOC, and organic forms of N and P and that there is much uncertainty regarding the feedback mechanisms associated with these pools. Thus, the leaching of DOC may be a mechanism for P removal from forest soils (Donald et al. 1993) as organic P is a key component of organic matter of soil and groundwater. At Bootleg Mountain, P concentrations did not vary significantly across the site, therefore spatial heterogeneity was not a major factor at this site; instead, it is temporal variation that influences the rates of cycling of nutrients in this ecosystem.

4.4.5 Summary

Temporal variation of DOC and DON concentrations in the forest floor may not be attributed to only one environmental factor. This reflects the diverse number of possible interactions and interdependences that make it difficult to determine an exact cause and effect under field conditions (Solinger et al. 2001). The organic layers of forest ecosystems are important sources of organic substances in the groundwater and surface

stream water (Kaiser et al. 2002). Hydrologic variability in soil horizons with high carbon contents may be more important than biotic controls (Kalbitz et al. 2000).

Creed and Band (1998b) discussed the idea that N was tightly cycling in forests with little or no export to the surface. This finding is substantiated by the observation of very low inorganic N contents, high C/N ratios (125 in snow, 120 in groundwater), and very little flushing of nutrients by snowmelt water. However, there is potential for loss of NO_3^- from these ecosystems if a certain threshold is reached. Rocky Mountain ecosystems are extremely responsive to slight increases in N availability (Baron et al. 2000). For example, fire may decrease organic matter, soil moisture, and increase P availability and pH in forest soils. Inorganic N could increase or decrease, depending on the season and water availability (Litton and Santelices 2003). Also, harvesting may influence the amount of drifting and snow accumulation which could potentially increase the amount of water entering the block during the spring melt period. A reduced leaf area index could increase the speed at which the snowmelt water would enter the system, possibly increasing the amount of NO_3^- being leached (Fahey and Knight 1986).

Spatially, the nutrients in the snow and groundwater were quite homogenous. The significant differences for the soil nutrient contents between Block 30A and the other blocks were not exhibited in the groundwater and snows. The only significant difference noted was that block 30A had consistently more water in the wells over the course of this study (Fig. 19), which can be related to the elevated moisture contents and low bulk densities also noted in block 30A (Chapter 3). High coefficients of variation were noted for nearly all the chemical variables at each sampling location indicating more heterogeneity within plots than between blocks.

Snow density, SWE, and pH in both the snow and groundwater were not important factors seasonally, annually, and in relation to nutrient levels, but variation in the groundwater levels influenced the amount of nutrients travelling through this system. Dissolved organic C and inorganic N and P contents were strongly correlated in both the snow and groundwater, with P likely being the key component influencing the concentrations and rates of cycling. This is likely because P is the more limiting nutrient in the snows and groundwater as compared to N being more limited in the soils. If this site is left undisturbed, it is likely that loss of NO_3^- to the groundwater and eventually to surface waters will be minimal as most inorganic inputs to this N-limited system would be immobilized (Johnson et al. 1997). There is still potential that there may be some leaching of NO_3^- during the spring snow melt flushes, especially if there were large accumulations of snow during the winter season (Johnson et al. 1997). To conclude, nutrients and groundwater levels were found to respond to the spring snowmelt. Both decreased seasonally, but varied little spatially and inter-annually. In relation to the soils, levels of DOC, N, and P track each other very closely. Future research should involve clearly defining the relationships between these components, especially by following their pathways as they are delivered via snow and rain, percolate through soils, and eventually end up in groundwater and surface waters.

Chapter 5
Determination of gross and net nitrogen mineralization and nitrification using ^{15}N isotopes in a lodgepole pine (*Pinus contorta* Doug.) forest

5.1 Introduction

Anthropogenic perturbations to the global nitrogen (N) cycle now exceed those of any other major biogeochemical cycle on Earth, yet the ability to predict how ecosystems will respond to the rapidly changing N cycle remains poor (Asner et al. 2001). In the face of this pronounced change, there is a need to understand better how transformations mediated by microbes, such as N fixation, nitrification, N mineralization, and denitrification (Likens et al. 1977) affect the cycling of nitrogen in a variaety of ecosystems, including forests. By studying the biogeochemistry and the microbiology of such systems, a better understanding of nutrient fluxes in terms of inputs, outputs and important processes can be achieved (Knowles 2000).

Nitrate and NH_4^+ in forest soils are subject to a variety of processes that link the soil to the groundwater. For example, increasing NO_3^- levels in N-limited soils could result in increased flow to the groundwater regime. Higher levels of NO_3^- in groundwater and, subsequently, in mountain streams could result in increased productivity and reduced quality of drinking water.

Nitrate concentrations are usually quite low in forest ecosystems and net nitrification rates have been found to be minimal in 30-d buried bag incubations (Robertson 1982, Vitousek et al. 1982, Aber et al. 1989, Davidson et al. 1992). Comparison of net and gross rates of nitrification and mineralization studies (Vitousek et al. 1982, Davidson et al. 1992, Stark and Hart 1997) indicate that net rates poorly predict gross rates and that

gross rates tend to be higher than anticipated. Consequently, nitrification is thought to be not an important part of the N cycle in most undisturbed forest ecosystems. It has been suggested that microbial biomass -C and –N is a major factor affecting soil N dynamics and is an excellent indicator of the low bacterial populations (Hart et al. 1994, Currie 1999, Compton and Boone 2002).

Logging activities such as clear-cutting and whole-tree harvesting have the potential to affect water and N outflow into the local reservoirs (Likens et al. 1977, Knight et al. 1991, Likens and Bormann 1995). Determining the N dynamics (particularly NO_3^- and NH_4^+) in the soils and water at Bootleg Mountain will potentially provide data for better management of drinking water following tree harvest. It is thus necessary to determine the current state of a forest ecosystem in order to determine the impacts that disturbances such as harvesting will have on NO_3^- and NH_4^+ and the subsequent potential fluxes to drinking water (Kroeze et al. 1989). Considering all the factors that regulate nutrient fluxes within this system, do N mineralization and nitrification offer a significant source of N to the groundwater of a lodgepole pine forest? In order to answer this question: 1) the gross and net rates of N mineralization and nitrification were measured; and 2) microbial biomass was estimated at the Bootleg Mountain study site.

5.2 Materials and methods

5.2.1 Site description

Each of the 6-one ha experimental blocks from the lodgepole pine forest at Bootleg Mountain were sub-divided into nine plots in order to evaluate soil heterogeneity and net and gross N mineralization and nitrification. Five plots were selected for installation of groundwater wells. Each of these was subdivided into quadrants and the quadrant located at the center for the lower left was selected to perform ^{15}N isotope dilution, buried bag,

and microbial biomass experiments (Fig. 4). A complete site description of the research site at Bootleg Mountain was presented in Chapter 2.

5.2.2 Gross nitrification and N mineralization using ^{15}N isotope dilutions

Sampling was performed in the six experimental blocks once during the summer of 2003 to determine site variability. In block at the center of the lower left quadrant, within each of five plots containing wells, the fresh litter (O1 layer) was removed from a 50 × 50 cm area and set aside. In each plot, the entire O2 layer (litter fragments and humus) was removed and placed in a plastic bucket and mixed. A sample (~50 g) was placed in a plastic bag and brought back to the lab for further analysis. Two molar KCl (50 mL) was added to each of three sub-samples (~ 5 g dry weight (dw) equivalent each) for determination of NO_3^--N and NH_4^+-N ions. Soil moisture was determined by drying soils at 105°C in an oven for 24 hrs. While still in the field, each of four subsamples (~50 g dw equivalent) were placed in 1 L glass Mason jars. With a needle and syringe (18 gage, 10 cm length), 6 mL of $(^{15}NH_4)_2SO_4$ solution was added in small aliquots to two of the jars. The remaining two jars received $K^{15}NO_3$ (6 mL) solution. These ^{15}N solutions contained N at 16 mg · L^{-1}, thus providing ^{15}N at ~2 μg · g^{-1} dw of O2 soil.

At the same time, the pool dilution technique was also applied to intact mineral soil cores as described by Davidson et al. (1991, 1992). Four pre-weighed PVC cores (4 cm diam. × 9 cm) were driven into the mineral soil layer. A larger metal cylinder (8 cm diam. × 9 cm) was then driven around each plastic core to form concentric circles. Both cores were then removed, and the soil from the outer core was placed in a plastic bag, mixed and extracted upon return to the lab (~5 g dw equivalent with 50 mL 2M KCl) for initial inorganic-N pool sizes. The smaller inner cores were weighed. Then, using large

syringes (18 gage, 10 cm length), small aliquots (6 mL total) of $(^{15}NH_4)_2SO_4$ or $K^{15}NO_3$ (16 mg · L^{-1}) was injected into two inner cores for each solution. The cores contained, on average, ~80 g dw of soil, giving an addition of ^{15}N at ~1.2 μg · g^{-1} dw of mineral soil. The cores were then capped and buried in the same holes for *in situ* incubation. The Mason jars were covered by the remaining O2 and O1 material. After 24 hours the samples were removed, taken to the laboratory, mixed, and extracted (~5 g dw equivalent in 50 mL 2 M KCl). All extraction solutions were filtered through filter papers (pre-rinsed with KCl, Whatman #1). Colorimetric analysis for NH_4^+-N and NO_3^--N was conducted as described in section 3.2.4.

For the ^{15}N analysis, sample extracts were prepared by a diffusion technique (Mackown et al. 1987, Brooks et al. 1989, Herman et al. 1995). The soil extract of a known volume (~50 mL) was placed in a capped plastic container (100 mL) to which 0.2 g of powdered MgO was added to adjust the solution to a pH of 10.5. The NH_4^+ in the solution was volatilized to NH_3 and trapped on a disk of glass fibre filter paper (1 cm diam.) acidified with 10 μL of 2.5 M $KHSO_4$. To measure the NO_3^- in an extract finely ground finely ground Devarda's alloy (0.4 g) was added to reduce the NO_3^- to NH_4^+ and then trapped on the filter paper as just described. After six days of incubation, the paper was removed, dried overnight in a dessicator, and wrapped in a tin capsule. The total N content and the ^{15}N isotope ratio (atom % ^{15}N) in the soils was determined at the University of Saskatchewan after combustion of the sample at 1000°C and passage of the gases through a reduction column at 550°C (Roboprep-CN Sample Preparation Unit, Europa Scientific Ltd., Crewe, UK) using an isotope ratio mass spectrometer (Tracermass, ANA-MS, Europa Scientific Ltd., Crewe, UK).

Gross N mineralization and nitrification rates were calculated using Kirkham and Bartholomew's (1954) isotope dilution model (Binkley and Hart 1989, Davidson et al. 1992). The equations of Kirkham and Bartholomew (1954) and Davidson et al. (1991) were as follows:

$$m = \frac{M_0 - M_1}{t} \times \frac{\log (H_0 M_1 / H_1 M_0)}{\log (M_0 / M_1)} \qquad (5.1)$$

$$c = \frac{M_0 - M_1}{t} \times \frac{\log (H_0 / H_1)}{\log (M_0 / M_1)} \qquad (5.2)$$

where M_0 = initial $^{14+15}N$ pool ($\mu g\ N \cdot g^{-1}$ dw)
M_1 = post-incubation $^{14+15}N$ pool ($\mu g\ N \cdot g^{-1}$ dw)
H_0 = initial ^{15}N pool ($\mu g\ N \cdot g^{-1}$ dw)
H_1 = post-incubation ^{15}N pool ($\mu g\ N \cdot g^{-1}$ dw)
m = mineralization rate ($\mu g\ N \cdot g^{-1}\ dw \cdot d^{-1}$)
c = consumption rate ($\mu g\ N \cdot g^{-1}\ dw \cdot d^{-1}$)
t = time (1 day for the present study)

and where $m \neq c$

For samples that used $^{15}NH_4^+$, the NH_4^+ pool was used for M and H. For $^{15}NO_3^-$ additions, the NO_3^- pool was used for M and H and the mineralization rate, m was changed to nitrification rate, n in $\mu g\ N \cdot g^{-1}\ dw \cdot d^{-1}$ (Davidson et al. 1991). After addition of $^{15}NO_3^-$ and $^{15}NH_4^+$ to the soil, the total NO_3^-, NH_4^+, $^{15}NO_3^-$, and $^{15}NH_4^+$ were measured in the 2M KCl extract. Calculations of gross rates into and out of the $^{15}NO_3^-$, and $^{15}NH_4^+$ pools require knowledge of the initial and final NO_3^-, NH_4^+, $^{15}NO_3^-$, and $^{15}NH_4^+$ pool sizes (Binkley and Hart 1989). Initial $^{14+15}NO_3^-$ and $^{14+15}NH_4^+$ pool sizes were determined from the extracts of the soils collected before the incubation. The initial $^{15}NO_3^-$ and $^{15}NH_4^+$ pools size is based on the amount injected into cores. Final pool sizes (M_1 and H_1) were determined from the extractions after a 24-hour incubation period

(Davidson et al. 1992). This gross consumption estimate includes microbial NH_4^+ immobilization and nitrification and microbial NO_3^- immobilization and possibly denitrification (Davidson et al. 1992).

5.2.3 Microbial biomass using chloroform fumigation incubations

From the Mason jars containing the $^{15}NH_4^+$ treated O2 material, four subsamples (10 g each) were weighed into 1-L glass Mason jars for immediate fumigation with chloroform to estimate microbial biomass –C and –N (Voroney and Paul 1984, Voroney et al. 1993). In this method, soil microorganisms are killed following the soil fumigation with chloroform ($CHCl_3$). Mineralization of dead microbial cells leads to a flush of CO_2 and accumulation of NH_4^+ over 10 days. The flush is directly proportional to the sizes of the microbial C and N pools (Voroney et al. 1993). The samples were placed in a dessicator lined with moist paper towels and $CHCl_3$ (50 mL) in a 100-mL beaker with a few boiling chips. The dessicator was then sealed and evacuated until the $CHCl_3$ boiled vigorously for ~1 min. After 24 hours in the sealed vacuum the $CHCl_3$ was removed and the dessicator was vented thoroughly in the fume hood. The jars were then capped and incubated for ten days.

Headspace CO_2 was then analyzed on a gas chromatograph (Varian 3800, Varian Canada Inc., Mississauga, Ont.), using a Poropak Q column (2 m × 3.18 mm SS, 80/100 mesh, Chromatographic Specialties Inc., Brockville, Ont.) and a thermal conductivity detector (TCD) at 150°C. The oven temperature was 45°C and the injector temperature was 110°C with a He carrier gas (25 mL min^{-1}). Standards of 1000 ppmv CO_2 were measured every 15 samples and the standard curve was linear between 69 to 83,333 ppmv CO_2.

The soil sample was extracted in 2 M KCl for MB-N determination. Calculations were based on the equations provided in Davidson et al. (1992), Jenkinson et al. (2004), and Voroney and Paul (1984):

$$\text{microbial biomass-C} = C_f/0.45, \quad (5.3)$$

$$\text{microbial biomass-N} = N_f/k_N, \quad (5.4)$$

$$k_N = 1.86 \times (C_f/N_f)^{-0.879}, \quad (5.5)$$

where C_f is the resulting flush of CO_2-C after fumigation, N_f is the flush of inorganic N, and k_N is the proportion of microbial biomass-N released as inorganic-N by chloroform fumigation. A constant ($k_C = 0.45$) representing the fraction of killed biomass C converted to CO_2 during the 10 day incubation period and was based on incubation studies on yeasts, fungi, actinomycetes, bacteria, and soil invertebrates (Jenkinson et al. 2004). No control was subtracted for the microbial biomass-C flush. N_f was calculated by subtracting the soil inorganic-N pool before and after the fumigation. Some limitations to this method such as the length of time of the incubations, the necessity of a control, and poor results in strongly acidic soils have been previously noted (Voroney et al. 1993, Harris et al. 1997, Jenkinson et al. 2004).

5.2.4 Net nitrification and N mineralization using buried bags incubations

At each plot, four more PVC soil cores (4 cm diam. × 9 cm) were taken from the mineral layer, placed in plastic Whirl-Pak ® bags (38 μm thickness), and buried at the sampling site. A subsample of the remaining O2 material from the bucket (~50 g dw) was also placed in a plastic bag and reburied within the O2 layer. After the 30-day incubation, the samples were retrieved, mixed, and extracted with KCl as previously described. All extraction solutions were filtered through pre-rinsed (with KCl) paper

filters (Whatman #1). Colorimetric analysis for NH_4^+-N and NO_3^--N was conducted as described in section 3.2.4.

The calculation of net nitrification is the change in the NO_3^- content of the sample during the 30-day incubation and was described by Davidson et al. (1992). Net mineralization was the change in the total inorganic-N pools during the incubation. The initial inorganic-N pool sizes were estimated from the initial pool sizes determined from the ^{15}N isotope dilution samples.

5.2.5 Statistical analyses

Statistics performed are described in section 2.3.

5.3 Results

Statistics for the variables measured at Bootleg Mountain were initially determined for each soil layer (Table 11).

5.3.1 Spatial variability of inorganic-N pool sizes

In all blocks, extractable NH_4^+-N was considerably higher than extractable NO_3^--N. The NO_3^--N pool was very small, with a range of 0.004 $\mu g \cdot g^{-1}$ dw (BDL) to 8.88 $\mu g \cdot g^{-1}$ dw in the O2 layer and 0.02 to 6.02 $\mu g \cdot g^{-1}$ dw in the mineral layer (Fig. 26). In the O2 layer, NO_3^--N in block 20 (0.25 ± 0.99 $\mu g \cdot g^{-1}$ dw) was significantly higher than block 28A (0.08 ± 0.02 $\mu g \cdot g^{-1}$ dw) and 28 (0.08 ± 0.12 $\mu g \cdot g^{-1}$ dw). In the mineral layer, block 20 (0.42 ± 1.12 $\mu g \cdot g^{-1}$ dw) was significantly higher than blocks 20A (0.08 ± 0.05 $\mu g \cdot g^{-1}$ dw) and 28 (0.05 ± 0.01 $\mu g \cdot g^{-1}$ dw).

For the extractable NH_4^+-N pool, the range of results was quite high (CV was 213.1% in the O2 layer and 446.5% in the mineral layer) (Fig. 26). Despite this larger variation, significant differences between the O2 and mineral layers in blocks 20A, 30, 28A, and 28

was observed. In the O2 layer, NH_4^+-N in block 30 (30.12 ± 47.60 μg · g^{-1} dw) was significantly higher than NH_4^+-N in blocks 20A (7.72 ± 13.52 μg · g^{-1} dw) and 20 (5.13 ± 9.23 μg · g^{-1} dw). NH_4^+-N in block 28 (21.27 ± 36.10 μg · g^{-1} dw) was also significantly higher than blocks 20A and 20. For the mineral layer, NH_4^+-N in block 30 (20.4 ± 61.9 μg · g^{-1} dw) was significantly higher than blocks 20A (3.11 ± 4.50 μg · g^{-1} dw), 20 (2.94 ± 2.62 μg · g^{-1} dw), 28A (2.03 ± 2.15 μg · g^{-1} dw), and 28 (1.81 ± 3.06 μg · g^{-1} dw).

5.3.2 Estimation of soil microbial biomass from chloroform fumigation incubations

The results of the microbial biomass tests were quite high, which may indicate a very high microbial activity. The overall averages for microbial biomass-C (MB-C) and microbial biomass-N (MB-N) were 5710 ± 2790 μg C · g^{-1} dw and 683 ± 385 μg N · g^{-1} dw, respectively (data not shown). This was partially expected, because chloroform fumigation incubations often do not produce reliable biomass comparisons in situations of low spatial and temporal variation and measures the total MB-C rather than the active part of the soil microbial community (Vandewerf and Verstraete 1987, Wardle and Ghani 1995, Bengtsson et al. 2003). This data was not considered any further.

5.3.3 Net rates of nitrification and mineralization from buried bag incubations

Net nitrification rates were very low in all blocks (0.0049 ± 0.0008 μg N · g^{-1} dw · d^{-1}) possibly indicating a very small NO_3^- pool and no overall increase of NO_3^- over time in the buried bags (Fig. 27). This could suggest rapid immobilization or denitrification of NO_3^- in the soils. There was no significant difference between the O2 and mineral layers. Furthermore, there were no significant differences between the blocks in the O2 layer. However, in the mineral layer, net nitrification in block 20 (0.0206 ± 0.0515 μg N · g^{-1}

dw · d^{-1}) was significantly higher than block 20A (-0.0009 ± 0.0024 μg N · g^{-1} dw · d^{-1}) which showed net immobilization of NO_3^-.

The NH_4^+-N pool size increased over the 30 day incubation, showing overall net mineralization of 0.43 ± 0.95 μg N · g^{-1} dw · d^{-1} for the O2 layer and 0.34 ± 1.21 μg N · g^{-1} dw · d^{-1} for the mineral layer (Fig. 27). Again there were no significant differences between the net mineralization rates in the O2 and mineral layers. There were no significant differences in the net mineralization rates between the blocks in the O2 layer. For the mineral layer, the rate of net mineralization in block 30 (1.31 ± 2.80 μg N · g^{-1} dw · d^{-1}) was significantly higher than those in blocks 20A (0.17 ± 0.18 μg N · g^{-1} dw · d^{-1}), 20 (0.12 ± 0.12 μg N · g^{-1} dw · d^{-1}), 28A (0.09 ± 0.09 μg N · g^{-1} dw · d^{-1}), and 28 (0.08 ± 0.13 μg N · g^{-1} dw · d^{-1}).

5.3.4 Gross rates of mineralization and nitrification from ^{15}N isotope dilutions

The gross rates of nitrification were low, ranging from -0.28 to 2.73 μg N · g^{-1} dw · d^{-1} in the O2 layer and -1.97 to 2.58 μg N · g^{-1} dw · d^{-1} in the mineral layer (Fig. 28). These rates were higher than those detected by the net nitrification method, but still indicated a very quick turnover of NO_3^- in these forest soils. The negative values observed should actually indicate ammonification or immobilization instead of nitrification. These low rates can also be related to the very small NO_3^- pool sizes. There was no significant difference between the gross nitrification rates in the O2 and the rates in the mineral layers for blocks 20A, 20, and 30A, but the gross nitrification rate in the mineral layer was significantly higher than the rate in the O2 layer for blocks 30, 28A, and 28. The gross nitrification rates in the O2 layer of block 30A (1.14 ± 0.95 μg N · g^{-1} dw · d^{-1}) were significantly higher than the rates in blocks 30 (0.04 ± 0.32 μg N · g^{-1} dw · d^{-1}) and

28 (0.03 ± 0.11 μg N · g^{-1} dw · d^{-1}), but there were no significant differences between the blocks for the average gross nitrification rates of the mineral layer.

Gross mineralization rates ranged between 1.56 and 19.1 μg N · g^{-1} dw · d^{-1} in the O2 layer and between -2.45 and 8.14 μg N · g^{-1} dw · d^{-1} in the mineral layer (Fig. 28). The negative results found in the mineral layer show that immobilization may be occurring instead of mineralization. As expected, these rates were higher than the rates found by the buried bag method. The gross mineralization rates in the O2 layer were found to be significantly higher than the rates measured in the mineral layer. There were no significant differences between the gross mineralization rates in blocks in both the O2 (overall average: 7.83 ± 4.19 μg N · g^{-1} dw · d^{-1}) and mineral (overall average: 2.13 ± 2.31 μg N · g^{-1} dw · d^{-1}) layers.

5.3.5 Soil microbial immobilization rates from ^{15}N isotope dilutions

Gross rates of NO_3^- consumption (microbial immobilization plus denitrification) showed no significant differences from block to block and layer to layer and ranged from 1.66 to 4.88 μg N · g^{-1} dw · d^{-1} in the O2 layer and from -1.02 to 4.31 μg N · g^{-1} dw · d^{-1} in the mineral layer (Fig. 29). In this case, negative results indicate that some nitrification may be occurring in the soils.

Gross rates of NH_4^+ consumption (microbial immobilization plus gross nitrification) had averages of 9.53 ± 3.63 μg N · g^{-1} dw · d^{-1} for the O2 layer and 3.03 ± 2.40 μg N · g^{-1} dw · d^{-1} for the mineral layer (Fig. 29). The immobilization rates in the O2 layer were significantly higher than the mineral layer for all blocks. For the O2 layer, block 28 (13.13 ± 3.33 μg N · g^{-1} dw · d^{-1}) was significantly higher than block 30A (6.49 ± 2.05 μg

$N \cdot g^{-1}$ dw $\cdot d^{-1}$). There were no significant differences between the blocks for the mineral layer.

5.3.6 Determination of correlations between N transformations and pool sizes

In general, the Pearson and the Spearman correlation coefficients were in agreement (Table 12). Spearman coefficients (rs) will not be mentioned unless they are different from the Pearson coefficients (r). The NO_3^--N pool was strongly positively correlated to net nitrification (r = 0.69) and weakly positively correlated to net mineralization (r = 0.18). The NH_4^+-N pool showed many correlations but the most interesting was the strong positive correlation to net mineralization (r = 0.59) and the negative correlation to gross nitrification (r = -0.28). Ammonium was also strongly positively correlated to gross mineralization (rs = 0.38) and gross NH_4^+ consumption (rs = 0.37).

Gross nitrification and gross mineralization were negatively correlated (r = -0.46, rs = -0.41), but not net nitrification and net mineralization, which were weakly positively correlated (r = 0.41). However, gross nitrification and gross mineralization were negatively correlated. As expected, gross nitrification was positively correlated to NO_3^- consumption (r = 0.58) and negatively correlated to NH_4^+ consumption (r = -0.51, rs = -0.40). Gross mineralization was also strongly positively correlated to NH_4^+ consumption (r = 0.96).

Table 10. Basic characteristics for the pool sizes and rates of N cycling.

		NO_3^--N (μg · g dw^{-1}) *	NH_4^+-N (μg · g dw^{-1})	NetNit * (μg · g dw^{-1} · d^{-1})	NetMin * (μg · g dw^{-1} · d^{-1})	GrossNit * (μg · g dw^{-1} · d^{-1})	GrossMin * (μg · g dw^{-1} · d^{-1})	NO_3Con * (μg · g dw^{-1} · d^{-1})	NH_4Con * (μg · g dw^{-1} · d^{-1})
O2	**mean**	0.13	14.1	0.004 L *	0.43	0.40	7.83	2.35	9.53
	CV (%) †	325.1	213.1	751.4	218.5	162.5	53.5	29.0	38.1
	min	0.004 L*	0.01 L *	-0.02	-0.06	-0.28	1.56	1.66	4.19
	max	8.88	198.8	0.29	5.10	2.75	19.1	4.88	18.5
Mineral	**mean**	0.16	5.86	0.005 L *	0.34	0.71	2.14	1.97	3.03
	CV (%) †	313.3	446.5	483.5	360.1	121.6	108.1	51.8	79.2
	min	0.02	0.11	-0.01	-0.09	-1.97	-2.45	-1.02	-1.37
	max	6.02	345.1	0.20	11.5	2.58	8.15	4.31	11.3

*** dw – dry soil weight; L – below detection limit; NetNit – net nitrification; NetMin – net mineralization; GrossNit – gross nitrification; GrossMin – gross mineralization; NO_3Con – gross NO_3^- consumption; NH_4Con – gross NH_4^+ consumption**
† CV (%) – coefficient of variation

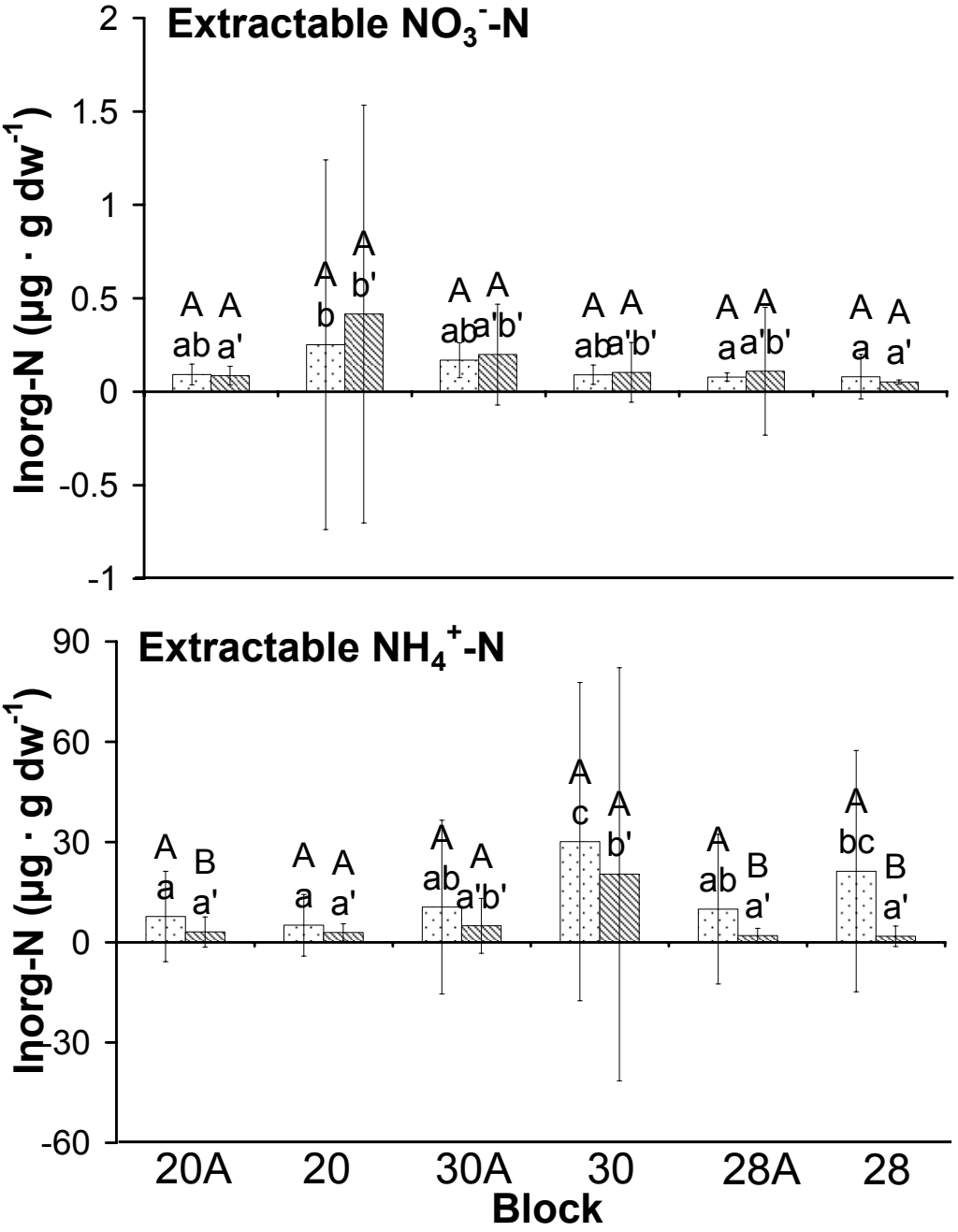

Figure 26. Extractable NO_3^--N and extractable NH_4^+-N levels in the ⬚ O2 layer and ▨ Mineral layer. Lower case letters indicate significant differences between blocks within the same soil layer ($p < 0.05$). Capital letters indicate significant differences between O2 and Mineral layers ($p < 0.05$). Inorg is Inorganic, dw is dry soil weight. Each bar shows the average (n = 5) and ± 1 SD.

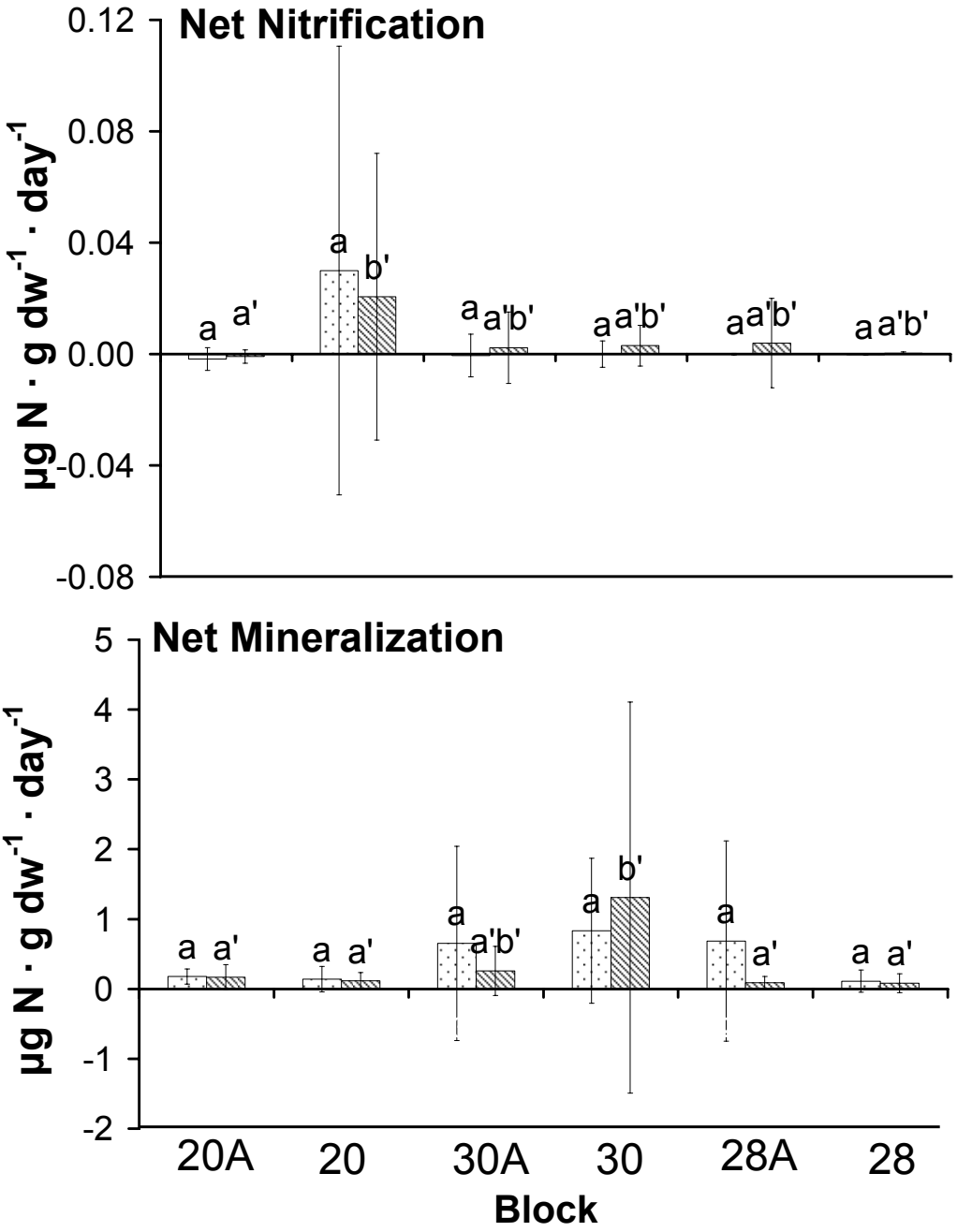

Figure 27. Net nitrification and N mineralization rates in the ⬚ O2 layer and ▨ Mineral layer. Lower case letters indicate significant differences between blocks within the same soil layer ($p < 0.05$). There was no significant difference between O2 and Mineral layers ($p < 0.05$). dw is dry soil weight. Each bar shows the average (n = 5) and ± 1 SD.

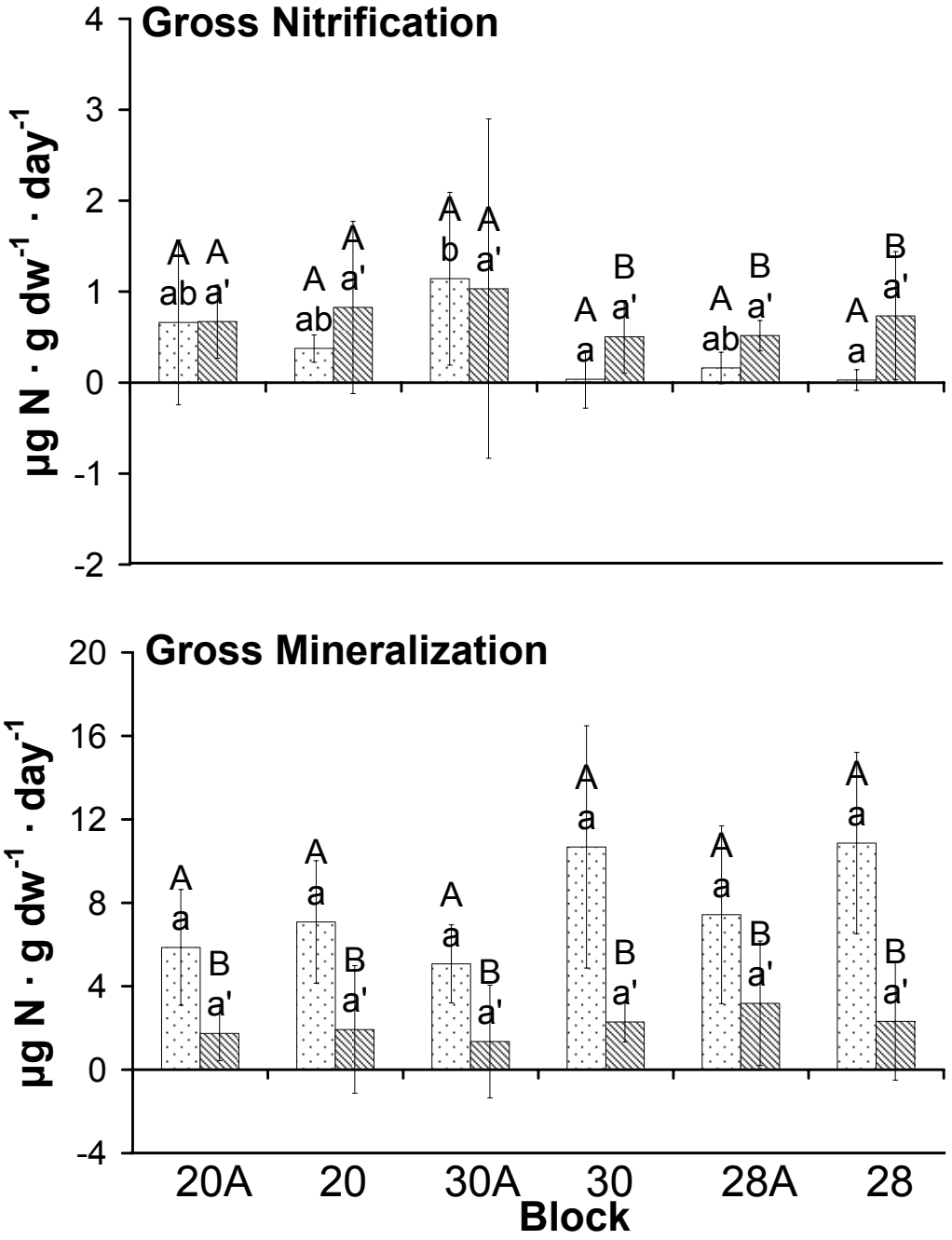

Figure 28. Gross nitrification and N mineralization rates in the ⊡ O2 layer and ▨ Mineral layer. Lower case letters indicate significant differences between blocks within the same soil layer ($p < 0.05$). Capital letters indicate significant differences between O2 and Mineral layers ($p < 0.05$). dw is dry soil weight. Each bar shows the average (n = 5) and ± 1 SD.

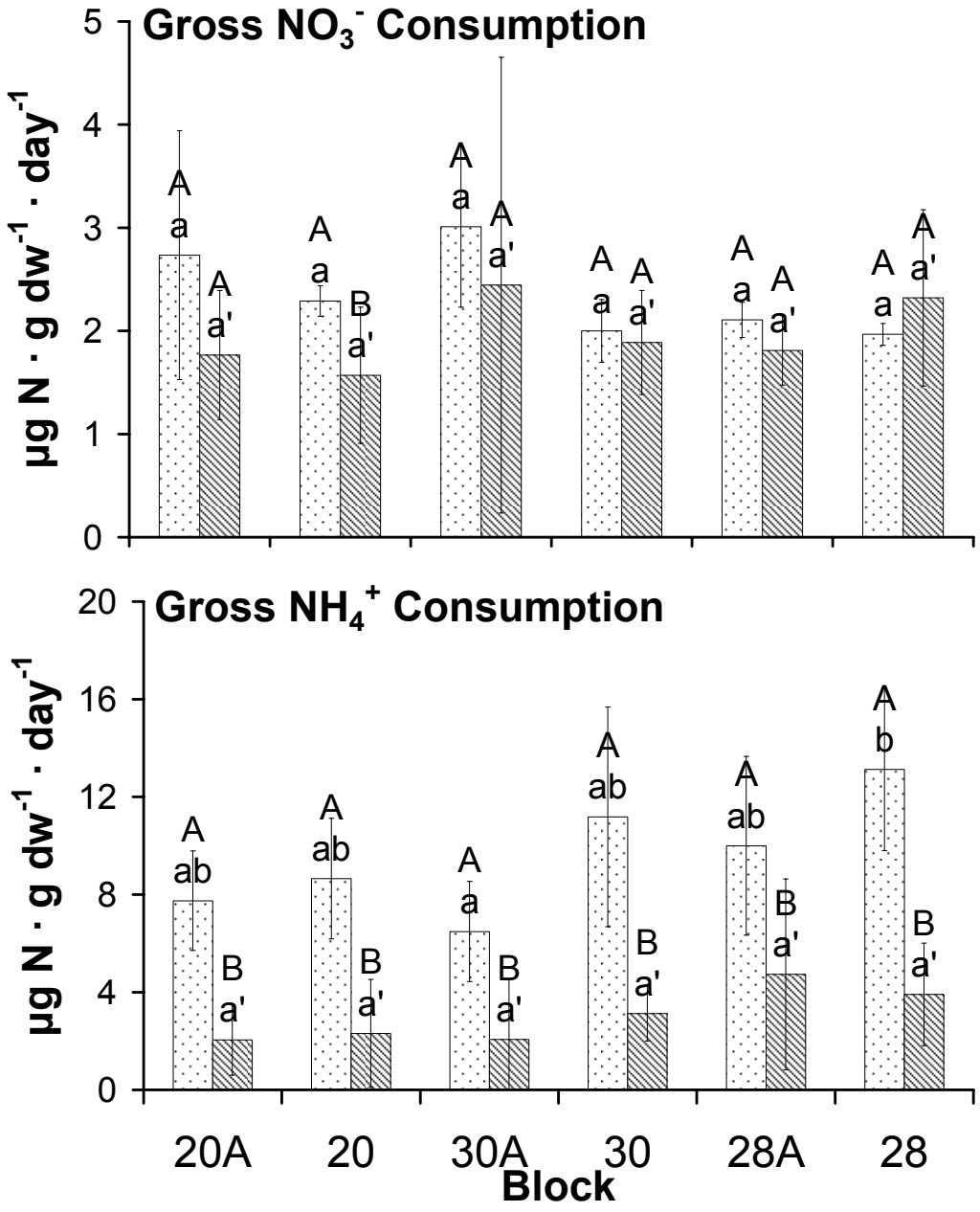

Figure 29. Gross consumption rates of NO_3^- and NH_4^+ in the ⬚ O2 layer and ▨ Mineral layer. Lower case letters indicate significant differences between blocks within the same soil layer ($p < 0.05$). Capital letters indicate significant differences between O2 and Mineral layers ($p < 0.05$). Each bar shows the average (n = 5) and ± 1 SD.

Table 11. Coefficients of correlation for N transformations and pool sizes. The correlation matrix was generated for data from all horizons, plots (wells), and blocks. For comparisons of gross rates, n = 60; for net rates, n = 210; and for comparisons including pool sizes n = 810.

	NO_3^--N †	NH_4^+-N †	NetNit †	NetMin †	GrossNit †	GrossMin	NO_3Con †	NH_4Con
NO_3^--N †	—	**.02**	**.28****	**.19****	**.08**	**.12**	**.23**	**.10**
NH_4^+-N †	.05	—	**.08**	**.57****	**-.27***	**.38****	**-.12**	**.37****
Net Nit †	.69**	.20*	—	**.15***	**.10**	**.09**	**.05**	**.06**
Net Min †	.18	.59**	.41**	—	**-.01**	**.10**	**-.08**	**.02**
GrossNit†	.17	-.28*	.17	-.06	—	**-.41****	**.61****	**-.40****
GrossMin	-.01	.38**	.25	.05	-.46**	—	**.09**	**.95****
NO_3 Con †	.19	-.10	.03	-.14	.58**	.02	—	**.17**
NH_4 Con	-.05	.37**	.08	-.01	-.51**	.96**	.10	—

*** Correlation is significant at the 0.05 level (two-tailed).**
**** Correlation is significant at the 0.01 level (two-tailed).**
† data log-transformed for normality for Pearson correlation coefficient determination
Pearson correlation coefficients calculated on the transformed data are shown in normal font in the bottom part of the table. Spearman non-parametric correlation coefficients calculated on raw data are shown in bold in the top half of the table. NetNit = Net Nitrification, NetMin = Net Mineralization, GrossNit = Gross Nitrification, GrossMin = Gross mineralization, NO_3Con = Gross NO_3^- Consumption, NH_4Con = Gross NH_4^+ Consumption.

5.4 Discussion

5.4.1 Rates of nitrogen mineralization in forest soils

Mineralization of soil N depends on a wide range of factors including C/N ratio and N content (Bengtsson et al. 2003). In the soils at Bootleg Mountain, a positive correlation of MB-C to net mineralization (data not shown) and a negative correlation to gross NO_3^- consumption were found. These variations in results exhibit the inherent difficulty in obtaining consistent estimations of microbial biomass (Vandewerf and Verstraete 1987, Wardle and Ghani 1995, Bengtsson et al. 2003). Variations in gross mineralization and immobilization rates could not be connected with corresponding variations in microbial biomass in laboratory experiments using soils from deciduous forests in Sweeden (Bengtsson et al. 2003). In contrast, Davidson et al. (1992) found positive correlations of MB-N to gross mineralization, gross nitrification, gross NH_4^+ consumption, and gross NO_3^- consumption in field incubations of soils from coniferous forests in the Sierra Nevada, California. Gross mineralization rate was found to be dependent on forest soil moisture and temperature, but not on microbial biomass-N (Puri and Ashman 1998).

The soils at Bootleg Mountain exhibited very low rates of net mineralization in comparison to the literature. In undisturbed temperate and boreal forests, a minimum of about 5-10 kg to a maximum of 100 kg of N is mineralized and taken up each year (Attiwill and Adams 1993). The soil mineral layer in a *Pinus patula* stand in South Africa, mineralized 5 $\mu g\ N \cdot d^{-1}$ (Dames et al. 2002). Net mineralization rates from laboratory incubations in the boreal conifer stands in northern Alberta were found to be -1.29 $\mu g \cdot g^{-1}\ dw \cdot d^{-1}$. This negative value indicates net assimilation, rather than mineralization and is likely a reflection of the method in that the samples were not under

actual environmental fluctuations occurring at a research site as in the buried bag method (Lindo and Visser 2003).

Rates of net mineralization may be lowered because of N limitation, but Magill and Aber (2000) demonstrated that microbial growth could also be limited by the lack of labile carbon (such as DOC) as an available energy source, even when levels are increased. Rapid immobilization of N will occur in the presence of a labile carbon source. Net mineralization rates in the soils of the European coniferous stands in the NITREX study ranged from 1.3 to 8.1 g $N \cdot m^{-2} \cdot yr^{-1}$ in the organic layer and from 2.2 to 9.0 g $N \cdot m^{-2} \cdot yr^{-1}$ in the mineral soil (Gundersen et al. 1998). In contrast to what was found at Bootleg Mountain, Gundersen et al. (1998) found that net and laboratory-determined gross rates of mineralization were significantly correlated. However, they did not determine field gross rates, so their data were not subject to external factors such as temperature, time of incubation, and soil moisture contents. In the soils of coniferous forest stands in the Sierra Nevada, California, Davidson et al. (1992) suggested that the poor correlation between gross and net rates of mineralization is probably due to multiple microbial processes that are occurring within the buried bags.

Net N mineralization was at its highest during the summer in the lodgepole pine ecosystems of southeastern Wyoming (20 mg $\cdot m^{-2} \cdot d^{-1}$) (Fahey et al. 1985) which was lower, but still close to the rates of 43 mg $\cdot m^{-2} \cdot d^{-1}$ and 34 mg $\cdot m^{-2} \cdot d^{-1}$ in the soil at Bootleg Mountain for the O2 and mineral layers, respectively. Also, rates of net mineralization were lower than the rates of gross mineralization, which fits with the apparent high demand of the soils for inorganic N. Thus, net mineralization may represent the amount of N available to plants. This difference between net and gross

mineralization was also observed in the mixed conifer stands in both the O2 (net mineralization: 0.14 – 1.14 μg N · g^{-1} dw · d^{-1} and gross mineralization: 20 – 41 μg N · g^{-1} dw · d^{-1}) and mineral layer (net mineralization: -0.02 – 0.10 μg N · g^{-1} dw · d^{-1} and gross mineralization: 2.0 – 5.7 μg N · g^{-1} dw · d^{-1}) [unpublished data from E. Davidson, S. Hart, J. Stark, and M. Firestone, quoted from Binkley and Hart (1989)]. These rates were quite similar to that found at Bootleg Mountain.

A large range of results for gross mineralization rates has been found. The soils at Bootleg Mountain exhibited high coefficients of variation (Table 11) and this range is also exhibited in the literature. In three soils from deciduous stands in southwestern Sweden the gross mineralization rates were found to be 22.5, 3.9, and 2.7 μg N · g^{-1} · d^{-1} (Bengtsson et al. 2003). In laboratory experiments of soils from the Harvard Research Forest, Compton and Boone (2002) found gross NH_4^+ mineralization to range between 17 and 80 μg N · g^{-1} · d^{-1}, and Davidson et al. (1991) found rates of 10-42 μg N · g^{-1} · d^{-1} in conifer stands at the Blodgett Research Forest in California. Gross mineralization seems to be a better estimate of available inorganic N in the soils at Bootleg Mountain.

5.4.2 Rates of nitrification in forest soils

The low concentration of NO_3^- found in forest soils has often been attributed to low rates of nitrification (Vitousek et al. 1982, Gosz and White 1986, Bengtsson et al. 2003). This is supported by the low net nitrification rates found during incubations. No net nitrification was detected in the soils from a mixed hardwood stand at the Harvard Forest and no NO_3^--N was detected in the laboratory incubated soils (Magill and Aber 2000). In contrast, Lindo and Visser (2003) in boreal conifer in northern Alberta stands found a net nitrification rate of 1.12 μg · g^{-1} dw · d^{-1} in soils with elevated concentrations of NH_4^+.

Net nitrification was -0.4 to 1.5 g N · m^{-2} · yr^{-1} in the organic layer and 0.9 to 3.2 g N · m^{-2} · yr^{-1} in the soils of the European coniferous stands for the NITREX study (Gundersen et al. 1998). As in the buried bags from Bootleg Mountains, Fahey et al. (1985) observed little to no net nitrification in the short-term (30 day) buried bags but during longer incubations (6 months), high NO_3^- accumulation was observed. There may be a long lag period before nitrification occurs (Gosz and White 1986, Hart et al. 1994). This is likely because the nitrifier populations have so little substrate and take a longer time to respond to higher NH_4^+ availability. As suggested by Fahey and Knight (1986) and Fahey et al. (1985) in the lodgepole pine ecosystems of Wyoming, it is probable that due to the relatively dry and aerobic conditions at Bootleg Mountain, in addition to extremely low availability of NO_3^-, losses of N via denitrification or volatilization are negligible. At both Bootleg Mountain and at the Blodgett Research Forest in California (Davidson et al. 1992), gross nitrification was greater than net nitrification. This finding may reflect immobilization of NO_3^- or low NO_3^- production from slow growing nitrifier populations during the buried bag experiment.

Gross nitrification rates in the forest soils at Blodgett Research Forest in California ranged between 20 and 100 mg · m^{-2} · d^{-1} (Davidson et al. 1991, Davidson et al. 1992). Also, a rate of 81 mg · m^{-2} · d^{-1} was determined in the top 10 cm mineral soil of a northern hardwood forest in plots with spring ephemerals (Zak et al. 1990). These examples are quite comparable to the rates found at Bootleg Mountain (O2 layer: 20.4 mg · m^{-2} · d^{-1}; Mineral layer: 36.2 mg · m^{-2} · d^{-1}), and still exhibit the inherently low N availability in forest soils in which most, if not all of the inorganic N tends to be immobilized, rather than nitrified or mineralized.

The positive relationship of net nitrification to net mineralization determined at Bootleg Mountain was also observed by Davidson et al. (1992) and is likely related to the method used and the concurrent production of NO_3^- and NH_4^+. In contrast, the negative correlation between gross rates of nitrification and mineralization is likely due to the high immobilization rates observed at Bootleg Mountain.

5.4.3 Rates of N immobilization in forest soils

Measurements of gross nitrification have suggested a rapid turnover of a small NO_3^- pool in forest soils in which the dominant fate of NO_3^- and NH_4^+ is immobilization (Bengtsson et al. 2003). Such immobilization can prevent the leakage of NO_3^- to ground and surface waters (Bengtsson et al. 2003). According to Fahey et al. (1985), higher rates of immobilization than mineralization and nitrification coupled to a lack of groundwater showed that lodgepole pine forests retain most of the N from precipitation. In the soils of Bootleg Mountain and at the Harvard Research forest (Dail et al. 2001), NO_3^- production via nitrification was matched by equal or greater rates of plant uptake and microbial immobilization which shows how tightly N is cycled within this ecosystem.

Despite the obvious importance of soil microorganisms in the turnover and retention of N in forest soils, the causes of variation in the degree of immobilization of N from one soil to another and between abiotic and biotic processes are not well known (Bengtsson et al. 2003). Magill and Aber (2000) concluded that immobilization of N by heterotrophic organisms appeared to be stimulated by additions of labile C because of greater availability of substrate for use by the microogranisms. Fahey and Knight (1986) suggested that the bulk of the competition for available mineral N is between the tree roots and decomposers (like fungi). Large amounts of labile C may be required to drive

the N-immobilization process in soil organic matter (Aber et al. 1998, Gundersen et al. 1998) and it is hypothesized that DOC concentrations would be high in N-limited systems and low at N-saturated conditions. Such a relationship in the groundwater was observed at Bootleg Mountain since TIN was negatively correlated to DOC in the groundwater (see Chapter 4). However, in the soils at Bootleg Mountain, the opposite relationship was noted (see Chapter 3). Nitrogen was so low in the soils that N saturation conditions were unlikely. In contrast to the apparent N limitation occurring in the soils from Bootleg Mountain, immobilization was not an important process in the soils for the NITREX study because N saturation had likely occurred and plants and microbes had more N than is required for metabolism (Gundersen et al. 1998).

Nitrate added to soil is immobilized rapidly and may include both abiotic and biotic pathways (Dail et al. 2001). In soils from Harvard Forest, Dail et al. (2001) found that 30-60% of added $^{15}NO_3^-$ was immobilized within 15 min. In the soils from Bootleg Mountain all of the added $^{15}NO_3^-$ was immobilized after 24 hours.

In future research, it would be important to determine the rate of 'fast' immobilization in the soils from Bootleg Mountain, as it is likely that the results would be very similar to that of Dail et al. (2001). There is a possibility that gross immobilization is stimulated by the addition of ^{15}N and may be overestimated by the isotope dilution method (Davidson et al. 1991). Rates of gross NO_3^- immobilization in the Harvard forest plots were found to be on average 125 mg $NO_3^- \cdot m^{-2} \cdot d^{-1}$ (Berntson and Aber 2000). Higher rates of immobilization (235 mg $NO_3^- \cdot m^{-2} \cdot d^{-1}$ in the O2 layer and 197 mg $NO_3^- \cdot m^{-2} \cdot d^{-1}$ in the mineral layer) were measured at Bootleg Mountain. Such elevated rates may reflect the general N deficiency in soils at Bootleg Mountain. Comparable to that found at Bootleg

Mountain (Table 10), Bengtsson et al. (2003) found gross NO_3^- immobilization rates to be 3.5, 1.5 and 0.1 μg $N \cdot g^{-1} \cdot d^{-1}$, respectively for the three soils studied in deciduous forests in southwestern Sweden. Furthermore, only after the immobilization capacity is reached, will NO_3^- leach from ecosystems (Berntson and Aber 2000). Currently, N saturation is not occurring at Bootleg Mountain which prevents any significant leaching of NO_3^- into the groundwater.

Gross NH_4^+ immobilization was found to be higher than gross NO_3^- immobilization in the soils which is consistent with the old and new forest stands in the Sierra Nevada (Davidson et al. 1992). The gross NH_4^+ immobilization rates (26.4 mg $N \cdot kg^{-1} \cdot d^{-1}$) were also higher than gross NO_3^- immobilization rates (2.8 mg $N \cdot kg^{-1} \cdot d^{-1}$) in the ground soils of a lowland forest in Costa Rica (Wanek et al. 2002). In the three soils of deciduous stands in southwestern Sweden, gross NH_4^+ immobilization was 37.5, 4.2 and 0 mg $N \cdot kg^{-1} \cdot d^{-1}$, respectively (Bengtsson et al. 2003). Also, immobilization rates varied between 0.5 and 1.7 mg $N \cdot kg^{-1} \cdot d^{-1}$ in sandy loams of a mature oak woodland (Puri and Ashman 1999). These findings were within the range of results found at Bootleg Mountain and could likely be related to either 1) the size of the ammonium pool; or 2) the preference of soil microbes for NH_4^+ for assimilation into amino acids. Ammonium rather than NO_3^- is preferentially used by most bacteria because they lack a specific nitrate reductase even though NO_3^- may be more easily assimilated or immobilized from the soil pore water.

5.4.4 Summary

Spatial heterogeneity across the research site did not play a major role in the distribution of nitrification and N mineralization rates in the soil at Bootleg Mountain.

Relative to the other blocks, Block 30A was only found to be significantly higher in the O2 layer for the rates of gross nitrification that were observed. Similarly, Block 30 had significantly higher rates of net mineralization in the mineral layer, which was likely related to the higher NH_4^+-N pools observed.

Along the different soil horizons, there was little difference between the O2 and mineral layers for most of the experiments performed except for determinations of gross mineralization and gross NH_4^+ consumption. The small difference between the O2 and mineral layers is likely due to the lower organic C contents in the mineral layer reported in Chapter 3. These changes in the C/N ratios in different soil layers may also affect the rates of mineralization (Bengtsson et al. 2003). However, there is still a need for further study on the mineralization processes occurring in these soils. Comparison of field and laboratory incubations would aid in the determination of experimental scaling (from plot to block to entire area) and prediction in the rates of mineralization within this ecosystem (Gundersen et al. 1998).

Due to the expense of determining gross rates by ^{15}N pool dilutions, only one measurement was obtained at each sampling location at Bootleg Mountain. The results yield the following conclusions: 1)inorganic N pools in the soils of this ecosystem are small; thus N tends to be limiting; 2) the chloroform fumigation method may not be a good estimate of microbial biomass in forest soils; 3) immobilization of both NH_4^+ and NO_3^- in the soils is of greater importance to N availability than mineralization and nitrification; 4) the determination of net rates underestimates mineralization and nitrification but still provides a cheap and easy way to estimate the transformations of NH_4^+ and NO_3^- in forest soils; 5) there is a possible lag time before nitrification will

occur in buried bags because NH_4^+ has to accumulate; and 6) NO_3^- is quickly and efficiently cycled at Bootleg and losses to the groundwater are likely to be minimal.

Nitrate is quite important in forest ecosystems and elevated levels due to anthropogenic inputs of the ion may disrupt the tight cycling currently occurring in the soils at Bootleg Mountain, as revealed by the research project. Harvesting could also change the fate of NO_3^- and may increase exports out of the system. This possibility continues to offer a research challenge. Future work should explore the effects of harvesting on soils like those of Bootleg Mountain in order to fully assess the mechanisms that control NO_3^- retention in lodgepole pine stands. The accelerating decimation of British Columbia's lodgepole pine forests by the mountain pine beetle and now the associated mass harvesting that is now underway adds a compelling dimension to such a research program.

Chapter 6
Overall conclusions

6.1 Interactions between the soil, snow, and water in lodgepole pine ecosystems

Water plays a large role in the pool sizes and cycling of nutrients. The significant differences between the organic and mineral layers observed in the variables studied at Bootleg Mountain showed how strongly the amount of water affected all aspects of this ecosystem. A threshold for soil moisture contents of approximately 50% affects the amounts of inorganic N that is available in soils (Prescott et al. 2003). Thus, ephemeral flushes of snowmelt with associated higher groundwater tables have the potential to introduce atmospheric nutrients and mobilize nutrients stored in the organic layer (Creed and Band 1998b). As the summer season progresses, groundwater levels and nutrient contents in the groundwater generally decrease, but this observation is often not obvious if only one variable at a time is considered (Knight et al. 1991). For example, the NO_3^- concentrations in the groundwater appeared to increase with decreasing amount of groundwater, but when the ratio of water/NO_3^- was determined, the seasonal decrease was observed. Nutrients in the soil, groundwater, and snow when considered individually are relatively homogeneous at the scale used in this study. However, the soil water contents and groundwater depths in the blocks introduced some of the spatial heterogeneity that was expected at Bootleg Mountain.

Dissolved organic C, N, and P are also tightly linked. It was hypothesized by Fahey and Yavitt (1988) that P dynamics may be the key component in lodgepole pine ecosystems and that rapid mineralization of organic P leads to responses in the N and

DOC pools. At Bootleg Mountain the C/N/P ratios in the snow, soil, and groundwater were 121/1/1, 132/0.6/1, and 4900/41/1, respectively. This indicates that N and P may be limiting at different times such that the snow was fairly limited in both N and P, the soil was limited in N and the groundwater was limited in P.

Though the relationship may be unclear in some analyses, fluxes of DOC are related to the N cycle in coniferous forests (Gundersen et al. 1998). Dissolved organic C in soil (1.50 ± 1.01 Mg · ha^{-1}) was greater than in the groundwater (0.16 ± 0.09 Mg · ha^{-1}) or in the snow (0.06 ± 0.04 Mg · ha^{-1}), showing that the main source of DOC was from particulate organic matter in the soils rather than an annual input via the snow (Michalzik et al. 2003).

In the soils at Bootleg Mountain, the total inorganic N pools were greater in the soil (7.24 ± 6.44 kg · ha^{-1}) than in the groundwater (1.31 ± 1.19 kg · ha^{-1}) or in the snow (0.46 ± 0.30 kg · ha^{-1}). In contrast, Fahey et al. (1985) found in the lodgepole pine forests of southeastern Wyoming that the inflow of N via precipitation exceeded the outflow of N (which was less than 5% of the input) when the N budget was determined. Consideration of the snow data from a sole sampling date made it difficult in this study to determine if there was a high retention of N in the Bootleg Mountain soils.

Ammonium was more dominant in the organic soil layers but had inventories equivalent to NO_3^--N in mineral layers. For the NH_4^+-N pools, soil (5.62 ± 5.90 kg · ha^{-1}) was greater than in the groundwater (0.40 ± 0.59 kg · ha^{-1}) and in the snow (0.12 ± 0.08 kg · ha^{-1}). The higher NH_4^+-N in the groundwater could be due to increased mineralization of organic N as the snowmelt water moves through the soil (Williams and

Melack 1991) or because NH_4^+-N adsorbs to sediment particles present in the groundwater (Ettema et al. 1999).

Immobilization of most, if not all, of the inorganic N was likely occurring at all soil depths. Indeed, the extremely low levels of NO_3^- seen in most forest ecosystems are likely caused by the high rate of immobilization. This leads to an efficient N cycle (Dail et al. 2001).

Phosphorus was found to be quite high in the organic layer and will tend to remain there unless it is mineralized or decomposed by soil microbial action (Litton and Santelices 2003). Phosphate pools in the soil (11.4 ± 11.2 kg · ha^{-1}) were greater than in the snow (0.47 ± 0.48 kg · ha^{-1}) or in the groundwater (0.03 ± 0.03 kg · ha^{-1}). This suggests that at Bootleg Mountain, PO_4^{3-} was being deposited into this ecosystem but very little PO_4^{3-} was flushed out of the soils during the spring. This same trend was exhibited in other studies that found that PO_4^{3-} was strongly retained by mineral soils that does not allow for significant phosphate leaching, even after a disturbance such as logging (Likens 1981, Piirainen et al. 2004, Fernandez-Perez et al. 2005).

Rates of mineralization and nitrification are also related to the moisture contents in the soils. Considering the seasonal differences in these rates would allow for determinations of the annual N fluxes through Bootleg Mountain. Although the buried bag method is a simple way to determine changes in the N pools, the net rates of mineralization and nitrification underestimate what was determined through ^{15}N pool dilution experiments for gross rates of mineralization and nitrification. The low inorganic N pool sizes, low rates of mineralization and nitrification, and small seasonal changes occurring in the groundwater all indicate a soil whose primary productivity is limited by N at Bootleg

Mountain. Following clear-cutting, rates of N mineralization and nitrification have been found to be elevated in the forest floors and mineral layers (Prescott et al. 2003). Coupled with the reports of elevated NO_3^- in the soil and drainage waters, harvesting may result in major changes to the tightly cycling N in these ecosystems (Vitousek et al. 1979, Likens and Bormann 1995).

Fluxes of inorganic N between the snow, soil, and groundwater are likely not going to change significantly over the season (Binkley and Hart 1989), but in the groundwater there were slightly increased levels of NO_3^- due to increased mobility during the spring snowmelt. Looking at the NO_3^- pools, again it was noted that the soil (3.07 ± 2.68 kg $\cdot$ ha^{-1}) was greater than in the groundwater (0.82 ± 1.10 kg $\cdot$ ha^{-1}) and in the snow (0.32 ± 0.26 kg $\cdot$ ha^{-1}). Lodgepole pine ecosystems retain most of the N deposited via precipitation and outputs are generally quite minimal.

Long-term monitoring at this site should develop a clearer picture of N, P, and C pools, the annual rates of cycling, and help in determining the factors that will allow the management of this ecosystem to ensure the quality of drinking water in the nearby reservoir. Phosphorus is highly retained in the soils, thus P tends to be low in the groundwater. Harvesting and the subsequent soil exposure will likely lead to the release of P and N into the ground and surface waters because of changes to the C/N/P ratios. However, since N is so quickly immobilized in these soils, there may be a lag period before an excess of N becomes available for leaching. The spring snowmelt period would likely result in the greatest leaching of NO_3^- after harvesting. A pattern of increased losses of nutrients to stream water has been observed elsewhere following both fires and harvesting (Kimmins 2004). This research could also be used for the prediction

of the effects of harvesting on Rocky Mountain ecosystems in that careful monitoring of the snow, soil, and groundwater post harvest could support future policies that would help to prevent losses of N and P from exceeding the limit where increased algal growth will occur in the drinking water reservoir.

6.2 Future research directions

Church and Driscoll (1997) suggested that the effects of disturbances (fire, harvesting) on N fluxes in ecosystems warrant investigation on both short- and long-term time scales. The extent and type of microbial transformations (N fixation, denitrification, nitrification, N mineralization) in soils, as well as enumeration of the microbes involved should also be considered in such work.

It is recommended that research should continue at the Bootleg Mountain site, as a sampling regime and experimental plots have already been established. Future disturbances should be monitored. Exploration of the effects of anthropogenic and non-anthropogenic disturbances will help to resolve uncertainties that surround our understanding of transformations in soils that are mediated by microbes. Specific processes of interest include N fixation, nitrification, N mineralization, and denitrification (Likens and Bormann 1995).

This before-harvest study has provided a database that will aid future predictions of the effects of increasing or decreasing a rate or a pool size at the Bootleg Mountain site. For example, changes to the rates of microbial activity in the soil, groundwater, and surface water may occur as a result of changing the system from being N limited to N saturated. Continued biogeochemical and microbial monitoring at Bootleg Mountain will provide an ability to evaluate the impacts of future tree harvesting on N cycling.

Bibliography

Aber, J.D., McDowell, W., Nadelhoffer, K.J., Magill, A., Berntson, G., Kamakea, M., McNulty, S., Currie, W., Rustand, L., and Fernandez, I. 1998. Nitrogen saturation in temperate forest ecosystems: hypothesis revisited. Bioscience **49**: 921-934.

Aber, J.D., Nadelhoffer, K.J., Steudler, P., and Melillo, J.M. 1989. Nitrogen saturation in northern forest ecosystems. Bioscience **39**(6): 378-386.

Adams, V.D. 1990. Water and Wastewater Examination Manual. Lewis Publishers, Boca Raton.

Addy, K.L., Gold, A.J., Groffman, P.M., and Jacinthe, P.A. 1999. Ground water nitrate removal in subsoil of forested and mowed riparian buffer zones. Journal of Environmental Quality **28**(3): 962-970.

Ander, P., Mishra, C., Farrell, R.L., and Eriksson, K.E.L. 1990. Redox reactions in lignin degradation - interactions between laccase, different peroxidases and cellobiose - quinone oxidoreductase. Journal of Biotechnology **13**(2-3): 189-198.

Arthur, M.A. and Fahey, T.J. 1992. Biomass and nutrients in an Engelmann spruce - sub-alpine fir forest in North Central Colorado - pools, annual production, and internal cycling. Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere **22**(3): 315-325.

Asner, G.P., Townsend, A.R., Riley, W.J., Matson, P.A., Neff, J.C., and Cleveland, C.C. 2001. Physical and biogeochemical controls over terrestrial ecosystem responses to nitrogen deposition. Biogeochemistry **54**(1): 1-39.

Attiwill, P.M. and Adams, M.A. 1993. Nutrient cycling in forests. New Phytologist **124**(4): 561-582.

Baron, J.S., Rueth, H.M., Wolfe, A.M., Nydick, K.R., Allstott, E.J., Minear, J.T., and Moraska, B. 2000. Ecosystem responses to nitrogen deposition in the Colorado Front Range. Ecosystems **3**(4): 352-368.

Bengtsson, G., Bengtson, P., and Mansson, K.F. 2003. Gross nitrogen mineralization-, immobilization-, and nitrification rates as a function of soil C/N ratio and microbial activity. Plant and Soil **35**(1): 143-154.

Berntson, G.M. and Aber, J.D. 2000. Fast nitrate immobilization in N saturated temperate forest soils. Soil Biology & Biochemistry **32**(2): 151-156.

Binkley, D., Burnham, H., and Allen, H.L. 1999. Water quality impacts of forest fertilization with nitrogen and phosphorus. Forest Ecology and Management **121**(3): 191-213.

Binkley, D. and Hart, S.C. 1989. The components of nitrogen availability assessments in forest soils. Advances in Soil Science **10**: 57-112.

Blackburn, T.H. and Knowles, R. 1993. Introduction. *In* Nitrogen Isotope Techniques. ed(s). R. Knowles and T.H. Blackburn. Academic Press, Inc., San Diego, Ca. pp. 1-10.

Bock, M.D. and Van Rees, K.C.J. 2002. Forest harvesting impacts on soil properties and vegetation communities in the Northwest Territories. Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere **32**(4): 713-724.

Boyer, E.W., Hornberger, G.M., Bencala, K.E., and McKnight, D.M. 1995. Variation of dissolved organic carbon during snowmelt in soil and streamwaters of two headwater catchments, Summit County, Colorado. Biogeochemistry of Snow-Covered Catchments. IAHS Publications **228**: 303-312.

Brooks, P.D., Stark, J.M., Mcinteer, B.B., and Preston, T. 1989. Diffusion method to prepare soil extracts for automated ^{15}N analysis. Soil Science Society of America Journal **53**(6): 1707-1711.

Brye, K.R., West, C.P., and Gbur, E.E. 2004. Soil quality differences under native tallgrass prairie across a climosequence in Arkansas. American Midland Naturalist **152**(2): 214-230.

Church, M.R. and Driscoll, C.T. 1997. Nitrogen cycling in forested catchments: A Chapman Conference. Global Biogeochemical Cycles **11**(4): 613-616.

Clough, T.J., Stevens, R.J., Laughlin, R.J., Sherlock, R.R., and Cameron, K.C. 2001. Transformations of inorganic-N in soil leachate under differing storage conditions. Soil Biology & Biochemistry **33**(11): 1473-1480.

Compton, J.E. and Boone, R.D. 2002. Soil nitrogen transformations and the role of light fraction organic matter in forest soils. Plant and Soil **34**(7): 933-943.

Coupé, R., Stewart, A.C., and Wikeem, B.W. 1991. Chapter 15: Englemann Spruce-Subalpine Fir Zone. *In* Ecosystems of British Columbia. ed(s). J. Pojar. B.C. Ministry of Forests, Victoria, B.C.

Creed, I.F. and Band, L.E. 1998a. Exploring functional similarity in the export of nitrate-N from forested catchments: A mechanistic modeling approach. Water Resources Research **34**(11): 3079-3093.

Creed, I.F. and Band, L.E. 1998b. Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. Water Resources Research **34**(11): 3105-3120.

Currie, W.S. 1999. The responsive C and N biogeochemistry of the temperate forest floor. Trends in Ecology & Evolution **14**(8): 316-320.

Currie, W.S., Aber, J.D., McDowell, W.H., Boone, R.D., and Magill, A.H. 1996. Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. Biogeochemistry **35**(3): 471-505.

Dail, D.B., Davidson, E.A., and Chorover, J. 2001. Rapid abiotic transformation of nitrate in an acid forest soil. Biogeochemistry **54**(2): 131-146.

Dames, J.F., Scholes, M.C., and Straker, C.J. 2002. Nutrient cycling in a *Pinus patula* plantation in the Mpumalanga Province, South Africa. Applied Soil Ecology **20**(3): 211-226.

Datry, I., Malard, F., and Gibert, J. 2004. Dynamics of solutes and dissolved oxygen in shallow urban groundwater below a stormwater infiltration basin. Science of the Total Environment **329**(1-3): 215-229.

Davidson, E.A., Chorover, J., and Dail, D.B. 2003. A mechanism of abiotic immobilization of nitrate in forest ecosystems: the ferrous wheel hypothesis. Global Change Biology **9**(2): 228-236.

Davidson, E.A., Hart, S.C., and Firestone, M.K. 1992. Internal cycling of nitrate in soils of a mature coniferous forest. Ecology **73**(4): 1148-1156.

Davidson, E.A., Hart, S.C., Shanks, C.A., and Firestone, M.K. 1991. Measuring gross nitrogen mineralization, immobilization, and nitrification by ^{15}N isotopic pool dilution in intact soil cores. Journal of Soil Science **42**(3): 335-349.

Donald, R.G., Anderson, D.W., and Stewart, J.W.B. 1993. Potential role of dissolved organic carbon in phosphorus transport in forested soils. Soil Science Society of America Journal **57**(6): 1611-1618.

Ebina, J., Tsutsui, T., and Shirai, T. 1983. Simultaneous determination of total nitrogen and total phosphorus in water using peroxodisulfate oxidation. Water Research **17**(12): 1721-1726.

Eno, C.H. 1960. Nitrate production in the field by incubating the soil in polyethylene bags. Soil Science Society of America Proceedings **24**: 277-279.

Environment-Canada. 2004. Canadian climate normals, Cranbrook, British Columbia. Environment Canada, Ottawa, Ont. [online] Available from http://climate.weatheroffice.ec.gc.ca/climate_normals/results_e.html [cited 1 March 2005].

Ettema, C.H., Lowrance, R., and Coleman, D.C. 1999. Riparian soil response to surface nitrogen input: temporal changes in denitrification, labile and microbial C and N pools, and bacterial and fungal respiration. Soil Biology & Biochemistry **31**(12): 1609-1624.

Fagre, D.B. 2002. Snowpack analysis of chemical loading in Glacier National Park. U.S. Geological Society. [online] Available from http://www.nrmsc.usgs.gov/research/snowpack_analysis.htm [cited 13 April 2003].

Fahey, T.J. and Knight, D.H. 1986. Lodgepole pine ecosystems. Bioscience **36**(9): 610-616.

Fahey, T.J. and Yavitt, J.B. 1988. Soil solution chemistry in lodgepole pine (*Pinus contorta ssp. latifolia*) ecosystems, Southeastern Wyoming, USA. Biogeochemistry **6**(2): 91-118.

Fahey, T.J., Yavitt, J.B., Pearson, J.A., and Knight, D.H. 1985. The nitrogen-cycle in lodgepole pine forests, Southeastern Wyoming. Biogeochemistry **1**(3): 257-275.

Fernandez-Perez, M., Flores-Cespedes, F., Gonzaalez-Pradas, E., Urena-Amate, M.D., Villafranca-Sanchez, M., Socias-Viciana, M., and Perez-Garcia, S. 2005. Effects of dissolved organic carbon on phosphate retention on two calcareous soils. Journal of Agricultural and Food Chemistry **53**(1): 84-89.

Fiedler, S. and Kalbitz, K. 2003. Concentrations and properties of dissolved organic matter in forest soils as affected by the redox regime. Soil Science **168**(11): 793-801.

Froehlich, H.A. 1979. Soil compaction from logging equipment - effects on growth of young ponderosa pine. Journal of Soil and Water Conservation **34**(6): 276-278.

Gee, G.W. and Bauder, J.W. 1986. Particle-Size Analysis *In* Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods - Agronomy Monograph No. 9. Second Edition. American Society of Agronomy-Soil Science Society of America, Madison, WI.

Gosz, J.R. and White, C.S. 1986. Seasonal and annual variation in nitrogen mineralization and nitrification along an elevational gradient in New Mexico. Biogeochemistry **2**(3): 281-297.

Groffman, P.M., Howard, G., Gold, A.J., and Nelson, W.M. 1996. Microbial nitrate processing in shallow groundwater in a riparian forest. Journal of Environmental Quality **25**(6): 1309-1316.

Gundersen, P., Emmett, B.A., Kjonaas, O.J., Koopmans, C.J., and Tietema, A. 1998. Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. Forest Ecology and Management **101**: 37-55.

Harris, D., Voroney, R.P., and Paul, E.A. 1997. Measurement of microbial biomass N : C by chloroform fumigation-incubation. Canadian Journal of Soil Science **77**(4): 507-514.

Hart, S.C., Nason, G.E., Myrold, D.D., and Perry, D.A. 1994. Dynamics of gross nitrogen transformations in an old-growth forest - the carbon connection. Ecology **75**(4): 880-891.

Hauer, F.R., Baron, J.S., Campbell, D.H., Fausch, K.D., Hostetler, S.W., Leavesley, G.H., Leavitt, P.R., McKnight, D.M., and Stanford, J.A. 1997. Assessment of climate change and freshwater ecosystems of the Rocky Mountains, USA and Canada. Hydrological Processes **11**(8): 903-924.

Hedin, L.O., von Fischer, J.C., Ostrom, N.E., Kennedy, B.P., Brown, M.G., and Robertson, G.P. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology **79**(2): 684-703.

Herman, D.J., Brooks, P.D., Ashraf, M., Azam, F., and Mulvaney, R.L. 1995. Evaluation of methods for ^{15}N analysis of inorganic nitrogen in soil extracts. 2. Diffusion methods. Communications in Soil Science and Plant Analysis **26**(11-12): 1675-1685.

Ingersoll, G.P. 2000. Snowpack chemistry at selected sites in Colorado and New Mexico during winter 1999-2000. U.S. Geological Society **Open-File Report 00-394**: 1-9.

Jenkinson, D.S., Brookes, P.C., and Powlson, D.S. 2004. Measuring soil microbial biomass. Soil Biology & Biochemistry **36**(1): 5-7.

Johnson, D.W., Susfalk, R.B., and Dahlgren, R.A. 1997. Nutrient fluxes in forests of the eastern Sierra Nevada Mountains, United States of America. Global Biogeochemical Cycles **11**(4): 673-681.

Kaiser, K., Guggenberger, G., Haumaier, L., and Zech, W. 2002. The composition of dissolved organic matter in forest soil solutions: changes induced by seasons and passage through the mineral soil. Organic Geochemistry **33**(3): 307-318.

Kaiser, K., Guggenberger, G., and Zech, W. 2001. Organically bound nutrients in dissolved organic matter fractions in seepage and pore water of weakly developed forest soils. Acta Hydrochimica Et Hydrobiologica **28**(7): 411-419.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., and Matzner, E. 2000. Controls on the dynamics of dissolved organic matter in soils: A review. Soil Science **165**(4): 277-304.

Kapoor, A. and Viraraghavan, T. 1997. Nitrate removal from drinking water - Review. Journal of Environmental Engineering-ASCE **123**(4): 371-380.

Kimmins, J.P. 2004. Forest Ecology: A Foundation for Sustainable Forest Management and Environmental Ethics in Forestry, 3rd Edition. Pearson Education, Inc., Upper Saddle River, NJ.

Kirkham, D. and Bartholomew, W.V. 1954. Equations for following nutrient transformation in soil, utilizating tracer data. Soil Science Society of America Journal **18**: 33-34.

Klute, A. ed. 1986. Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods - Agronomy Monograph No. 9. Second Edition. American Society of Agronomy-Soil Science Society of America, Madison, WI.

Knight, D.H., Fahey, T.J., and Running, S.W. 1985. Water and nutrient outflow from contrasting lodgepole pine forests in Wyoming. Ecological Monographs **55**(1): 29-48.

Knight, D.H., Yavitt, J.B., and Joyce, G.D. 1991. Water and nitrogen outflow from lodgepole pine forest after two levels of tree mortality. Forest Ecology and Management **46**(3-4): 215-225.

Knowles, R. 1975. Interpretation of recent ^{15}N studies of nitrogen in forest systems. *In* Forest soils and forest land management. Proceedings of the 4th North American Forestry Soil Conference, Laval University, Quebec. August 1973. ed(s). C.H. Winget. Laval University Press. pp. 53-65.

Knowles, R. 2000. Nitrogen cycle. Encyclopedia of Microbiology **3**: 379-391.

Kroeze, C., Vanfaassen, H.G., and Deruiter, P.C. 1989. Potential denitrification rates in acid soils under pine forest. Netherlands Journal of Agricultural Science **37**(4): 345-354.

Lea, E.C. 1989. Biophysical resources of the East Kootenay area: vegetation groups and types. *In* Ministry of Environment Technical Report 5, 1989. BC Environment.

Likens, G.E. ed. 1981. Some Perspectives of the Major Biogeochemical Cycles. John Wiley and Sons, Chichester, UK.

Likens, G.E. and Bormann, F.H. 1995. Biogeochemistry of a Forested Ecosystem, 2nd ed. Springer-Verlag, New York.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S., and Johnson, N.M. 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York.

Lindo, Z. and Visser, S. 2003. Microbial biomass, nitrogen and phosphorus mineralization, and mesofauna in boreal conifer and deciduous forest floors following partial and clear-cut harvesting. Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere **33**(9): 1610-1620.

Litton, C.M. and Santelices, R. 2003. Effect of wildfire on soil physical and chemical properties in a *Nothofagus glauca* forest, Chile. Revista Chilena de Historia Natural **76**: 529-542.

Mackown, C.T., Brooks, P.D., and Smith, M.S. 1987. Diffusion of ^{15}N Kjeldahl digests for isotope analysis. Soil Science Society of America Journal **51**(1): 87-90.

Magill, A.H. and Aber, J.D. 2000. Variation in soil net mineralization rates with dissolved organic carbon additions. Soil Biology & Biochemistry **32**(5): 597-601.

Male, D.H. and Gray, D.M. 1981. Handbook of Snow: Principles, Processes, Management and Use. Pergamon Press Canada, Willowdale, Ont.

Mcdowell, W.H., Currie, W.S., Aber, J.D., and Yano, Y. 1998. Effects of chronic nitrogen amendments on production of dissolved organic carbon and nitrogen in forest soils. Water Air and Soil Pollution **105**(1-2): 175-182.

Michalzik, B., Kalbitz, K., Park, J.H., Solinger, S., and Matzner, E. 2001. Fluxes and concentrations of dissolved organic carbon and nitrogen - a synthesis for temperate forests. Biogeochemistry **52**(2): 173-205.

Michalzik, B., Tipping, E., Mulder, J., Lancho, J.F.G., Matzner, E., Bryant, C.L., Clarke, N., Lofts, S., and Esteban, M.A.V. 2003. Modelling the production and transport of dissolved organic carbon in forest soils. Biogeochemistry **66**(3): 241-264.

Microsoft-Corporation. 2003. Microsoft Office Excel 2003. Part of Microsoft Office Profesional Edition 2003. Microsoft Corporation, Redmond, Wa.

Moore, T.R. 2003. Dissolved organic carbon in a northern boreal landscape. Global Biogeochemical Cycles **17**(4): 1-8.

Mullen, M.D. 1999. Transformations of Other Elements. *In* Principles and Applications of Soil Microbiology. ed(s). D.A. Zuberer. Prentic Hall Inc., New Jersey. pp. 370-377.

Mulvaney, R.L. 1996. Nitrogen - Inorganic forms. *In* Methods of Soil Analysis, Part 3. Chemical Methods, Vol. 3. ed(s). American Society of Agronomy-Soil Science Society of America, Madison, WI, USA.

Munch, J.M., Totsche, K.U., and Kaiser, K. 2002. Physicochemical factors controlling the release of dissolved organic carbon from columns of forest subsoils. European Journal of Soil Science **53**(2): 311-320.

Myrold, D.D. 1999. Transformations of nitrogen. *In* Principles and Applications of Soil Microbiology. ed(s). D.A. Zuberer. Prentice Hall, New Jersey. pp. 259-294.

Norwitz, G. and Keliher, P.N. 1986. Study of organic interferences in the spectrophotometric determination of nitrite using composite diazotization-coupling reagents. Analyst **111**(9): 1033-1033.

Nyberg, R.C. and Fahey, T.J. 1988. Soil hydrology in lodgepole pine ecosystems in Southeastern Wyoming. Soil Science Society of America Journal **52**(3): 844-849.

OI-Analytical. 2001a. Ammonia in soil and plant extracts by segmented flow analysis (SFA). Publication #15330501. OI Analytical Methodology, College Station TX.

OI-Analytical. 2001b. Nitrate plus nitrite nitrogen and nitrite nitrogen in soil and plant extracts by segmented flow analysis (SFA). Publication #15300301. OI Analytical Methodology. OI Analytical, College Station, TX.

Paul, K.I., Polglase, P.J., O'Connell, A.M., Carlyle, J.C., Smethurst, P.J., and Khanna, P.K. 2003. Defining the relation between soil water content and net nitrogen mineralization. European Journal of Soil Science **54**(1): 39-47.

Peterjohn, W.T. and Correll, D.L. 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. Ecology **65**(5): 1466-1475.

Piatek, K.B., Harrington, C.A., and DeBell, D.S. 2003. Site preparation effects on 20 year survival and growth of Douglas-fir (*Pseudotsuga menziesii*) and on selected soil properties. Western Journal of Applied Forestry **18**(1): 44-51.

Piirainen, S., Finer, L., Mannerkoski, H., and Starr, M. 2004. Effects of forest clear-cutting on the sulphur, phosphorus and base cations fluxes through podzolic soil horizons. Biogeochemistry **69**(3): 405-424.

Prescott, C.E., Hope, G.D., and Blevins, L.L. 2003. Effect of gap size on litter decomposition and soil nitrate concentrations in a high-elevation spruce-fir forest. Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere **33**(11): 2210-2220.

Puri, G. and Ashman, M.R. 1998. Relationship between soil microbial biomass and gross N mineralisation. Soil Biology & Biochemistry **30**(2): 251-256.

Puri, G. and Ashman, M.R. 1999. Microbial immobilization of ^{15}N-labelled ammonium and nitrate in a temperate woodland soil. Soil Biology & Biochemistry **31**(6): 929-931.

Qualls, R.G. and Haines, B.L. 1992. Biodegradability of dissolved organic-matter in forest throughfall, soil solution, and stream water. Soil Science Society of America Journal **56**(2): 578-586.

Rhine, E.D., Sims, G.K., Mulvaney, R.L., and Pratt, E.J. 1998. Improving the Berthelot reaction for determining ammonium in soil extracts and water. Soil Science Society of America Journal **62**(2): 473-480.

Robertson, G.P. 1982. Nitrification in forested ecosystems. Philosophical Transactions of the Royal Society of London Series B-Biological Sciences **296**(1082): 445-457.

Schimel, J.P. and Firestone, M.K. 1989. Nitrogen incorporation and flow through a coniferous forest soil-profile. Soil Science Society of America Journal **53**(3): 779-784.

Schmidt, M.G., Macdonald, S.E., and Rothwell, R.L. 1996. Impacts of harvesting and mechanical site preparation on soil chemical properties of mixed-wood boreal forest sites in Alberta. Canadian Journal of Soil Science **76**(4): 531-540.

Schwesig, D., Kalbitz, K., and Matzner, E. 2003. Mineralization of dissolved organic carbon in mineral soil solution of two forest soils. Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde **166**(5): 585-593.

Shimadzu-Corporation. 2001. PC-Controlled TOC Analyzer TOD-VCPH/CPN and TOC-Control V Software User Manual. Shimadzu, Kyoto, Japan.

Sievering, H., Rusch, D., and Marquez, L. 1996. Nitric acid, particulate nitrate and ammonium in the continental free troposphere: nitrogen deposition to an alpine tundra ecosystem. Atmospheric Environment **30**(14): 2527-2537.

Simmons, R.C., Gold, A.J., and Groffman, P.M. 1992. Nitrate dynamics in riparian forests - groundwater studies. Journal of Environmental Quality **21**(4): 659-665.

Small, H. and Bowman, B. 1998. Ion chromatography: A historical perspective. American Laboratory **30**(21): 56C-+.

Sokal, R.R. and Rohlf, F.J. 1981. Biometry: The Principles and Practice of Statistics in Biological Research. W. H. Freeman and Company, New York.

Solinger, S., Kalbitz, K., and Matzner, E. 2001. Controls on the dynamics of dissolved organic carbon and nitrogen in a Central European deciduous forest. Biogeochemistry **55**(3): 327-349.

Spalding, R.F. and Exner, M.E. 1993. Occurrence of nitrate in groundwater - a review. Journal of Environmental Quality **22**(3): 392-402.

SPSS-Inc. 2003. SPSS 12.0 for Windows. Version 12.0. SPSS Inc., Chicago Ill.

Stark, J.M. and Hart, S.C. 1997. High rates of nitrification and nitrate turnover in undisturbed coniferous forests. Nature **385**(6611): 61-64.

Startsev, N.A., McNabb, D.H., and Startsev, A.D. 1998. Soil biological activity in recent clearcuts in west-central Alberta. Canadian Journal of Soil Science **78**(1): 69-76.

Stumm, W. and Morgan, J.J. 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd Edition. John Wiley & Sons, Inc., New York.

Subler, S., Parmelee, R.W., and Allen, M.F. 1995. Comparison of buried bag and PVC core methods for in situ measurement of nitrogen mineralization rates in an agricultural soil. Communications in Soil Science and Plant Analysis **26**(15-16): 2369-2381.

Tietema, A., Beier, C., deVisser, P.H.B., Emmett, B.A., Gundersen, P., Kjonaas, O.J., and Koopmans, C.J. 1997. Nitrate leaching in coniferous forest ecosystems: the European field-scale manipulation experiments NITREX (nitrogen saturation experiments) and EXMAN (experimental manipulation of forest ecosystems). Global Biogeochemical Cycles **11**(4): 617-626.

Vancleve, K. and White, R. 1980. Forest-floor nitrogen dynamics in a 60-year-old paper birch ecosystem in Interior Alaska. Plant and Soil **54**(3): 359-381.

Vandewerf, H. and Verstraete, W. 1987. Estimation of active soil microbial biomass by mathematical-analysis of respiration curves - calibration of the test procedure. Soil Biology & Biochemistry **19**(3): 261-265.

Vanmiegroet, H. and Cole, D.W. 1984. The impact of nitrification on soil acidification and cation leaching in a red alder ecosystem. Journal of Environmental Quality **13**(4): 586-590.

Verchot, L.V., Franklin, E.C., and Gilliam, J.W. 1997. Nitrogen cycling in piedmont vegetated filter zones. 1. Surface soil processes. Journal of Environmental Quality **26**(2): 327-336.

Verchot, L.V., Holmes, Z., Mulon, L., Groffman, P.M., and Lovett, G.M. 2001. Gross vs net rates of N mineralization and nitrification as indicators of functional differences between forest types. Soil Biology & Biochemistry **33**(14): 1889-1901.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., and Tilman, D.G. 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecological Applications **7**(3): 737-750.

Vitousek, P.M., Gosz, J.R., Grier, C.C., Melillo, J.M., and Reiners, W.A. 1982. A comparative-analysis of potential nitrification and nitrate mobility in forest ecosystems. Ecological Monographs **52**(2): 155-177.

Vitousek, P.M., Gosz, J.R., Grier, C.C., Melillo, J.M., Reiners, W.A., and Todd, R.L. 1979. Nitrate losses from disturbed ecosystems. Science **204**(4392): 469-474.

Vitousek, P.M. and Howarth, R.W. 1991. Nitrogen limitation on land and in the sea - how can it occur. Biogeochemistry **13**(2): 87-115.

Vitousek, P.M. and Matson, P. 1988. Nitrogen transformations in a range of tropical forest soils. Soil Biology and Biochemistry **20**: 361-367.

Vitousek, P.M. and Matson, P.A. 1985. Disturbance, nitrogen availability, and nitrogen losses in an intensively managed loblolly-pine plantation. Ecology **66**(4): 1360-1376.

Vitousek, P.M. and Melillo, J.M. 1979. Nitrate losses from disturbed forests - patterns and mechanisms. Forest Science **25**(4): 605-619.

Volk, C., Wood, L., Johnson, B., Robinson, J., Zhu, H.W., and Kaplan, L. 2002. Monitoring dissolved organic carbon in surface and drinking waters. Journal of Environmental Monitoring **4**: 43-47.

Voroney, R.P. and Paul, E.A. 1984. Determination of Kc and Kn in situ for calibration of the chloroform fumigation incubation method. Soil Biology & Biochemistry **16**(1): 9-14.

Voroney, R.P., Winter, J.P., and Beyaert, R.P. 1993. Chapter 28 Soil microbial biomass C and N. *In* Soil Sampling and Methods of Analysis. ed(s). M.R. Carter. CRC Press Inc., Boca Raton, Florida. pp. 277-286.

Wanek, W., Arndt, S.K., Huber, W., and Popp, M. 2002. Nitrogen nutrition during ontogeny of hemiepiphytic *Clusia* species. Functional Plant Biology **29**: 733-740.

Wardle, D.A. and Ghani, A. 1995. Why is the strength of relationships between pairs of methods for estimating soil microbial biomass often so variable? Soil Biology & Biochemistry **27**(6): 821-828.

Wells, W.H., Putt, D.J., Halleran, W.H., and Wallace, C. 1998. Matthew Creek Terrain Interpretation. William H. Wells Consulting, Cranbrook, B.C.

Wilde, S.A. 1958. Forest Soils: Their Properties and Relation to Silviculture. The Ronald Press Company, New York.

Williams, M.W., Bardsley, T., and Rikkers, M. 1998. Overestimation of snow depth and inorganic nitrogen wetfall using NADP data, Niwot Ridge, Colorado. Atmospheric Environment **32**(22): 3827-3833.

Williams, M.W., Baron, J.S., Caine, N., Sommerfeld, R., and Sanford, R. 1996. Nitrogen saturation in the Rocky Mountains. Environmental Science & Technology **30**(2): 640-646.

Williams, M.W. and Melack, J.M. 1991. Solute chemistry of snowmelt and runoff in an alpine basin, Sierra-Nevada. Water Resources Research **27**(7): 1575-1588.

Zak, D.R., Groffman, P.M., Pregitzer, K.S., Christensen, S., and Tiedje, J.M. 1990. The vernal dam - plant microbe competition for nitrogen in northern hardwood forests. Ecology **71**(2): 651-656.

Zechmeister-Boltenstern, S. 2001. New insights into mechanisms of nitrogen turnover and N_2O-emissions from forest soils. Phyton-Annales Rei Botanicae **41**(3): 143-158.

Zellweger-Analytics. 1999. QuikChem Method 10-115-01-1-8 Determination of orthophosphate by flow injection analysis colorimetry. Zellweger Analytics Lachat Instruments Division, Milwaukee, WI.

Zuberer, D.A. 1999. Biological Dinitrogen Fixation: Introduction and Nonsymbiotic. *In* Principles and Applications of Soil Microbiology. ed(s). D.A. Zuberer. Prentice Hall, New Jersey. pp. 295-321.

Appendix A
Additional site description and soils data

Table A 1. List of plants from Bootleg Mountain.

Vegetation Types
Trees
Lodgepole Pine (*Pinus contorta*)
Subalpine Fir (*Abies lasiocarpa*)
Englemann Spruce (*Picea engelmannii*)
Interior Douglas-Fir (*Pseudotsuga menziesii*)
Shrubs
Black Gooseberry (*Ribes lacustre*)
Thimbleberry *(Rubus parvillorus*)
Sitka Alder (*Alnus crispa*)
False Azalea (*Menziesia ferruginea*)
Black Huckleberry (*Vaccinium membranaceum*)
Grouseberry (*Vaccinium scoparium*)
Herbs and Wildflowers
White Hawkweed (*Hieracium albiflorum*)
Heart-Leaved Arnica (*Arnica cordifolia*)
Pathfinder (*Adencocaulon bicolor*)
Arctic Lupine (*Lupinus arcticus*)
Stream Violet (*Viola glabella*)
Sweet-Scented Bedstraw (*Gallium triflorum*)
Baneberry (*Actaea rubra*)
Mountain Sweet-Cicely (*Osmorhiza chilensis*)
Bunchberry (*Cornus canadensis*)
Brewer's Mitrewort (*Mitella breweri*)
One-Leaved Foamflower (*Tiarella unifoliata*)
Single Delight (*Moneses uniflora*)
One-Sided Wintergreen (*Orhilia secunda*)
Fairyslipper (*Calypso bulbosa*)
Rattlesnake Plantain (*Goodyera oblongifolia*)
Broad-Leaved Twayblade (*Listera convallariodies*)
False Solomon's Seal (*Smilacina racemosa*)
Clasping Twisted Stalk (*Streptopus amplexifolius*)
Queen's Cup (*Clintonia uniflora*)
Indian Hellebore (*Veratrum viride*)
Oregon Woodsia (*Woodsia oregana*)
Spiny Wood Fern (*Dryopteria expansa*)
Lady Fern (*Athyrium filix-femina*)
Mountain Holly Fern (*Polystichum lonchitis*)
Oak Fern (*Gymnocarpium dryopteris*)

Table A 1. Continued

Vegetation Types
Mosses and Lichens
Fir Clubmoss (*Lycopodium selago*)
Hanging Basket Moss (*Rhytidiadelphus loreus*)
Pipecleaner Moss (*Rhytidiopsis robusta*)
Yellow-Green Cushion Moss (*Dicranoweisia crispula*)
Broom Moss (*Dicranum scoparium*)
Shadow Ruffle (*Cetraria chlorophylla*)
Ragbag (*Platismatia glauca*)
Monk's Hood (*Hypogymnia physodes*)
Horn Cladonia (*Cladonia cornuta*)
Wolf Lichen (*Letharia vulpina*)
Common Witch's Hair (*Alectoria sarmentosa*)
Speckled Horsehair (*Bryoria fuscenscens*)
Edible Horsehair (*Bryoria fremontii*)

Table A 2. Groundwater well GPS coordinates.

Well	x-coordinate	y-coordinate	Elevation
20A-1	563970.1	5503726.3	1714.1
20A-2	563958.5	5503759.9	1716.7
20A-3	563951.2	5503784.6	1721.5
20A-4	563939.6	5503750.3	1714.9
20A-5	563980.7	5503769.5	1709.8
20-1	564051.6	5503757.9	1694.1
20-2	564045.5	5503783.9	1699.6
20-3	564039.4	5503813.4	1709.5
20-4	564021.0	5503779.8	1699.7
20-5	564068.4	5503785.9	1697.8
30A-1	564052.7	5503559.6	1713.0
30A-2	564047.6	5503571.6	1728.7
30A-3	564043.6	5503594.4	1713.4
30A-4	564037.0	5503565.3	1723.7
30A-5	564055.6	5503572.7	1720.5
30-1	564123.7	5503575.4	1690.3
30-2	564114.3	5503600.2	1704.9
30-3	564111.3	5503624.9	1697.4
30-4	564100.2	5503601.2	1711.8
30-5	564133.8	5503605.4	1702.2
28A-1	564132.4	5503404.8	1705.6
28A-2	564130.7	5503415.2	1709.7
28A-3	564120.3	5503431.5	1719.6
28A-4	564112.7	5503405.1	1716.8
28A-5	564137.0	5503409.9	1711.4
28-1	564182.6	5503384.4	1705.3
28-2	564180.0	5503429.3	1683.4
28-3	564180.2	5503443.9	1701.8
28-4	564158.4	5503405.4	1707.2
28-5	564200.7	5503420.3	1697.2

34A-2 Soil Pit

Vegetation: *thimbleberry, false azalea, arnica, grouseberry, cushion moss, clasping twisted stalk, pipe cleaner moss, subalpine fir, lodgepole pine, Engelmann spruce, one-sided wintergreen, low bilberry*
Surface: *90% canopy*
CWD – medium
Widths of Layers (cm):

	N	E	S	W	Avg
1	18	14	21	15	17
2	47	4	29	37	40
Total	65	60	50	52	57

Bulk Density:
1. 0-14 cm to NE of pit
2. horizontal @ 12 cm, length = 8.5 cm, depth = 9.5 cm on the W side of pit

Samples Taken:
0-17 cm
7-37 cm
37-57 cm
physical

SU1 = 57.0 cm
SU2 = 53.4 cm
TL = 200.2 cm
Total Depth of Pit: upslope = 142.4 cm
downslope = 125.9 cm

1 *no herbs where pit is, needles, sticks, pine cones, moss, lots of decaying wood, roots, yellow and white fungal mycelia, very thick humic layer, loose dry, charcoal beneath surface.*

2 *rocks, silt loam, grey colour, lots of roots.*

70 cm & below
light grey silt loam, very loose, dry, lots of rocks.

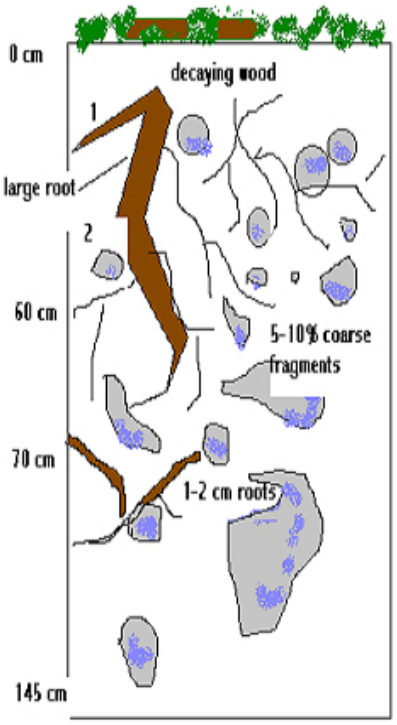

Figure A 1. Soil pit description.

Table A 3. Site and soil layer characteristics.

		Organic Layer		Mineral Layer 1		Mineral Layer 2	
Well	**% Canopy**	**Width of Layer (cm)**	**Colour/Texture**	**Width of Layer (cm)**	**Colour/Texture**	**Width of Layer (cm)**	**Seepage (cm)**
20A-1	70	0-16	Humus	16-20	Light brown, loam	20-63	n/a
20A-2	70	0-12	Humus, charcoal	12-46	Light brown, sandy silt loam, charcoal, some red	46-67	n/a
20A-3	60	0-13	Dark black humus, charcoal	13-30	Sandy silt, grey-brown	30-62	43
20A-4	70	0-12	Reddish brown, charcoal, decaying wood	12-36	Brown sandy silt	36-67	n/a
20A-5	50	0-15	Reddish orangey brown, charcoal	15-25	Red-orange, silt loam	25-64	n/a
20-1	70	0-10	Humus, blackish red brown, silt loam	10-33	Silt loam, grey brown, red layer @ 32.5 cm	33-62	n/a
20-2	20	0-15	Brown-black humus, some red	15-52	Reddish light brown silt loam, charcoal	52-68	n/a
20-3	70	0-21	Black humus, decaying wood	21-43	Tan grey, silty sand	43-61	60
20-4	30	0-11	Blackish-brown	11-28	Reddish dark brown, silty	28-63	30
20-5	50	0-13	Sandy humus, charcoal	13-30	Silt loam, light tan	30-61	n/a
30A-1	60	0-14	Humus	14-32	Grey silt, orange mottles	32-66	60
30A-2	60	0-10	Humus	10-30	Grey silt	30-60	30
30A-3	60	0-18	Humus	18-37	Grey silt	37-61	70
30A-4	60	0-19	Red humus, grey	19-35	Grey silt	35-61	n/a
30A-5	50	0-27	Humus, red, charcoal, decayed wood	27-47	Dark brown, sandy silt	47-66	n/a

Table A 3. Continued.

		Organic Layer		Mineral Layer 1		Mineral Layer 2	
Well	**% Canopy**	**Width of Layer (cm)**	**Colour/Texture**	**Width of Layer (cm)**	**Colour/Texture**	**Width of Layer (cm)**	**Seepage (cm)**
30-1	50	0-15	Reddish brown humus, charcoal	15-34	Grey silty-clayey, light-brown reddish silty clay	34-63	140
30-2	50	0-18	Humus, charcoal	18-50	Sandy silt, grey becoming mottled with roange/red	50-61	n/a
30-3	50	0-12	Brown humus, charcoal	12-30	Sand silt grey, clayey	30-60	60
30-4	60	0-19	Brown-black humus	19-52	Silt, grey brown	52-60	n/a
30-5	70	0-19	Brown-black humus	19-39	Grey brown tan, silt with blue-grey chunks	39-62	n/a
28A-1	35	0-17	Humus, charcoal, decaying wood	17-45	Red-brown silt loam, orange mottles	45-59	n/a
28A-2	50	0-14	Humus, decaying wood	14-38	Reddish silt loam, charcoal	38-62	143
28A-3	86	0-19	Humus, decaying wood	19-42	Grey brown silt	42-60	n/a
28A-4	5	0-18	Humus, charcoal	18-48	Reddish brown silt loam	48-64	n/a
28A-5	25	0-19	Humus, decaying wood	19-33	Red brown silt	33-61	60
28-1	10	0-10	Dark brown, charcoal	10-36	Grey-brown, silt loam	36-70	n/a
28-1	96	0-14	Humus, decaying wood	14-32	Grey tan brown silt	32-70	n/a
28-3	80	0-17	Humus, charcoal	17-40	Red-brown silt loam with some grey	40-58	n/a
28-4	50	0-12	Humus, charcoal, ash, decaying wood	12-30	Reddish silt	30-58	n/a
28-5	80	0-11	Grey-brown soil	11-43	Orange-brown loam	43-63	n/a

Table A 4. Soil sample statistics by block.

Block			GMC * ($g \cdot g^{-1}$)	Bulk Density ($g \cdot cm^{-3}$)	DOC ($mg \cdot g\ dw^{-1}$)	NO_2^- ($\mu g \cdot g\ dw^{-1}$) ‡	NO_3^- ($\mu g \cdot g\ dw^{-1}$) ‡	NO_3^- ($\mu g \cdot g\ dw^{-1}$) §	NH_4^+ ($\mu g \cdot g\ dw^{-1}$) §	TIN ($\mu g \cdot g\ dw^{-1}$) §	PO_4^{3-} ($\mu g \cdot g\ dw^{-1}$) ‡	TDP ($\mu g \cdot g\ dw^{-1}$) ‡
20A	Org	mean	1.14	0.45	0.36	0.56	0.73	0.63	1.89	2.51	4.41	5.07
		CV (%)	69.4	40.0	53.1	215.0	36.4	132.2	61.6	74.3	95.9	79.4
		min	0.51	0.25	0.16	0.00	0.41	0.06	0.38	0.43	0.74	1.13
		max	2.48	0.69	0.65	2.72	1.06	2.00	3.35	5.35	10.69	10.20
	Min1	mean	0.43	0.89	0.16	0.02	1.09	0.47	1.02	1.49	0.10	0.25
		CV (%)	42.2	22.0	63.1	176.5	108.3	102.7	25.5	39.1	58.2	58.5
		min	0.20	0.67	0.06	0.00	0.40	0.04	0.76	0.80	0.04	0.05
		max	0.70	1.11	0.29	0.10	3.15	1.21	1.37	2.27	0.17	0.44
	Min2	mean	0.27	n/a	0.11	0.01	0.48	0.20	0.46	0.65	0.08	0.20
		CV (%)	37.9	n/a	72.1	124.8	61.7	74.5	47.7	21.0	111.5	24.1
		min	0.21	n/a	0.04	0.00	0.17	0.05	0.29	0.44	0.01	0.15
		max	0.44	n/a	0.21	0.02	0.93	0.37	0.71	0.81	0.23	0.25
20	Org	mean	1.79	0.33	0.50	0.02	1.52	2.30	1.59	3.89	3.81	5.36
		CV (%)	21.0	74.4	44.7	175.5	74.6	92.5	37.5	54.3	49.6	47.4
		min	1.29	0.13	0.28	0.00	0.64	0.55	0.68	2.52	1.39	2.25
		max	2.16	0.67	0.81	0.10	3.19	6.00	2.19	7.58	6.53	9.13
	Min1	mean	0.31	0.85	0.09	0.04	0.75	0.52	0.54	1.07	0.11	0.38
		CV (%)	32.6	17.2	41.9	84.4	61.7	115.8	85.5	74.5	44.2	27.8
		min	0.16	0.61	0.06	0.00	0.41	0.16	0.20	0.43	0.05	0.25
		max	0.45	0.98	0.16	0.08	1.56	1.61	1.33	2.18	0.18	0.48
	Min2	mean	0.21	n/a	0.05	0.02	0.63	0.40	0.20	0.60	0.04	0.22
		CV (%)	21.0	n/a	17.4	86.9	48.8	66.3	69.7	54.1	54.2	31.2
		min	0.18	n/a	0.04	0.00	0.31	0.03	0.07	0.10	0.02	0.11
		max	0.28	n/a	0.07	0.04	1.03	0.76	0.43	0.96	0.07	0.28

Table A 4. Continued.

Block			GMC * ($g \cdot g^{-1}$)	Bulk Density ($g \cdot cm^{-3}$)	DOC ($mg \cdot g\ dw^{-1}$)	NO_2^- ($\mu g \cdot g\ dw^{-1}$) ‡	NO_3^- ($\mu g \cdot g\ dw^{-1}$) ‡	NO_3^- ($\mu g \cdot g\ dw^{-1}$) §	NH_4^+ ($\mu g \cdot g\ dw^{-1}$) §	TIN ($\mu g \cdot g\ dw^{-1}$) §	PO_4^{3-} ($\mu g \cdot g\ dw^{-1}$) ‡	TDP ($\mu g \cdot g\ dw^{-1}$) ‡
30A	Org	mean	2.30	0.13	n/a	0.93	3.04	1.84	3.52	5.36	6.28	9.40
		CV (%)	12.0	32.4	n/a	95.5	109.7	211.3	103.6	100.5	82.8	82.9
		min	2.03	0.08	n/a	0.01	0.31	0.07	0.35	0.49	1.00	1.78
		max	2.71	0.17	n/a	2.07	8.72	8.80	9.46	12.44	13.90	21.92
	Min1	mean	0.73	0.21	n/a	0.04	1.10	0.10	0.81	0.91	0.33	0.79
		CV (%)	36.8	63.0	n/a	199.4	90.5	104.5	47.7	48.1	92.6	106.1
		min	0.42	0.10	n/a	0.00	0.33	0.04	0.47	0.51	0.03	0.18
		max	1.08	0.43	n/a	0.18	2.84	0.27	1.37	1.42	0.78	2.25
	Min2	mean	0.46	0.54	n/a	0.14	0.56	0.06	0.92	0.98	0.05	0.35
		CV (%)	53.0	20.6	n/a	195.6	55.3	105.7	73.4	72.1	113.7	67.6
		min	0.25	0.46	n/a	0.00	0.30	0.02	0.26	0.28	0.01	0.10
		max	0.84	0.62	n/a	0.63	1.06	0.17	1.83	1.87	0.16	0.62
30	Org	mean	1.48	0.21	0.99	0.94	0.81	0.14	3.50	3.64	10.81	15.73
		CV (%)	31.1	33.1	97.6	175.6	69.9	122.7	118.3	118.3	135.0	113.4
		min	0.84	0.12	0.35	0.00	0.20	0.04	0.70	0.74	0.72	1.26
		max	1.91	0.28	2.68	3.81	1.62	0.44	10.65	11.09	35.00	44.55
	Min1	mean	0.26	0.70	0.18	0.01	0.53	0.06	0.39	0.45	0.10	0.38
		CV (%)	65.6	49.2	51.3	113.7	38.4	79.1	49.7	43.5	51.7	62.2
		min	0.01	0.35	0.08	0.00	0.35	0.03	0.08	0.11	0.02	0.12
		max	0.46	1.25	0.26	0.03	0.87	0.14	0.54	0.59	0.17	0.64
	Min2	mean	0.20	n/a	0.13	0.01	0.60	0.05	0.53	0.58	0.04	0.41
		CV (%)	38.8	n/a	52.7	109.6	68.1	73.7	85.2	82.2	71.7	55.5
		min	0.16	n/a	0.06	0.00	0.35	0.02	0.06	0.08	0.01	0.21
		max	0.34	n/a	0.20	0.03	1.33	0.12	1.01	1.13	0.08	0.81

Table A 4. Continued.

			GMC * ($g \cdot g^{-1}$)	Bulk Density ($g \cdot cm^{-3}$)	DOC ($mg \cdot g\ dw^{-1}$)	NO_2^- ($\mu g \cdot g\ dw^{-1}$) ‡	NO_3^- ($\mu g \cdot g\ dw^{-1}$) ‡	NO_3^- ($\mu g \cdot g\ dw^{-1}$) §	NH_4^+ ($\mu g \cdot g\ dw^{-1}$) §	TIN ($\mu g \cdot g\ dw^{-1}$) §	PO_4^{3-} ($\mu g \cdot g\ dw^{-1}$) ‡	TDP ($\mu g \cdot g\ dw^{-1}$) ‡
28A	Org	mean	1.16	0.23	1.25	0.02	0.42	0.14	2.23	2.38	8.65	14.79
		CV (%)	44.0	55.8	61.1	172.5	12.2	111.7	88.4	89.7	65.0	59.9
		min	0.60	0.07	0.46	0.00	0.35	0.06	0.92	1.01	2.36	4.21
		max	1.66	0.36	2.33	0.10	0.48	0.43	5.72	6.15	16.40	24.35
	Min1	mean	0.34	0.94	0.10	0.01	0.24	0.05	0.42	0.47	0.08	0.26
		CV (%)	48.0	30.8	128.8	142.5	54.1	15.7	149.6	135.6	66.1	79.0
		min	0.17	0.59	0.03	0.00	0.10	0.04	0.11	0.15	0.01	0.03
		max	0.55	1.36	0.32	0.04	0.41	0.05	1.55	1.61	0.13	0.55
	Min2	mean	0.20	n/a	0.09	0.01	0.27	0.04	0.33	0.38	0.01	0.20
		CV (%)	29.5	n/a	133.5	130.1	39.3	10.9	150.9	133.5	9.01	104.1
		min	0.16	n/a	0.02	0.00	0.19	0.04	0.10	0.14	0.01	0.04
		max	0.30	n/a	0.31	0.03	0.45	0.05	1.23	1.27	0.01	0.58
28	Org	mean	0.84	0.23	0.84	0.24	0.56	0.09	4.85	4.94	11.93	17.67
		CV (%)	62.5	61.1	74.2	102.3	67.9	77.9	134.8	131.7	47.0	46.4
		min	0.18	0.13	0.03	0.00	0.09	0.03	1.38	1.60	6.33	8.27
		max	1.45	0.48	1.69	0.58	1.08	0.22	16.50	16.55	19.09	26.90
	Min1	mean	0.19	0.67	0.05	0.00	0.19	0.04	0.16	0.20	0.09	0.23
		CV (%)	35.9	23.1	34.3	32.0	34.7	13.1	84.0	68.6	40.0	64.1
		min	0.10	0.51	0.02	0.00	0.09	0.04	0.09	0.12	0.05	0.08
		max	0.26	0.88	0.07	0.01	0.27	0.05	0.40	0.44	0.14	0.43
	Min2	mean	0.14	n/a	0.20	0.00	0.23	0.04	0.11	0.15	0.09	0.39
		CV (%)	26.2	n/a	182.6	8.4	38.9	16.8	24.1	17.4	117.1	47.9
		min	0.10	n/a	0.02	0.00	0.15	0.04	0.09	0.13	0.01	0.12
		max	0.20	n/a	0.84	0.00	0.36	0.05	0.16	0.19	0.24	0.54

Table A 4. Continued.

* Org – Organic soil layer; Min1 – Mineral Layer 1; Min2 – Mineral Layer 2; GMC – Gravimetric Moisture Content; L – below detection limit
† CV (%) – coefficient of variation
‡ Soil was extracted with ultrapure H_2O
§ Soil was extracted with KCl

Appendix B
Additional hydrology data

Table B 1. Snow sampling locations.

Transect #	Block	Distance along Transect (m)	Distance off Transect (m)
1	20A	0	N40
		25	S32
		50	N36
		75	S22
	20	100	N30
		125	N20
		150	S22
	34A	175	N42
		200	S45
		225	N2
		250	N14
2	21	0	N18
		25	S17
		50	S28
		75	S12
	33A	100	S44
		125	S26
		150	N24
	33	175	S4
		200	N10
		225	N13
3	30A	0	S12
		25	0
		50	S6
		75	N24
	30	100	N19
		125	N34
		150	N43
	33X	175	N36
		200	S37
		225	N29
4	29	0	N24
		25	N7
		50	S30
		75	N28
	32A	100	S43
		125	S3
		150	N15
		175	N29
	32	200	S43
		225	N14
		250	S45
		275	S39

Table B 1. Continued.

5	28A	0	S35
		25	S22
		50	S11
		75	S2
	28	100	S10
		125	N17
		150	N25
		175	N13

Table B 2. Snow statistics by block.

	Year		SD ($g \cdot cm^{-3}$)	SWE * (cm water)	pH	Cond. * (uS)	DOC * ($mg \cdot L^{-1}$)	NO_2^- ($\mu g \cdot L^{-1}$)	NO_3^- ($\mu g \cdot L^{-1}$)	NH_4^+ ($\mu g \cdot L^{-1}$)	TDN * ($\mu g \cdot L^{-1}$)	TN * ($\mu g \cdot L^{-1}$)	PO_4^{3-} ($\mu g \cdot L^{-1}$)	TP * ($\mu g \cdot L^{-1}$)
Block 20A	2003	mean	0.41	29.4	6.17	12.1	6.44	4.53	79.71	13.94	88.47	377.93	54.64	106.16
		CV (%)	17.9	41.9	7.6	60.7	56.7	29.8	37.9	40.1	10.3	37.2	91.1	59.1
		Min	0.33	20.7	5.80	6.5	2.38	3.32	44.74	8.38	78.05	183.96	7.58	54.99
		Max	0.50	47.1	6.84	22.2	9.45	5.76	117.76	21.72	95.19	513.88	121.04	194.27
	2004	Mean	0.42	43.8	5.62	8.0	6.66	0.30	55.47	11.16	557.94	776.59	124.82	210.75
		CV (%)	52.2	17.6	4.2	63.4	96.0	0.0	37.8	31.0	42.0	105.0	140.6	106.9
		Min	0.10	33.0	5.46	3.8	1.85	0.30	36.91	8.38	375.21	229.36	14.17	59.85
		Max	0.56	51.2	5.97	14.9	15.6	0.30	85.46	16.16	883.85	1990.31	385.08	545.42
Block 20	2003	Mean	0.50	35.5	5.86	6.3	5.58	2.92	32.41	13.94	43.08	472.13	56.07	111.81
		CV (%)	6.2	3.1	2.9	11.4	55.3	94.5	86.2	42.2	31.4	38.0	89.0	32.2
		Min	0.46	34.7	5.76	5.5	3.26	0.30	0.45	7.27	34.15	301.53	15.78	70.29
		Max	0.52	36.8	6.06	6.9	9.08	5.79	52.29	18.38	58.66	659.43	111.86	134.48
	2004	Mean	0.53	42.4	5.49	6.2	4.36	0.30	51.55	46.01	533.87	1452.86	59.32	98.53
		CV (%)	4.8	11.8	3.6	24.4	76.5	0.0	20.3	102.6	45.7	97.5	100.4	63.5
		Min	0.51	36.7	5.32	4.8	1.37	0.30	39.52	6.81	302.78	284.59	17.18	28.13
		Max	0.56	46.0	5.71	7.8	7.96	0.30	58.31	98.38	788.99	3027.86	127.47	147.94
Block 30A	2003	Mean	0.41	32.3	5.37	7.2	11.33	4.20	11.46	12.99	33.02	1004.01	52.86	200.77
		CV (%)	18.4	20.6	3.4	43.4	103.7	68.0	192.1	53.0	37.5	81.0	163.2	81.3
		Min	0.34	22.9	5.15	3.3	0.94	0.30	0.45	6.81	23.01	139.88	0.90	11.54
		Max	0.49	38.0	5.59	10.2	27.97	7.00	44.49	22.83	46.88	1938.90	180.81	375.06
	2004	Mean	0.48	34.5	5.35	9.4	5.18	0.30	33.61	12.71	541.97	1166.54	68.65	213.29
		CV (%)†	11.7	10.5	2.8	9.6	43.6	0.0	138.3	53.5	27.0	65.7	79.5	79.0
		Min	0.39	30.7	5.17	8.6	1.82	0.30	0.45	6.81	370.39	171.44	15.25	16.92
		Max	0.52	38.4	5.52	10.5	6.69	0.30	99.08	20.61	713.72	1833.99	133.64	427.27

Table B 2. Continued.

	Year		SD ($g \cdot cm^{-3}$)	SWE * (cm water)	pH	Cond. * (uS)	DOC * ($mg \cdot L^{-1}$)	NO_2^- ($\mu g \cdot L^{-1}$)	NO_3^- ($\mu g \cdot L^{-1}$)	NH_4^+ ($\mu g \cdot L^{-1}$)	TDN * ($\mu g \cdot L^{-1}$)	TN * ($\mu g \cdot L^{-1}$)	PO_4^{3-} ($\mu g \cdot L^{-1}$)	TP * ($\mu g \cdot L^{-1}$)
Block 30	2003	Mean	0.46	32.12	5.38	6.4	5.19	0.27	10.28	8.82	324.96	517.03	31.21	109.97
		CV (%)†	7.9	13.8	2.7	14.6	17.9	16.2	83.2	39.4	81.9	37.9	41.7	67.3
		Min	0.43	27.26	5.22	5.6	4.13	0.22	4.32	6.81	24.41	302.22	19.53	38.85
		Max	0.50	35.94	5.50	7.4	5.83	0.30	20.08	12.83	530.37	685.92	45.22	186.51
	2004	Mean	0.48	36.61	5.30	9.0	6.14	0.30	28.57	8.82	406.04	1128.00	60.48	112.37
		CV (%)†	10.7	6.4	5.2	35.6	82.1	0.0	93.5	39.4	32.3	52.2	88.9	74.6
		Min	0.44	34.73	5.03	6.0	2.61	0.30	0.45	6.81	280.38	574.33	13.95	60.23
		Max	0.54	39.24	5.58	12.4	11.91	0.30	53.61	12.83	542.22	1746.65	119.30	209.02
Block 28A	2003	Mean	0.44	33.98	5.39	7.0	6.51	0.30	32.75	8.99	513.81	379.01	44.04	88.32
		CV (%)†	16.3	30.7	5.2	50.9	113.1	0.0	67.9	31.8	58.2	65.0	120.2	130.4
		Min	0.35	19.63	4.99	3.7	0.94	0.30	0.45	6.81	277.79	120.58	0.90	3.98
		Max	0.52	41.90	5.61	12.1	16.60	0.30	48.27	12.83	912.26	696.86	116.95	254.47
	2004	Mean	0.45	41.15	5.16	9.9	6.86	0.30	36.68	13.38	296.01	262.14	48.75	49.35
		CV (%)†	10.9	16.8	1.0	46.5	76.6	0.0	71.3	27.5	93.6	105.0	122.1	59.6
		Min	0.40	35.86	5.09	4.4	0.52	0.30	0.45	8.38	52.37	114.30	4.84	28.71
		Max	0.51	51.30	5.21	14.1	11.41	0.30	58.61	17.27	565.26	674.92	134.20	80.43
Block 28	2003	Mean	0.48	37.02	5.25	9.6	10.11	1.37	27.89	9.26	519.83	409.33	55.01	74.24
		CV (%)†	4.8	17.1	3.8	41.2	78.4	156.2	68.0	49.7	26.9	20.9	116.4	96.9
		Min	0.45	30.12	4.99	5.3	4.15	0.30	0.45	6.81	413.82	281.53	17.55	29.86
		Max	0.50	44.72	5.48	13.7	19.11	4.58	44.13	16.16	718.16	460.79	150.89	181.59
	2004	Mean	0.38	32.08	5.27	9.9	6.41	0.30	30.89	22.88	562.29	173.34	20.54	82.88
		CV (%)†	14.1	5.6	4.3	36.7	59.2	0.0	170.6	49.9	28.9	46.8	85.4	102.0
		Min	0.32	30.86	4.99	5.7	2.31	0.30	0.45	7.27	425.37	102.63	0.90	28.71
		Max	0.45	34.76	5.55	14.6	11.45	0.30	109.82	33.03	797.26	270.50	39.43	208.40

* SWE – Snow water equivalent; Cond. – Conductivity; DOC – Dissolved organic carbon; TOC – Total organic carbon; L – below detection limit; TDN – total dissolved nitrogen; TN – Total nitrogen; TP – Total phosphorus

† CV (%) – coefficient of variation

Table B 3. Subsurface water sampling statistics by sampling date.

Date		GWD (cm)	Temp* (°C)	pH	Cond* (µS)	DOC * ($mg \cdot L^{-1}$)	NO_2^- ($\mu g \cdot L^{-1}$)	NO_3^- ($\mu g \cdot L^{-1}$)	NH_4^+ ($\mu g \cdot L^{-1}$)	TDN * ($\mu g \cdot L^{-1}$)	TN * ($\mu g \cdot L^{-1}$)	PO_4^{3-} ($\mu g \cdot L^{-1}$)	TP * ($\mu g \cdot L^{-1}$)
4-Jun-2002	mean	-45.3	18.1	6.19	54.8	29.3	0.3	18.4	16.7	3449.0	5581.8	3.3	2144.0
	CV(%)	89.3	9.0	7.85	146.3	57.7	48.5	60.9	49.3	73.6	49.0	143.3	66.9
	min	-121.6	16.5	5.67	13.8	0.01L	0.3	7.8	6.8L	1766.3	2260.3	0.9	646.9
	max	-1.8	20.7	7.20	287.4	58.5	0.8	44.9	32.5	10506.6	12702.6	16.3	5549.6
25-Jun-2002	mean	-81.0	16.0	6.38	0.4	26.5	0.3	14.4	15.7	1825.9	2010.0	1.3	218.7
	CV(%)	58.9	7.7	4.23	24.3	47.5	27.7	69.2	41.6	43.7	50.0	56.2	113.1
	min	-138.9	15.0	5.90	0.3	13.2	0.3	0.4	6.8L	513.6	602.6	0.9	18.7
	max	-3.8	19.0	6.60	0.6	51.0	0.6	29.6	27.5	3127.6	3737.1	3.2	730.0
30-Jul-2002	mean	-116.6	13.2	6.58	nd	20.1	1.0	18.7	nd	1319.5	1433.3	2.9	281.3
	stdev	40.6	1.4	0.27	nd	15.9	2.1	20.6	nd	899.8	894.2	2.4	351.5
	min	-165.0	12.0	6.05	nd	10.1	0.01L	0.01L	nd	0.01L	218.0	0.01L	14.8
	max	-27.7	16.5	6.90	nd	64.0	7.2	68.2	nd	2559.6	2868.7	6.5	1078.2
22-Aug-2002	mean	-118.7	16.3	6.83	nd	10.4	14.5	11.6	nd	656.3	725.1	1.2	222.2
	CV(%)	36.6	3.9	2.93	nd	50.5	177.0	110.3	nd	34.9	83.5	51.9	143.2
	min	-165.0	15.5	6.55	nd	5.9	0.3	0.4	nd	432.2	246.4	0.9	7.6
	max	-27.2	17.0	7.10	nd	22.2	64.7	37.1	nd	1089.2	1753.6	2.6	819.9
28-Sep-2002	mean	-121.0	16.9	6.13	34.0	19.7	16.1	19.0	nd	496.4	369.5	3.8	74.8
	CV(%)	32.2	5.2	1.98	26.0	74.7	125.6	76.3	nd	45.2	30.7	122.7	67.6
	min	-165.0	16.1	6.03	25.1	8.6	0.3	4.5	nd	203.4	153.2	0.9	18.1
	max	-28.4	18.6	6.36	46.9	52.4	50.0	39.9	nd	844.7	511.3	14.2	154.7
14-May-2003	mean	-63.4	14.6	6.25	29.5	12.4	3.6	154.4	39.6	496.3	597.6	2.1	448.5
	CV(%)	57.0	16.9	12.6	41.6	79.1	64.1	212.7	192.1	71.6	142.0	150.8	190.3
	min	-146.4	11.7	5.07	15.2	0.01L	0.01L	0.01L	6.8L	0.01L	7.5	0.01L	8.9
	max	-16.2	20.4	7.76	81.6	40.7	7.5	1260.6	319.5	1229.3	4329.4	14.6	3698.5
21-May-2003	mean	-75.9	16.1	6.56	29.6	9.2	3.3	114.9	68.9	440.0	369.5	1.4	178.7
	CV(%)	47.19	7.9	7.36	104.3	70.8	159.3	239.1	250.0	93.3	66.4	125.0	96.5
	min	-146.4	13.3	5.88	15.1	0.01L	0.3	11.5	6.8L	3.8	49.5	0.9	4.2
	max	-20.0	18.5	7.49	168.8	26.5	25.0	1353.3	800.6	1390.4	1146.0	9.7	553.3

Table B 3. Continued.

Date		GWD (cm)	Temp* (°C)	pH	Cond* (µS)	DOC * ($mg \cdot L^{-1}$)	NO_2^- ($\mu g \cdot L^{-1}$)	NO_3^- ($\mu g \cdot L^{-1}$)	NH_4^+ ($\mu g \cdot L^{-1}$)	TDN * ($\mu g \cdot L^{-1}$)	TN * ($\mu g \cdot L^{-1}$)	PO_4^{3-} ($\mu g \cdot L^{-1}$)	TP * ($\mu g \cdot L^{-1}$)
28-May-2003	mean	-63.2	17.1	5.76	25.7	12.5	6.1	112.0	13.0	587.0	300.1	1.5	127.5
	CV(%)	66.4	8.0	3.79	69.7	57.8	41.2	242.5	92.2	44.9	68.5	110.3	81.0
	min	-141.9	14.9	4.92	13.3	0.01L	0.3	8.6	6.8L	242.8	22.1	0.9	6.9
	max	-3.0	20.3	6.04	105.5	29.4	12.3	1310.2	61.2	1454.7	972.1	7.7	380.8
3-Jun-2003	mean	-77.1	16.1	5.73	22.0	10.6	3.2	60.3	12.3	517.5	170.3	1.4	56.3
	CV(%)	58.3	5.1	4.70	23.7	54.1	103.6	135.9	98.9	50.0	58.3	57.2	104.8
	min	-150.4	15.0	5.18	13.6	2.5	0.3	7.2	6.8L	186.2	5.4	0.9	6.3
	max	-0.5	17.8	6.07	36.1	22.3	10.2	351.1	59.2	917.4	352.4	3.3	228.3
17-Jun-2003	mean	-96.1	18.7	5.42	36.1	9.6	5.7	66.3	12.34	684.2	298.1	1.0	119.1
	CV(%)	45.3	10.1	7.41	108.0	62.0	104.5	90.7	76.0	83.0	70.9	48.7	89.3
	min	-156.4	15.6	4.98	17.7	0.01L	0.01L	0.01L	0.01L	0.01L	7.5	0.01L	13.6
	max	-18.8	22.0	6.65	189.7	21.7	25.9	228.5	42.1	1167.1	751.8	2.5	384.6
2-Jul-2003	mean	-106.6	17.5	6.12	35.6	7.1	6.1	51.0	13.9	711.2	281.7	10.6	81.3
	CV(%)	37.4	3.6	4.50	41.8	57.1	98.0	57.3	61.5	40.5	136.2	244.7	65.1
	min	-157.0	16.3	5.86	20.4	0.01L	0.3	14.1	6.8L	161.1	7.5	0.9	3.3
	max	-27.1	18.6	7.01	80.9	14.1	20.4	109.2	35.7	1234.1	1505.3	99.4	153.2
24-Jul-2003	mean	-119.7	18.7	6.91	55.8	8.2	4.2	24.5	31.4	485.9	776.7	2.0	236.7
	stdev	37.6	1.6	0.32	37.9	4.6	5.3	14.3	35.2	363.7	943.8	2.0	187.9
	min	-165.0	16.3	6.33	26.8	0.01L	0.01L	0.01L	0.01L	0.01L	89.8	0.01L	22.1
	max	-26.9	21.5	7.41	159.3	15.3	16.5	42.5	122.0	1046.7	3347.8	6.6	510.2
12-Aug-2003	mean	-124.12	18.3	6.61	49.2	6.9	9.6	22.4	70.5	438.0	441.5	22.6	84.0
	CV(%)	28.04	7.9	6.71	70.0	57.4	64.0	62.2	201.9	75.0	70.6	271.8	78.6
	min	-165.00	17.0	6.04	23.5	0.01L	0.01L	0.01L	0.01L	0.01L	109.6	0.01L	20.3
	max	-27.00	21.6	7.28	130.1	12.5	20.8	43.7	408.0	927.5	1043.7	174.7	204.9

GWD – Depth to groundwater; Temp – Temperature; Cond. – Conductivity; DOC – Dissolved organic carbon; L – below detection limit; TDN – total dissolved nitrogen; TN – Total nitrogen; TP – Total phosphorus; CV (%) – coefficient of variation, nd – no data

Table B 4. Subsurface water statistics by block.

Block		GWD (cm)	Temp (°C)	pH	Cond (µS)	DOC ($mg \cdot L^{-1}$)	NO_2^- ($\mu g \cdot L^{-1}$)	NO_3^- ($\mu g \cdot L^{-1}$)	NH_4^+ ($\mu g \cdot L^{-1}$)	TDN * ($\mu g \cdot L^{-1}$)	TN * ($\mu g \cdot L^{-1}$)	PO_4^{3-} ($\mu g \cdot L^{-1}$)	TP * ($\mu g \cdot L^{-1}$)
20A	mean	-99.4	16.8	6.30	58.6	9.0	4.8	21.1	72.6	1,147.8	1,542.7	1.7	283.1
	CV(%)	45.9	12.5	9.37	120.6	102.4	136.1	94.3	245.5	196.6	191.7	185.2	222.6
	min	-136.4	13.8	5.18	0.4	0.01L	0.01L	0.01L	6.8L	0.01L	5.4	0.01L	4.2
	max	-1.8	21.6	7.20	287.4	42.2	27.9	98.4	800.6	10,506.6	12,702.6	16.3	2,702.0
20	mean	-77.1	16.4	6.10	28.3	16.2	2.7	50.7	41.4	949.7	1,352.7	4.2	568.8
	CV(%)	52.1	11.8	9.94	95.3	62.0	114.0	154.1	317.0	100.77	123.0	370.2	208.8
	min	-142.2	13.3	5.03	0.3	0.01L	0.01L	0.01L	0.01L	0.01L	94.6	0.01L	12.0
	max	-0.5	20.7	7.49	168.8	46.4	12.3	400.6	783.7	3,193.9	6,086.6	99.4	5,549.6
30A	mean	-74.6	16.8	6.09	26.9	16.6	5.8	22.7	34.8	660.1	480.1	5.5	127.6
	CV(%)	60.9	10.5	8.41	39.6	52.4	163.4	74.0	241.8	74.3	111.2	459.8	173.9
	min	-151.7	12.0	4.98	0.4	0.01L	0.3	0.4	6.8L	186.2	21.6	0.9	3.3
	max	-15.8	20.4	7.28	44.5	51.0	50.0	71.2	408.0	2,519.3	3,058.4	174.7	1,310.9
30	mean	-88.3	16.6	6.20	30.3	13.7	4.8	55.0	20.1	892.0	679.6	2.8	354.0
	CV(%)	40.9	10.3	8.49	49.5	88.8	119.2	58.3	66.4	78.2	158.2	175.1	163.7
	min	-157.0	12.8	4.92	0.4	0.01L	0.01L	0.01L	0.01L	0.01L	35.9	0.01L	40.1
	max	-28.9	20.4	7.41	90.4	58.5	25.9	135.7	63.5	3,992.5	6,364.9	28.0	3,459.4
28A	mean	-109.0	16.1	6.29	24.2	7.0	7.2	259.8	8.3	616.7	368.0	1.3	139.6
	CV(%)	49.3	17.6	11.76	27.2	159.1	183.1	169.4	65.4	88.5	110.4	62.9	118.3
	min	-165.0	11.7	5.40	13.8	1.9	0.3	7.2	0.01L	14.9	7.5	0.9	8.9
	max	-16.2	22.0	7.76	40.9	64.0	64.7	1,353.3	27.7	2,293.7	1,608.0	3.6	639.4
28	mean	-132.5	17.4	5.87	27.3	8.0	4.2	55.2	21.4	689.6	451.0	1.7	216.7
	CV(%)	21.9	18.0	12.04	85.9	54.9	74.6	44.2	98.3	67.1	57.8	42.6	53.2
	min	-156.5	12.5	5.07	13.3	0.01L	0.3	14.1	6.8L	45.1	76.2	0.9	87.8
	max	-30.1	21.2	7.57	81.6	17.5	8.7	90.9	61.2	1,390.4	826.4	2.7	382.9

GWD – Depth to groundwater; Temp – Temperature; Cond. – Conductivity; DOC – Dissolved organic carbon; L – below detection limit; TDN – total dissolved nitrogen; TN – Total nitrogen; TP – Total phosphorus; CV (%) – coefficient of variation.