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# Ecohydrological Analysis of the Transport of Nitrate and Ammonium in Sandy Desert Soils in Southern California

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Environmental Sciences

by

Julie Marie Scanlan

March 2012

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- Dr. Jiří Šimůnek, Chairperson
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# ABSTRACT OF THE DISSERTATION

## Ecohydrological Analysis of the Transport of Nitrate and Ammonium in Sandy Desert Soils in Southern California

by

Julie Marie Scanlan

Doctor of Philosophy, Graduate Program in Environmental Sciences
University of California, Riverside, March 2012
Dr. Jiří Šimůnek, Chairperson

Disruptions of the hydrological and nitrogen cycles in arid regions can seriously impact desert ecosystems by altering the fire cycle and exacerbating shifts in vegetation. With the potential for nitrogen deposition, spread of invasive species, and climate change to alter the hydrological and nitrogen cycles, understanding these cycles is necessary for assessing the threats to desert ecosystems. This dissertation explores the connections between the hydrological and nitrogen cycles in sandy soils in arid ecosystems. An analysis of the hydrological cycle suggested that the water flux at highly negative potentials during the dry summers contributes significantly to the total annual water flux at two study sites in the Sonoran desert. Because commonly-used soil hydraulic models do not accurately approximate the retention curve at highly negative potentials, predictions of liquid water flow at moderate potentials during the growing season were inaccurate due to very dry initial conditions. An examination of how monthly nitrate measurements throughout the top 100cm of soil varied with precipitation at the same study sites showed how strongly the hydrological cycle affects the nitrogen cycle in the desert. After rapid nitrate creation followed the first rains of the growing season, the leaching of nitrate with subsequent rainfalls was likely a major factor causing nitrogen limitation in annual plants. Significantly greater nitrate in the soil in plots fertilized with ammonium nitrate relative to unfertilized plots throughout the dry summer suggested that a considerable amount of nitrate in the soil was not taken up by plants. Variations in ammonium measurements with precipitation in the soil at the sites were similarly analyzed. Results suggest that the adsorption of ammonium is likely an important factor in increasing nitrogen availability to short-rooted plants through inhibiting leaching. Identifying how the hydrological cycle influences the nitrogen cycle in arid ecosystems is critical for predicting how deserts will change in the future.

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## General Introduction

The innovations of modern science have given humankind the ability to better understand the complex, interconnected processes of the living world, as well as a greater capacity to affect these processes in often unintended and detrimental ways. The pursuit of further advancements in the knowledge and understanding of the chemical, physical, and biological processes of the natural world is critical if humanity desires to control the impact it has on the planet. The complexity and interconnectivity of life on Earth necessitates the analysis of not only individual natural processes but also of how different processes relate to each other.

The nitrogen (N) cycle is among the processes critical to life on Earth currently being altered by human activities. Despite nitrogen composing approximately 78% of the atmosphere, its availability to life is severely restricted by the inability of most organisms to break the triple bonds of the abundant elemental nitrogen ($N_2$). The anthropogenic release of biologically-available N can eliminate natural restrictions on N availability in ecosystems and destabilize the N cycle.

Between 1860 and 1990, the amount of reactive N being created by humans is estimated to have increased by an order of magnitude, with human activity estimated to be responsible for about 40% of reactive N created worldwide by 1990 (Galloway et al., 2004). Most human fixation of reactive N is done in the creation of fertilizer through the Haber-Bosch process, but fossil fuel combustion can also fix a substantial amount of N (Galloway et al., 2004). Fossil fuel combustion is the primary source of human emissions of nitrogen oxides ($NO_x$) into the atmosphere while modern agricultural practices release most anthropogenic ammonia ($NH_3$) (Galloway et al., 2004). In the United States, the release of anthropogenic N into environments is estimated to have doubled between 1961 and 1997 alone as a result of increased fossil fuel combustion and fertilizer use (Howarth et al., 2002). Because N is commonly found to be a limiting nutrient in many varied ecosystems throughout the world (LeBauer and Treseder, 2008; Vitousek and Howarth, 1991), the deposition of extra biologically-available N from human activities into ecosystems has a great potential to cause widespread environmental problems.

### *Consequences of the Increased Availability of Nitrogen*

The effects of increased biologically-available N have been observed in terrestrial and aquatic ecosystems throughout the world (Adams, 2003; Smith et al., 1999; Vitousek et al., 1997). Eutrophication of lakes, streams, and estuaries from the concurrent loading of the commonly-limiting nutrients nitrogen and phosphorous is a prevalent water quality issue in the United States that can result in algal blooms, oxygen depletion, fish kills, loss of biodiversity, and the impairment of the water for human use (Carpenter et al., 1998; Smith et al., 1999). Agricultural and residential runoff and groundwater discharge are responsible for much of the aquatic eutrophication (Carpenter et al., 1998), but the atmospheric deposition of N can also contribute a substantial amount of N to many watersheds and raise the concentration of nitrate in water bodies (Fenn and Poth, 1999; Michalski et al., 2004; Riggan et al., 1985).

Human activities are estimated to have at least doubled the rate of input of reactive N into the N cycle of terrestrial ecosystems worldwide (Vitousek et al., 1997). N deposition can result in N saturation (Aber et al., 1989; Fenn et al., 1998; Williams et al., 1996) and accelerated soil acidification (Bobbink et al., 1998; Wood et al., 2007), but the alteration of vegetation composition appears to be the most widespread problem. These changes in vegetation are shaped by alterations to many components of the terrestrial N cycle resulting from increases in bioavailable N. With the addition of anthropogenic N, changes have been observed in the rates of N mineralization (Fenn et al., 2003a; Fenn et al., 1996; Magill et al., 1997; Vourlitis and Zorba, 2007), nitrification (Fenn et al., 2003a; Fenn et al., 1996; Magill et al., 1997), and denitrification (Hanson et al., 1994) in various ecosystems and the sensitivity of many lichens to disturbance may result in the alteration of nitrogen-fixation rates in some communities with added N as well (Evans and Belnap, 1999). The potential for the deposited N to be assimilated in many ecosystems has been confirmed by the measurement of elevated N tissue concentrations resulting from the addition of anthropogenic N (Magill et al., 2004; Padgett and Allen, 1999; Rueth and Baron, 2002; Vourlitis et al., 2009). In addition to augmenting assimilation, increased N availability has corresponded to a decrease in the abundance of mycorrhizae in some studies (Egerton-Warburton and Allen, 2000; Lilleskov et al., 2011; Treseder, 2004), which can alter how water and nutrients are absorbed. Although the N content of litter is often positively correlated with the rates of decomposition, the observed effects of N deposition on decomposition rates have varied between increased rates, decreased rates, and no change (Hobbie, 2005; Knorr et al., 2005).

The broad effects of anthropogenic N on the terrestrial N cycle have corresponded to changes in vegetation. Competitive advantages may be altered with increased biologically-available N, leading to the competitive exclusion of plants adapted to low-N conditions by nitrophilic species and resulting in the loss of diversity(Bobbink et al., 2010; Tilman, 1987). Shifts in vegetation and decreases in species richness have been observed to coincide with elevated N deposition in many different environments, including forests (Allen et al., 2007; Gilliam, 2006), semiarid shrublands (Padgett and Allen, 1999; Wood et al., 2006), grasslands (Bobbink et al., 1998; Clark and Tilman, 2008; Stevens et al., 2004; Tilman, 1993), wetlands (Bobbink et al., 1998), alpine tundras (Bowman and Steltzer, 1998; Theodose and Bowman, 1997), and deserts (Brooks, 2003). The expansions of some ecosystems at the expense of others have likely been impelled by N deposition, including the expansion of forests into grassland in the Great Plains of North America (Kochy and Wilson, 2001) and the spread of grasslands into coastal sage scrub in southern California (Padgett et al., 1999; Wood et al., 2006).

Although many shifts in vegetation have been observed to result from N deposition favoring the spread of some native species over others (Bobbink et al., 1998; Bowman and Steltzer, 1998; Stevens et al., 2004; Tilman, 1987), N deposition is of particular concern in ecosystems threatened by invasive species. Because the spread of invasive species can cause a decline in the abundance and diversity of native vegetation (Mack et al., 2000) and elevated levels of nutrients can aid the spread of invasive species (Burke and Grime, 1996; DeFalco et al., 2003), anthropogenic N deposition and invasive species have the potential to work in conjunction to induce vegetative change. Moreover, the composition of plant species greatly affects N cycling in ecosystems (Knops et al., 2002), resulting in invasive species altering N fixation and decomposition rates, the amount of biomass, and other changes even in the absence of elevated bioavailable N (Ehrenfeld, 2003), which can lead to a greater potential for disruption when N deposition and the spread of invasive species are coupled. This facilitation of the spread of exotics by N has most frequently been observed in arid and semi-arid ecosystems of the southwestern United States (Brooks, 2003; DeFalco et al., 2003; Huenneke et al., 1990; Padgett and Allen, 1999; Rao and Allen, 2010).

### *Nitrogen Deposition in Southern California*

Southern California is among the regions of the United States that have experienced consequences from the deposition of anthropogenic N. The substantial amount of $NO_x$ released by automobiles in the Los Angeles area is supplemented by atmospheric $NH_x$ from Californian agricultural production, resulting in the annual deposition of 20-45 kg/ha in many chaparral and coniferous forests in the South Coast Air Basin (Fenn et al., 2003b). A sizable portion of the N deposition in southern California occurs as dry deposition (Fenn et al., 2003b; Padgett and Bytnerowicz, 2001; Riggan et al., 1985), which can accumulate on the surfaces of the plants and the soil throughout the dry summers and becomes available for plant uptake with the first rains (Padgett et al., 1999).

The consequences of anthropogenic N deposition have been observed in many Californian ecosystems. Coastal sage scrub, a common semiarid shrubland in southern California, has declined over the last 70 years with the spread of invasive exotic annuals

(Minnich and Dezzani, 1998) and the change in N availability has been identified as contributing factor (Padgett et al., 1999; Wood et al., 2006). The semi-arid coniferous forests of southern California have also been subject to high N deposition (Bytnerowicz and Fenn, 1996), which has resulted in instances of acidification (Wood et al., 2007) and saturation (Fenn et al., 1996). Higher emissions of NO and $N_2O$, increased rates of mineralization and nitrification, high soil acidity, N enrichment of the soils and plant tissues, and increased $NO_3$ leaching have all been observed in southern Californian forests (Fenn et al., 1996). In conjunction with the pollutant ozone, which can cause foliage loss in pines in southern California, N deposition can also contribute to increased litter accumulation by enhancing leaf growth, which can increase the potential for fires (Fenn et al., 2003a). With most of the western Sierra Nevada above the critical load required to protect sensitive lichen communities (Fenn et al., 2008), it is clear that the effects of elevated N levels in California are widespread.

### *Nitrogen and Invasives in the Californian Deserts*

Most deserts in California receive relatively little N deposition compared to many Californian shrublands and coniferous forests (Fenn et al., 2003b); however, over decades, chronic low levels of deposition have resulted in decreased diversity in grasslands (Clark and Tilman, 2008) and the naturally low N availability of arid ecosystems could amplify the effects of added N. Moreover, the leaching of nutrients deep into the soil below the root zones is estimated to be negligible in many arid ecosystems (Peterjohn and Schlesinger, 1990), increasing the potential for N accumulation in the biomass and soil. Because N often co-limits productivity in arid regions along with water (Gutierrez and Whitford, 1987; Hooper and Johnson, 1999; Yahdjian et al., 2011), serious changes to arid ecosystems could result from a significant accumulation of N.

In the Mojave and Sonoran Deserts of southern California, invasive annual grass and forb species have been spreading to the detriment of many native species (Barrows et al., 2009; Brooks, 2000; DeFalco et al., 2007; Steers and Allen, 2010). While both native and invasive annuals have been observed to respond with greater productivity to an increase in N (DeFalco et al., 2003; Rao and Allen, 2010; Salo et al., 2005), N fertilization has been observed to be more favorable to many exotic annuals when grown in competition with native species (Allen et al., 2009; Brooks, 2003; DeFalco et al., 2003).

The spread of invasive species in the Californian deserts has consequences beyond a loss of native diversity. The increase in the frequency and intensity of fires in arid regions in southern California during the last few decades has likely been contributed to by increased ground cover by exotic species, which change the fuel properties, contribute to the fuel load, and help carry fires between shrubs (Brooks et al., 2004; Brooks and Minnich, 2006; Brown and Minnich, 1986). N deposition amplifies the hazards of fire by increasing the growth of both annual natives and invasives above the threshold needed to carry fire (Brooks, 2003; Rao et al., 2010). Because limited fuel has resulted in fires historically being rare in creosote scrub and other arid ecosystems (Brooks and Matchett, 2006), many shrubs are poorly adapted to fire (Brown and Minnich, 1986) and the faster recovery from the exotics following fires can increase the likelihood that the land will again burn (Brooks et al., 2004).

### *The Hydrological and Nitrogen Cycles in the Desert*

The relationship between the hydrological cycle and the N cycle is especially pronounced in deserts due to the importance of the infrequent precipitation for soil microbial processes (Austin et al., 2004; Schwinning and Sala, 2004; Stark and Firestone, 1995), as well as for assimilation and leaching. Precipitation is also a critical factor in determining the relative success of invasive and native annuals in the California deserts (Brooks, 2003; Rao and Allen, 2010) and in determining the size and frequency of wildfires (Brown and Minnich, 1986). Therefore, the destabilization of the hydrological cycle by climate change could have repercussions in the N cycle, the fire cycle, and the spread of invasive species in the Californian deserts.

Much of the understanding of the hydrology of desert soils has been derived from techniques and models created for agricultural soils, which have traditionally been more extensively studied. However, the applicability of understanding developed from studying agricultural soils to desert soils is limited by the prominent contribution of water vapor transport to total water flux in desert soils. In the deep vadose zones of coarse textured soils that have been below the depth of percolation during the Holocene, upward vapor flow dominates water transport (Scanlon et al., 2003; Walvoord et al., 2002). Near the surfaces of desert soils, both seasonal downward liquid flow and vapor flow are important, which requires that both states, as well as heat, be considered simultaneously when making models and predictions of the systems. Only within the last decade have hydrological models become sophisticated enough to concurrently represent the movement and interactions between the strongly coupled processes. The current version of the widely-used numerical model HYDRUS-1D (Šimůnek et al., 2008) includes vapor flow and heat transport components (Saito et al., 2006), which could be useful in deserts. However, the van Genuchten (Van Genuchten, 1980) and Brooks-Corey (Brooks and Corey, 1964) hydraulic property models are not accurate at very low water contents (Khaleel et al., 1995; Nimmo, 1991; Rossi and Nimmo, 1994). While errors produced by inaccuracy at extremely low water contents may be negligible in agricultural soils, the errors would be magnified in soils that are frequently very dry. Additionally, the extreme soil hydraulic properties of the frequently sandy desert soils and the limitations on measuring water content and water flow with instruments originally created for agricultural soils produce further complications when trying to understand and represent the hydrology of desert soils.

The challenges in understanding water flow are reflected in challenges in understanding the desert N cycle. The mechanism for the frequent accumulation of $NO_3$ throughout the Holocene in deserts near the bottoms of root zones (Hartsough et al., 2001; Marion et al., 2008; Walvoord et al., 2003) and beneath desert pavement (Graham et al., 2008) is not clearly understood. With all precipitation being removed from vegetated soil annually by evapotranspiration (Andraski, 1997; Kemp et al., 1997; Sandvig and Phillips, 2006), deep-rooted perennials are expected to absorb the $NO_3$ when taking up the water. The accumulation of a nutrient that is frequently co-limiting in arid ecosystems below the soil surface remains enigmatic.

### *Objectives of this Dissertation*

The primary goal of this dissertation is to further the knowledge of the hydrological and N cycles in arid regions by analyzing some of the physical and chemical processes that underlie shifts in vegetation. The following three chapters focus on hydrology, $NO_3$, and $NH_4$ in desert ecosystems with the intent of attaining a greater understanding of the desert N cycle through the examination of contributing components.

Chapter 1 entails an analysis of two years of hourly water potential data taken from dielectric matric water potential sensors (MPS-1s) at two sites in the Sonoran Desert in southern California. Models were created using HYDRUS-1D with the inclusion of heat and vapor flow components for the purpose of assessing the extent to which the model can recreate field measurements of matric potential in the desert. Issues with applying the model to measurements of water potential in desert ecosystems are analyzed in relation to variations between measurements and model predictions for the purpose of highlighting potential deficiencies in the current understanding of the hydrology in the desert.

In chapter 2, extractable nitrate ($NO_3$) concentrations taken from soil cores collected monthly for two years at the Sonoran Desert sites are examined in relation to the timing of precipitation events for the purpose of studying how the hydrological cycle is driving the production and movement of $NO_3$ in the soil. The differences in the measurements of $NO_3$ in plots fertilized with ammonium nitrate ($NH_4NO_3$) and control plots are the focus of an analysis of the potential fate and transport of anthropogenic deposition. Monthly measurements over a dry summer establish differences between fertilized and unfertilized plots that extend beyond the end of the growing season, as well as create a basis for the analysis of changes observed throughout winter.

The effect of the hydrological cycle on measurements of ammonium ($NH_4$) in the soil cores is similarly analyzed in Chapter 3. The difference in the potential uptake by annual and perennial plants of deposited $NH_4$ and $NO_3$ due to the differences in mobility in the soil is a primary focus. Measurements throughout the summer and during the rainy season help establish the role of $NH_4$ in the desert N cycle.

This dissertation is intended to contribute to the growing body of knowledge of the effects of N deposition throughout the world, as well as to increase the understanding of the ecohydrology of traditionally overlooked arid ecosystems. Advancement in the understanding of the N cycle in the desert soils can aid in the prediction of how N deposition may alter species composition and the fire cycle and in the determination of a strategy to preserve the beauty and diversity of desert ecosystems.

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# **Chapter 1** Evaluation of the applicability of the van Genuchten-Mualem model for simulating water flow during the rainy season in sandy desert soils

## Abstract

The model HYDRUS-1D was used to evaluate measurements taken by dielectric matric potential sensors (MPS-1) over two years at two sites in the Sonoran Desert dominated by creosote bush (*Larrea tridentata*). Although numerous variables were altered in an attempt to fit the models to the data, the HYDRUS-1D model consistently vastly underestimated the timing of the decline in potential (Ψ) at the end of the growing seasons. Neutron probe data showed that a sizeable amount of water was depleted over the summer after Ψ measured by the MPS-1s fell below -500kPa, the lower limit of the sensors. The inability of the model to reproduce the field measurements may result from established inaccuracies at very low water contents of the van Genuchten-Mualem functions, which predicted negligible removable water below -500kPa in the sandy soil. The results suggest that the water flux at highly negative potentials during the dry summers contributes substantially to the total annual flux and cannot be ignored when modeling liquid water flow in sandy desert sites if the starting conditions are dry. Further research is needed to establish the proportion of winter precipitation remaining until the

dry summer, to ascertain the role of vapor flow and condensation in the removal of water throughout the summer, to evaluate the relationship between capillary flow and vapor flow used by the model HYDRUS-1D, and to determine the impact of dry season evapotranspiration on nutrient uptake by plants.

## Introduction

Although the infrequent rain events and often loosely-structured sandy soil may give rise to the perception that the hydrology of a desert soil is simple, the importance of the flow of water vapor, in addition to the flow of liquid water, results in a system of some complexity. Modeling a system where liquid water, heat, and water vapor are important is difficult due to the strong coupling of the highly non-linear equations representing these processes (Saito et al., 2006). The current version of the widely-used numerical model HYDRUS-1D (Šimůnek et al., 2008) is capable of simultaneously modeling the flows of liquid water, water vapor, and heat, offering the comprehensive model necessary for representing the desert soils. However, the most common soil hydraulic property models, the van Genuchten-Mualem model (Van Genuchten, 1980) and the Brooks-Corey model (Brooks and Corey, 1964), function poorly at very low water contents (Khaleel et al., 1995; Nimmo, 1991; Rossi and Nimmo, 1994). In modeling concentrated on liquid flow, which remains the primary focus of HYDRUS-1D, inaccuracies at very low water contents ($\theta$) often do not matter since the vast majority of liquid water flow occurs at medium and high $\theta$, particularly in sandy soils. However, the prolonged periods of extreme dryness in desert soils could potentially magnify the effects of inaccuracies at very low $\theta$ and affect the modeling of liquid flow.

### *The Importance of Water in Desert Ecosystems*

Deserts have received increased attention in recent years because of their applicability as locations for hazardous waste storage (Andraski, 1997; Gee et al., 1994), nuclear waste storage (Flint et al., 2001; Stuckless and Dudley, 2002), and landfills (Young et al., 2006); the influence of anthropogenic deposition of nitrate and ammonium on the spread of invasive species (Brooks, 2003; DeFalco et al., 2003; Rao and Allen, 2010); the increased potential for wildfires as a result of vegetation shifts (Brooks and Minnich, 2006; Rao et al., 2010); and the unusual properties of the deep vadose zone (Scanlon et al., 2003; Walvoord et al., 2002b).

The hydrological cycle strongly influences other biological and chemical processes in the desert, with the timing and amount of precipitation determining biogeochemical cycles (Austin et al., 2004; Schwinning and Sala, 2004) and the growth of plants (Lundholm and Larson, 2004; Ogle and Reynolds, 2004). Water is generally considered the main factor limiting productivity in the desert (Noy-Meir, 1973), with the nutrient nitrogen being a secondary limitation (Gutierrez and Whitford, 1987; Hooper and Johnson, 1999; Yahdjian et al., 2011). Understanding the hydrological cycle in deserts is very important for the evaluation of potential shifts in vegetation and nutrient cycling, as well as for evaluating the applicability of desert sites for future waste storage.

### *The Hydrology of the Desert*

The hydrology of desert systems is unusual in that all water infiltrating many vegetated soils is commonly removed annually through evapotranspiration, resulting in no deep drainage at many sites (Andraski, 1997; Kemp et al., 1997; Sandvig and Phillips, 2006). Estimates for the last time water percolated into the deep vadose zone below the root zones at many vegetated locations in the deserts of the American southwest generally range from 10,000-20,000 years ago (Phillips, 1994; Sandvig and Phillips, 2006; Scanlon et al., 2003; Tyler et al., 1996; Walvoord et al., 2002a). The net flux in the deep vadose zones at these sites is often upward (Andraski, 1997; Scanlon et al., 2003; Walvoord et al., 2002b) and they have been in a gradually drying following a climatic shift thousands of years ago (Walvoord et al., 2002b).

In the deep vadose zones of coarse textured soils in arid regions, which can extend to depths of more than 200m, vapor flow is an important component of total water flux (Scanlon et al., 2003; Walvoord et al., 2002b). Liquid flow is more important near the surface due to infiltration of water on an annual basis, but both isothermal and thermal vapor flow can significantly contribute to the total water flux (Scanlon and Milly, 1994) and must be considered along with liquid flow when modeling desert systems.

### *Modeling Water in Desert Soils*

Many modern models of vapor transport in soils are descended from a mathematical formulation of the movement of water vapor and liquid water in the soil as a result of both pressure head and thermal gradients developed by Philip and de Vries (1957). The model HYDRUS numerically solves an equation derived from the formulations of Philip and de Vries (1957), which governs the flow of liquid water and water vapor (Saito et al., 2006):

$$\frac{\partial \theta_T(h)}{\partial t} = \frac{\partial}{\partial x}\left[\left(K + K_{vh}\right)\left(\frac{\partial h}{\partial x} + \cos\alpha\right) + \left(K_{LT} + K_{vT}\right)\frac{\partial T}{\partial x}\right] - S(h)$$

where $\theta_T$ is the sum of the volumetric liquid and vapor water contents, $h$ is the pressure head, $T$ is the temperature, $S$ is the sink term, $x$ is the spatial coordinate, $\alpha$ is the angle of flow relative to the vertical axis, and $K$, $K_{LT}$, $K_{vh}$, and $K_{vT}$ are the liquid isothermal, liquid thermal, vapor isothermal, and vapor thermal hydraulic conductivities, respectively. This model has replicated moisture and temperature measurements well in numerous studies (Deb et al., 2011; Kato et al., 2011; Saito et al., 2006; Sakai et al., 2009; Zeng et al., 2009; Zhao et al., 2010).

### *Measuring Liquid Water Flow in the Desert*

Measuring water in sandy desert soils can be challenging because many instruments and techniques that were originally designed primarily for agricultural soils are less effective in the desert. Methods of water measurement that have been determined to be applicable in desert soils include the use of lysimeters to estimate evapotranspiration and deep percolation (Allison et al., 1994; Gee et al., 1994); neutron probe measurements to estimate the change in water storage (Scanlon and Milly, 1994); tracers, such as chloride, to evaluate long-term flow processes in arid environments (Allison and Hughes, 1983; Kwicklis et al., 2006; Phillips, 1994; Sandvig and Phillips, 2006; Scanlon et al., 2003) and psychrometers to measure very low water potentials (Scanlon et al., 2003).

In order to study the water uptake of plants following precipitation, measurements of water flow at high and medium water potentials (Ψ) are most important since little liquid flow occurs at very low Ψ in sandy soil.  Continuous measurements are necessary in arid regions because precipitation events are generally brief and infrequent.  The recently-developed dielectric water potential sensors (MPS-1s), which measure the water potential of the soil by using a solid matrix equilibration technique (MPS-1, 2008), have the capacity to be simple way to measure the flow of liquid water in desert soils.  After the buried porous ceramic disks achieve hydraulic equilibrium with the soil, the MPS-1s determine the Ψ by measuring the dielectric permittivity of the ceramic disks.  While the sensors cannot measure osmotic potential, osmotic potential is generally much less than matric potential in the vadose zones of desert soils (Walvoord et al., 2002b). Temperature sensitivity and hysteresis effects of the MPS-1s are small (Malazian et al., 2011).  A major drawback of the sensors is the specified lower limit of -500kPa (MPS-1, 2008), which is an order of magnitude higher than typical Ψ measured in desert soil when it is dry.  However, in a study focused solely on liquid water flow and nutrient uptake by plants, it was hypothesized that measuring Ψ below -500kPa is unimportant since the steep unsaturated hydraulic conductivity functions of sandy desert soils are expected to result in negligible water flow at very low Ψ.

### *Intent of the Analysis*

Being able to take reliable hourly or daily measurements of matric potential during and following the rains in arid regions would be useful for creating models for the fate and transport of nutrients and chemicals in the desert soil. Similarly, a comprehensive model for liquid, vapor, and heat transport is beneficial for understanding the desert hydrological cycle. The purpose of this analysis is to determine whether the vapor transport model of HYDRUS-1D can reasonably replicate the data from the MPS-1 sensors. This will test the hypothesis that water flow at very low Ψ has negligible effects on liquid water flow for sandy soils, because the steep hydraulic conductivity and water retention curves created by HYDRUS-1D for sandy soils predict a miniscule loss of water for when Ψ is reduced below -500kPa.

## Materials and Methods

### *The Study Sites*

The two study sites, Wide Canyon (WC) and Pinto Basin (PB), are located in the Colorado Desert portion of the Sonoran Desert in Joshua Tree National Park (JOTR) in southern California (Figure 1.1). Wide Canyon (33.943°N; 116.395°W; 501 meters above sea level) is situated approximately 20 kilometers northeast of the city of Palm Springs in the southwestern part of JOTR and Pinto Basin (33.832°N; 115.758°W; 744m above sea level) is located approximately 100 kilometers east of WC at the center of JOTR. The study area consisted of nine 6m x 6m plots centered on creosote bushes (*Larrea tridentata)* spread over <1ha.

On-site weather stations have been collecting temperature and precipitation data hourly since 2005. Precipitation at PB and WC occurs primarily during the winter and early spring. Based on precipitation data collected by the National Weather Service (NWS) between 1900 and 1995 at a nearby station in Palm Springs (33.83°N 116.50°W), the average annual precipitation at WC is estimated to be 144mm. The closest long-term station to PB was the NWS weather station at the Hayfield Pump Plant (33.70°N 115.63°W), which estimated an average annual rainfall of 98mm between 1933 and 1995. Figure 1.2 shows the yearly winter precipitation and the average winter and summer temperatures measured at PB and WC from 2005 to 2010. Three years of below average rainfall at both sites preceded the start of the study in November 2008, including severe droughts during the winters of 2005-2006 and 2006-2007. Precipitation was also below average during the winter of 2008-2009, with 7.4cm of rain at WC and 6.4cm at PB. The winter of 2009-2010 was the first in which above average precipitation fell since the winter of 2004-2005, with rainfall measured to be 17.9cm at WC and 15.1cm at PB. Precipitation generally occurred on or near the same days at the two sites (Figure 1.3). Although occasional summer rains are common, less than one centimeter of rain fell between May 1 and October 31 at either site in 2009 and 2010. Average temperatures during the growing season and the dry season were consistent at the sites between 2005 and 2010. While average summer and winter high temperatures at PB and WC were similar, greater variation was observed in low temperatures between the sites.

### *Water Potential and Water Content Measurements*

The MPS-1s measured the matric potential at the depths of 5cm, 10cm, 15cm, 20cm, 25cm, 50cm, and 70cm in the soil of two plots at PB and WC between November 2008 and May 2010 for the purpose of better understanding the water and nutrient flow in desert soils. 30kg/ha of ammonium nitrate was added to one plot in which the sensors had been installed at each site because N fertilization alters plant composition at these sites (Allen et al., 2009; Rao and Allen, 2010; Schneider, 2010) and the influence of annual plants on water flow was of interest. The two sets of sensors, which help establish the precision of the measurements, were located approximately 8m apart at Wide Canyon and 11m apart at Pinto Basin.

The sensors were specified to have an accuracy of approximately +/-5kPa between the $\Psi$ of -10kPa and -50kPa and an accuracy of about +/-20% between -50kPa and -500kPa (MPS-1, 2008). While the sensors were stated not to need calibration (MPS-1, 2008), Malazian et al. (2011) evaluated the sensors and found a high variability between sensors and that factory calibration underestimated applied pressures by about 40%, both of which can be improved by one point calibration. Since this was unknown at the time of installation, these calibrations were not done. The uncertainty in the sensor measurements is not expected to greatly impact the overall trends, which are the primary focus in attempting to fit the HYDRUS model to the data.

In accordance with the suggestion of Malazian et al. (2011), the sensors were submitted to a wetting and drying cycle prior to field installation. Although there is some uncertainty in ensuring good physical contact with the surrounding soil (Malazian et al., 2011), the sensors were coated with a finer textured soil before inserting them into the sandy soil to increase the potential for good hydraulic contact.

The fit of the HYDRUS-1D model to the timing of the measurements rather than the accuracy of it fits to the measurements at a given time takes priority due to some uncertainties in the measurements and in the model. The steep retention and hydraulic conductivity curves of the sandy soil are expected to result in a rapid decline in $\Psi$ as the soil moisture approaches the residual water content ($\theta_r$). Accurately predicting the timing at which these steep declines occur is the primary focus in fitting the model. The timing of declines between -15kPa and -100Pa are of greatest interest because above -15kPa the $\Psi$ measurements have little sensitivity to changes in $\theta$ and below -100kPa minute changes in $\theta$ result in extreme changes in $\Psi$. Focusing on fitting the timing of the declines from -15kPa to -100kPa allows the best evaluation of the accuracy of the water retention and hydraulic conductivity functions.

A neutron probe was also used to measure water at 20cm intervals from 15cm-115cm in 9 plots at each site monthly from November 2008 and January 2009. Because site-specific calibration data was not obtained during that time, predicted $\theta$ from the raw neutron probe counts have an uncertainty resulting from being estimated from previous calibrations at other similar locations. As a result, the $\theta$ predicted from the neutron probe measurements will only be used in a limited capacity to analyze trends observed in the MPS-1 data and HYDRUS-1D models.

### *Rosetta and HYDRUS-1D*

The van Genuchten-Mualem functions (Van Genuchten, 1980) were used to estimate the retention and hydraulic conductivity functions in the model HYDRUS-1D:

$$\theta(h) = \begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m} & h < 0 \\ \\ \theta_s & h \geq 0 \end{cases}$$

$$K(h) = K_s S_e^l [1 - (1 - S_e^{1/m})^m]^2 \qquad \text{where} \quad m = 1 - 1/n \ , \quad n > 1$$

where $\theta_r$ and $\theta_s$ are respectively the residual and saturated water contents, $\alpha$ is the inverse of the air-entry value; $h$ is the pressure head, $K_s$ is the saturated hydraulic conductivity, $n$ is a pore-size distribution index, $l$ is a pore-connectivity parameter, and $S_e$ is the effective saturation:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$$

Because the MPS-1s measure potential in kilopascals rather than pressure head in centimeters, modeling results will be expressed as $\Psi$ in kilopascals for comparison to experimental data.

Estimates for the values of these hydraulic parameters are required for the solution of the van Genuchten-Mualem functions. Due to the difficulty of obtaining direct measurements, parameters were estimated based on the particle-size distribution of the soil using the neural network analysis-based pedotransfer function (PTF) model Rosetta (Schaap et al., 2001). Particle-size distribution was analyzed using the hydrometer method for 10 samples collected throughout the top 100cm at the edge of a creosote bush in 9 plots at each sites. Differences under creosote bushes and in the interspaces, such as higher sand contents measured under shrub canopies (Caldwell et al., 2008), required that all samples be taken at the approximately the same distance from the shrubs at which the MPS-1s were installed. The particle-size distribution is representative of the proximity to the creosote bushes at which all measurements were done but may not reflect the sites overall. Spatial variability results in some uncertainty in the PTF, which is generally greater than the PTF intrinsic uncertainty and can result in significant errors (Deng et al., 2009). Despite their wide use, significant uncertainties exist in PTF predictions of hydraulic parameters (Vereecken et al., 2010). However, the predictions are expected to be adequate for simulating general trends of the MPS-1 measurements.

Gravel comprised approximately 31% of the soil by weight at WC and 20% at PB but was assumed to have a negligible contribution to $\Psi$. Because of spatial variability at the sites, only the particle-size distributions from plots near the sensors were used to determine the soil hydraulic parameters. The MPS-1s at Wide Canyon were located in the northern part of the site where there was no consistent pattern with depth and little variation between plots. Soil hydraulic parameters were determined by the average particle size distribution of plots in which the sensors were installed, which were approximated to be uniform with depth.

Table 1.1 shows the soil hydraulic parameters as well as the particle size distribution measurements from WC and PB used to calculate them. Although no consistent pattern of variation was observed with space or depth at PB, irregularly distributed high silt percentages of 13-20% were common amidst more typical silt measurements of 8-10%. Because of the inconsistency between measurements in the plots, hydraulic properties were determined at PB using an average of four plots in the vicinity of the sensors to represent the average particle-size distributions around creosote bushes near the sensors. A uniform distribution with depth was assumed at PB since no pattern in the variations was observed.

Vapor flow and heat transport are modeled by HYDRUS-1D as described by Saito et al. (2006). The volumetric water content of vapor ($\theta_v$) is approximated by:

$$\theta_v = \rho_v \frac{\theta_s - \theta}{\rho_w} = \rho_{vs} H_r \frac{\theta_s - \theta}{\rho_w}$$

where $\rho_w$ is the density of liquid water, $\rho_v$ is the vapor density, and $\rho_{vs}$ is the saturated vapor density, and $H_\mathrm{r}$ is the relative humidity given by (Philip and de Vries, 1957):

$$H_r = \exp\left[\frac{hMg}{RT}\right]$$

where $M$ is the molecular weight of water in mass/mol, $g$ is gravitational acceleration, $R$ is the universal gas constant, and $T$ is the temperature.

$\rho_{vs}$ is a function of temperature:

$$\rho_{vs} = 10^{-3}\frac{\exp\left(31.3716 - \frac{6014.79}{T} - 7.92495\cdot 10^{-3}T\right)}{T}$$

The thermal hydraulic conductivity function ($K_{LT}$) is described as follows:

$$K_{LT}(T) = K_{Lh}(h)\left(hG_{wT}\frac{1}{\gamma_0}\frac{d\gamma}{dT}\right)$$

where $K_{Lh}$ is the isothermal liquid hydraulic conductivity, $G_{wT}$ is the gain factor representing the temperature dependence of the retention curve (which is 7 for sand), $\gamma_0$ is the surface tension of the water at 25°C (71.89 g $s^{-2}$), and $\gamma$ is the surface tension of the water given by:

$$\gamma = 75.6 - 0.1425T - 2.38\cdot 10^{-4}T^2$$

The isothermal vapor hydraulic conductivity ($K_{vh}$) is approximated as:

$$K_{vh} = \frac{D_v}{\rho_w} \rho_{vs} \frac{Mg}{R_u T} H_r$$

where $D_v$ is the vapor diffusivity in soil given by:

$$D_v = \tau_g a_v D_a$$

where $\tau_g$ is the tortuosity factor, $a_v$ is the porosity filled with air, and $D_a$ is the diffusivity of water vapor in air at a given temperature:

$$D_a = 2.12 \cdot 10^{-5} \left( \frac{T}{273.15} \right)^2$$

The thermal vapor hydraulic conductivity is described as follows:

$$K_{vT} = \frac{D_v}{\rho_w} \eta_e H_r \frac{d\rho_{vs}}{dT}$$

where $\eta_e$ is the enhancement factor describing increases in thermal vapor flux due to increased gradients in temperature in the air phase and liquid-islands (Philip and de Vries, 1957), given by an equation derived by Cass et al. (1984) and expressed as:

$$\eta_e = 9.5 + 3\frac{\theta}{\theta_s} - 8.5 \exp\left\{ -\left[ \left( 1 + \frac{2.6}{\sqrt{f_c}} \right) \frac{\theta}{\theta_s} \right]^4 \right\}$$

where $f_c$ is the fraction of clay by mass in the soil.

Heat transport was estimated in the HYDRUS-1D model using the default thermal parameters for sand, atmospheric temperatures as the upper boundary condition, and a zero gradient lower boundary condition.

### *Vegetation*

Both sites are dominated by creosote bush, long-lived flowering evergreens found throughout the Sonoran, Mojave, and Chihuahua Deserts. The creosote bushes are widely spread across the sites, with complex extensive root systems underlying the spaces between them. Annuals grow at greater densities under and around creosote bush and other desert shrubs, which have greater nutrients beneath their canopies relative to the interspaces (Garner and Steinberger, 1989; Reynolds et al., 1999; Schade and Hobbie, 2005; Schlesinger and Pilmanis, 1998; Schlesinger et al., 1996). Drought during the winters of 2005-2006 and 2006-2007 resulted in many creosote bushes losing leaves and branches. During the study from 2008-2010, the health of the creosote bushes appeared to improve with new growth at the base of the plants.

MPS-1s were installed on the southeast side of the creosote bushes approximately 0.5m from the edge of the canopy, within the radial spread of the lateral roots of the shrubs, which is expected to be greater than 2m based on previous studies (Gibbens and Lenz, 2001). The vertical root distribution is considered an unknown that can be fitted to the data for the purpose of modeling. Creosote bush rooting depth is expected to be limited by the depth of water flow when there are no other restrictions (Wallace and Romney, 1972); therefore, the entire depth of percolation is expected to be included in the root zones at WC and PB. The proximity of deep roots to the sensors is unknown since roots can extend a distance in the horizontal plane before veering into the soil, reaching several meters depth (Gibbens and Lenz, 2001).

The initial estimation of creosote bush root distribution with depth reflects the varied observations of several studies. Wallace et al. (1980), who excavated three creosote bushes in increments of 10cm to a depth of 50cm in Rock Valley at the Nevada Testing Site, found that root biomass was similar from 0-10cm and 10-20cm but much less in lower intervals. Schwinning and Hooten (2009) fit a curve to the root biomass measured by Wallace et al. (1980) that decreased about 5% per centimeter below 15cm. The presence of a caliche layer 30-50cm at Rock Valley, as well as the low precipitation, likely affected the rooting depth (Wallace et al., 1980), limiting the applicability of the measurements to WC and PB, which do not have shallow caliche layers. Yeaton et al. (1977) found greater biomass density of creosote bush roots between 10-30cm in a Sonoran Desert mixed shrub community. Sandvig and Phillips (2006) observed fairly constant root density in the top 30cm, a decline from 30-50cm, and a smaller but steady root density below 50cm at a New Mexico sites. Estimation of the root distribution is further complicated by the greater importance of fine roots than coarse roots in taking up water. Wilcox et al. (2004) found creosote bush to have the greatest number of fine roots between 20cm and 40cm, few roots below 60cm, more fine roots between canopies than under canopies, and a greater number of active roots in lower soil moistures at the

Nevada Test Site. With these conflicting studies, the initial creosote bush root distribution used estimates a constant root density from 10 to 40cm, a linear decline in root density above 10cm, and a 5% per cm decline below 40cm as shown in Figure 1.4.

Input parameters for the Feddes root water uptake model (Feddes et al., 1974) were also uncertain due to limited data on uptake by desert plants. Creosote bush is expected to be very efficient at taking up water. A maximum rate of uptake was estimated to begin at -100cm, above which water is seldom maintained long in a sandy desert soil. Below -1000cm, the efficiency of water uptake is estimated to decrease, primarily due to the very low hydraulic conductivity, which would be expected to hinder the transport of water from the vicinity of the MPS-1s to the roots for uptake. -5000cm is chosen as the wilting point due to the inability of the MPS-1s to measure below this. Although xylem-pressure-potential measurements of creosote bush in the Sonoran deserts could be as low as -65000cm (Nilsen et al., 1984), the van Genuchten-Mualem retention and hydraulic conductivity curves suggest miniscule difference between -5000cm and -65000cm in water content or conductivity.

Root compensation for water stress can be included in HYDRUS-1D, which experimental evidence has suggested allows plants to meet transpiration demands by taking up more water in areas of the root zone where it is available to compensate for stresses in other areas of the root zone (Simunek and Hopmans, 2009). As a result of compensation, plants are estimated to transpire at the potential rate above a critical ratio of calculated actual transpiration to potential transpiration ($T_0$). Because desert plants are expected to have a great ability to compensate for stress (Simunek and Hopmans, 2009), an initial estimate of 0.1 for the critical value of the water stress index above which compensation occurs was chosen. Therefore, except when the soil was very dry, the actual transpiration was predicted to be equal to $T_0$.

The Hargreaves equation (Hargreaves, 1994) was used to predict potential evapotranspiration ($ET_0$) since it requires only temperature data and is less impacted by aridity than the alternative Penman-Montieth model (Hargreaves and Allen, 2003). $T_0$ was estimated as a proportion of $ET_0$ as determined by the surface fraction covered. Estimated shrub cover is 9.5% +/- 2.7% at Pinto Basin and 18.1% +/- 3.8% at Wide Canyon (Rao and Allen, 2010). The coverage of creosote bush leaves was small relative to the soil covered by the plant. The leaf area index estimate of 0.65 x cover (Kemp et al., 1997) is reasonably applicable for Wide Canyon and Pinto Basin. The surface cover fraction is therefore estimated to be 6.2% +/- 1.8% at PB and 11.8% +/- 2.5% at WC.

The water uptake of winter annual plants was incorporated into the model HYDRUS-1D as a second set of roots that would grow while the distribution of creosote bush roots remained constant. The native forbs *Chaenactis fremontii* and *Malacothrix glabrata* and the invasive grass *Schismus barbatus* were the most common annuals, all of which are considered part of the same root system in the model. The winter annuals contribute to $ET_0$ in the model only in the top 20cm of soil, below which annual roots were seldom found at PB and WC.

Growth of annuals was estimated to begin at the first significant rainfall of the winter season and peak when plant surveys were conducted. The length of the roots at a given time ($L_R$) was approximated by the Verhulst-Pearl logistic growth function:

$$f_r(t) = \frac{L_0}{L_0 + (L_m - L_0)\, e^{-rt}}$$

$$L_R(t) = L_m \;\, f_r(t)$$

where $L_m$ is the maximum root depth, $L_0$ is the root depth at the start of the growing season, $r$ the growth rate, and $t$ is time. $r$ was estimated using the assumption that the roots will reach 50% of their length after 50% of the growing season.

The surface cover fraction of the annuals ($SF_a$), which determines their contribution to total transpiration, was considered proportional to $L_R$:

$$SF_a(t) = p * SF_m * L_R(t) / L_m$$

$SF_m$ is the maximum surface fraction covered by the annuals. The variable p is necessary to account for uncertainty in the influence of nearby annuals, since sensors are between the densely populated undershrub of the creosote bushes and the more sparse interspaces.

The summation of the surface fraction cover of the annuals and the surface cover fraction of perennial shrubs ($SF_c$) determines the percentage of $ET_0$ accounted for by potential transpiration ($T_0$) at any given time:

$$T_0(t) = ET_0\,(t)\,(SF_a(t) + SF_c)$$

The percentage of total potential transpiration done by the annuals at any given time can be determined from an estimate of the surface fraction covered by the annuals by the equation:

$$T_{ann}(t)/T_0(t) = SF_a(t) / (SF_a(t) + SF_c)$$

where $T_{ann}(t)$ is the transpiration done by the annuals at a given time.

Determining the percentage of water and nutrients taken up by desert annuals would be a useful function of this model, but annuals are only considered separately in this analysis to assess whether their inclusion could potentially improve the fit of the model to the MPS-1 sensor data.

## Results

The HYDRUS-1D model was unable to reasonably reproduce the MPS-1 data without unrealistic assumptions. Figure 1.5 shows the measurements of $\Psi$ by the sensors as compared to the model's predictions at depths of 10cm and 70 cm in the WC control plot when the model used the previously described initial estimates for creosote bush root distribution, surface cover fraction, and soil hydraulic parameters with no annual plants considered. Only two depths for the WC control plot are shown, but the general trends were representative of the model's predictions for all depths in all plots at both sites. The model consistently severely underestimates the timing of when the measured $\Psi$ sharply declines as the soil dries. The sharp decline is due to the steep water retention curve and unsaturated hydraulic curve predicted by the van Genuchten-Mualem (VGM) model (Figure 1.6). Sharp decreases in the measured Ψ as the soil dries occur weeks earlier than is predicted by the model.

Numerous attempts to rectify this problem failed to significantly improve the discrepancy with reasonable input assumptions. Increasing the rate of transpiration by raising the surface cover fraction allowed for the creation of models that could fit the data fairly well (Figure 1.7). Although this decreases the evaporation, it allows for more efficient water removal deep in the soil. Table 1.2 shows the surface cover fractions that produced the best fit of the data for each year. The high surface cover fractions necessary to improve the fit of the models suggest that transpiration by the deep-rooted shrubs is unlikely to account for the rapid decline in Ψ observed in the measured data. The significant increase the second year is also not likely to be accounted for by significantly increased creosote bush uptake.

By including the secondary root system to simulate the growth of the annuals, the surface fraction can reasonably be increased. Figure 1.8 shows the model for the WC control plot when annuals are considered, but is representative of all plots both years. Estimated annual surface coverage of 15% improved uptake in the top 20%, but the model continued to predict the soil drying too slowly below the root zones of the annuals. Transpiration by creosote bush remains too small to account for the decline in Ψ below the root zones of the annuals. Although the estimated $ET_0$ of the site would be more than sufficient to remove the water from the soil (Figure 1.9), the water below 20cm appears to be accessible only to deep-rooted plants with low surface coverage.  With an estimated surface cover fraction of 11.8% at WC, the cumulative $T_0$ from the shrub cover was only 3.5cm (about 20% of the 2009-2010 winter precipitation) by the end of March 2010, when most of the sensors had declined.  With so little estimated $T_0$ reducing water below 20cm, a factor besides transpiration likely accounts for the measured decline in $\Psi$.

The potential for an underestimation of percolation below the zone of the sensors by the model to account for its underestimation of the rate of the decline in $\Psi$ was examined by varying the soil hydraulic parameters.  Inverse fits produced no results due to the magnitude of the divergence between the measured and modeled $\Psi$.  Alterations to the parameters that improved the timing of the soil drying resulted in greater inaccuracies in other parts of the model.  Preferential flow, which has been observed to a depth of 50cm along creosote roots (Martinez-Meza and Whitford, 1996),  may alter the amount of water percolating below the sensor zones.  The impact of preferential flow is unknown, but nothing suggests that it could completely rectify the discrepancy between the model and the measurements. The likelihood of greater percolation below 70cm than the model predicts significantly reducing the $\theta$ is unlikely because the models often over-predicted the depth of water flow into dry soil, as can be observed in Figure 1.5, where the modeled $\Psi$ at 70cm in the winter of 2009-2010 at WC increases prior to when the measured $\Psi$ increases.  Moreover, water percolating below the sensors would still contribute to transpiration, since creosote bush root depth is expected to be limited by the depth of water percolation when their growth is not otherwise restricted (Wallace and Romney, 1972), with roots having been measured to reach depths of 3m or more (Gibbens and

Lenz, 2001). Attempts to fit the data by estimating creosote bush water uptake only between 15cm and 75cm to maximize uptake in the root zones of the sensors still underestimated the timing of the decline of the measured $\Psi$ when reasonable shrub covers were input.

Because neither transpiration nor deeper percolation can account for the rate at which the measured $\Psi$ decreased, a substantial amount of the precipitation may have remained in the soil when the sensors measurements declined. Although the retention curve predicted by the VGM model would allow only about 0.003 $cm^3/cm^3$ of water removable from the soil below -500kPa before $\theta_r$ is reached, the neutron probe readings from 9 plots at each site indicate a significant decrease in $\theta$ throughout the summer of 2009 (Figure 1.10). Because insufficient site-specific calibration data was obtained, there is some uncertainty in the measurements, particularly estimates of a $\theta$ of essentially zero. However, trends clearly suggested significant moisture remained to be removed after the MPS-1 measurements declined. In late February and early March, when most sensor readings had sharply declined, estimated $\theta$ remained elevated relative to $\theta$ the previous November in the top 95cm at each site. Table 1.3 shows the mean $\theta$ measured and the standard deviations of the means in the late spring and late fall of 2009 after the soil had dried. The differences in the means are statistically significant, with the small decline in the base reading of the neutron probe considered. Field observations when soil cores were taken throughout the summer also suggested the presence of greater moisture in early summer relative to late summer. Rough calculations extrapolating the neutron probe readings over the soil above the depth they were taken suggest a loss of about 1.9cm at

WC and 3.4cm at PB between April and November 2009, or about 26% and 53% of the previous winter's precipitation. There is little certainty in these estimates of the amount of water removed from soil, but they support the hypothesis that the water flux at very low $\Psi$ during the summer contributes significantly to the overall flux despite the predictions of the VGM model.

## Discussion

The inability of HYDRUS-1D to reproduce $\Psi$ measured by the MPS-1s most likely results from the loss of a significant proportion of the rainfall at low $\Psi$ during the summer. The VGM functions are not accurate at very low $\theta$ (Khaleel et al., 1995; Nimmo, 1991; Rossi and Nimmo, 1994), which could result in an underestimation of the amount of water that is removed from the soil as $\Psi$ becomes very low. Although the modeling was intended to focus on water flow at medium and high $\theta$, which are expected to dominate during the growing season, the initial conditions of the soil were very dry. Differences between the van Genuchten-Mualem (VGM) model's approximation of the very dry region and the true retention function seemed to be significant enough to cause the model to considerably underestimate the water necessary to increase the $\Psi$ from highly negative values (~5000kPa) to moderately negative values (~500kPa). Because HYDRUS-1D cannot account for the VGM model's underestimation of water depletion in the very dry region by allowing initial water contents below $\theta_r$, an accurate model cannot be created for water flow during the growing season that starts with dry conditions. Consistent with the neutron probe estimates, the extent of the errors observed in the HYDRUS-1D model imply that the water flux at very low Ψ during summer contributes substantially to the total annual water flux.

### *The VGM Model at Very Low Water Contents*

Accuracy in the very dry range is generally not important in the van Genuchten-Mualem and Brooks-Corey (BC) soil hydraulic properties models because the vast majority of liquid water flow occurs in the wet and moderately-wet ranges. At very low $\theta$, the VGM model and the Brooks-Corey model approach $\theta_r$, which is frequently a poorly-defined variable set to a convenient value. Hydraulic continuity is estimated to cease at $\theta_r$, with the matric potential approaching negative infinity and the hydraulic conductivity approaching zero. However, the assumption that Ψ becomes infinitely negative at a nonzero $\theta_r$ is not well-supported by experimental evidence and it has been shown that the VGM and the BC models do not accurately represent very dry soils (Nimmo, 1991; Ross et al., 1991).

Numerous hydraulic property models have been proposed over the past twenty years that attempt to accurately describe the dry range. Rossi and Nimmo (1994) created water retention curves extending to oven dryness based on the combination of a power function and a logarithmic dependence of $\theta$ on Ψ. Andraski and Jacobson (2000) evaluated the Rossi-Nimmo (RN) function in comparison to the BC function and found the RN function better simulated data measured in a desert soil under dry conditions. Another model for retention curves covering saturation to oven-dryness was created by

Groenevelt and Grant (2004), who fit the data on a semi-logarithmic scale. Webb (2000) proposed that simply extending the capillary pressure function into the dry range could improve simulations.

The inclusion of the contribution of adsorptive forces, in addition to capillary forces, to matric potential has been the focus of many models encompassing the dry region. Fayer and Simmons (1995) replaced $\theta_r$ in the BC and VGM models with an adsorption equation formulated by Campbell and Shiozawa (1992). Khlosi et al. (2006) similarly modified the Kosugi (1999) model using the Campbell and Shiozawa adsorption equation. Tuller et al. (1999) created a model that incorporates adsorption and simulated a more realistic pore space geometry. Silva and Grifoll (2007) proposed a water retention function incorporating the Brunauer-Emmett-Teller adsorption isotherm in the dry range, while applying the BC function in the wet range.

Although the Fayer-Simmons model has been partially-integrated into HYDRUS (Sakai et al., 2009), the model is not yet useable for data from PB and WC because water uptake by roots was not integrated in the model.

### *Vapor Flow in the Dry Range*

The consideration of nonzero $\theta_r$ at which the hydraulic conductivity is zero and the $\Psi$ is infinitely negative is particularly problematic when vapor flow is important (Prunty, 2003). Because in the formulation used in the HYDRUS-1D model for relative humidity $H_r$ is dependent on pressure head (and therefore on $\Psi$), if $\Psi$ is predicted by the VGM and BC models to become infinitely negative at $\theta_r$, $H_r$ will be predicted to be zero at $\theta_r$. This allows no consideration of equilibration between liquid water and water vapor for $\theta < \theta_r$ when $\Psi$ is taken to be infinite at $\theta_r$, which is inaccurate since both adsorbed water and capillary condensation can be evaporated. The importance of accurately estimating an adsorptive component of $\Psi$ when describing the liquid-vapor interface was emphasized by Philip (1977), who found that the Kelvin equation could not account for the effects of adsorption. The temperature independence of $H_r$ becoming zero at a nonzero $\theta_r$ makes the problem even more evident, since the reduction of soil water to oven-dry conditions involves the removal of $\theta_r$ by evaporation due to heat.

### *Issues in the Model of the MPS-1 Measurements*

A seemingly minor discrepancy of the VGM model at very low $\theta$ could significantly affect its ability to predict water flow in the moderately wet range in the desert. Figure 1.11 shows a hypothetical retention curve for WC in comparison to the VGM model that would be generally consistent with the predictions of dry region models, such as the Rossi-Nimmo models. The differences between the models could result in substantially different estimates of water flow during the growing season in the desert. Measurements of -8000kPa are not unusual in root zones in deserts (Andraski, 1997; Scanlon et al., 2003). Whereas the difference $\theta$ between -500kPa and -8000kPa is only 0.00045cm$^3$ cm$^{-3}$ in the VGM retention curve, the difference is 0.01558cm$^3$ cm$^{-3}$ in the hypothetical retention curve. Approximately 1.48cm of water would be necessary to raise the profile from -8000kPa to -500kPa in the top 95cm in the hypothetical curve, compared to only 0.043cm predicted by the VGM model. Considering that the neutron probe readings suggested water percolated to approximately 95cm in the winter of 2008-2009, the hypothetical curve predicts 20% of the precipitation would have been necessary to raise the Ψ to -500kPa at WC, compared to the VGM curves' estimation of 0.6%. This would result in 20% of the water from winter precipitation remaining in the soil when the Ψ measured by the MPS-1s declines below -500kPa, while the VGM model would not decline below -500kPa until only 0.6% of the precipitation remained. This could account for the discrepancy between the timing of the MPS-1s rapid decline in Ψ at the end of the season and the timing of the decline in Ψ predicted by HYDRUS. While the hypothetical example demonstrates the potential for inaccuracies in the VGM model at very low $\theta$ to result in problems in the HYDRUS-1D model similar to those observed, the actual shapes of the retention curves in the very dry region at WC and PB are unknown. The issues with the HYDRUS model and the neutron probe measurements suggest that an estimate of the removal of ~20% or more of the precipitation at very low Ψ during the summer of 2009 may be reasonable.

To use the VGM model to approximate the MPS-1 data in the moderately wet range at WC and PB, the initial $\theta$ would need to be set below an effective $\theta_r$ to account for the underestimation by the VGM curve of the water necessary to raise the Ψ in the dry range. Although the model would remain inaccurate in the approach of $\theta_r$, the majority of water flow on the daily time scale occurs at Ψ at which the VGM model is useful. The percent of the precipitation estimated to raise the $\theta$ to the effective residual water content for the VGM model would be given by:

$$\text{Effective precipitation} = P - \int(\theta_r - \theta_i)\, dl \qquad \text{when} \quad \theta_i < \theta_r$$

where $P$ is precipitation, $\theta_i$ is the initial water content before the precipitation at any given depth, and in integration is done over the depth of the water flow. The $\theta_r$ here is only considered a fitting parameter that allows application of the VGM model at moderate $\theta$ but does not truly represent the very dry range.

### *Depletion of Water During the Summer*

Both the neutron probe measurements and the HYDRUS-1D results suggest considerable water removal during the summer at very low $\Psi$. Neutron probe measurements by Andraski (1997) in the top 50cm of a vegetated Mojave Desert soil showed similar continued declines in $\theta$ throughout summer after the measured $\Psi$ had declined to highly negative values. The cause for the reduction in $\theta$ is insufficiently understood, with further study being necessary for the determination of the relative contributions of vapor flow, capillary flow, and film flow to this reduction. Although the VGM model does not represent liquid flow well at very low $\theta$, it is expected that hydraulic continuity in the sandy soil would be greatly reduced during the dry summer. With the potential for both isothermal and thermal vapor flow to contribute substantially the total water flux in desert soils (Scanlon and Milly, 1994) and its increasing importance at very low $\theta$, vapor flow processes are likely responsible for a significant amount of the water reduction.

The well-established effect of desert vegetation on the water flux even deep in the soil (Andraski, 1997; Sandvig and Phillips, 2006; Scanlon et al., 2005; Walvoord and Phillips, 2004) makes it probable that water is not lost solely to evaporation during summer. The highly negative matric potentials found in the deep root zones of vegetated desert soils can induce upward fluxes that contribute to drying the soil below (Scanlon et al., 2003; Walvoord et al., 2002b). The water potential of creosote bush tissues as low as -7.8 MPa have been measured (Odening et al., 1974), indicating the capacity for creosote bush to continue to uptake water in extremely dry conditions. The greater length of active fine roots of creosote bush in conditions of low water availability (Wilcox et al., 2004) and the continued creosote bush metabolical activity throughout the dry season (Oechel et al., 1972) further suggest that vegetation may contribute to water removal in soil throughout the summer. More water available for capillary flow at low $\Psi$ than predicted by the VGM model would make the reduction to these very negative $\Psi$ more advantageous than simply allowing uptake of the miniscule amount of water predicted by the VGM model, but with little hydraulic continuity predicted, it is unclear how the water is transported through the sandy soil to the roots.

Several studies have shown that downward thermal vapor fluxes in the root zones can result in condensation in desert soils, which could potentially be taken up by plants. Sakai et al. (2009) evaluated the condensation of water vapor at the cooler base of a sandy soil column, which was followed by upward liquid flow driven by matric potential gradients and evaporation at a moisture front. Similar condensation and subsequent liquid flow was observed by Garcia et al. (2011) at the base of the creosote bush root zone in simulations of vapor flow and liquid water flow at a Mojave Desert site. Garcia et al. (2011) hypothesized that this may provide a source of water for the plants during the driest periods of the year. Gran et al. (2011) found that condensation of downward-moving vapor below the evaporation front can result in the solution being diluted below the evaporation front in columns of salty soils. Even in absence of the thermal gradients, condensation of vapor water on and near roots could play a role in water transport in desert soils. With minimal hydraulic continuity likely in the sandy soil during summer, capillary flow through soil is expected to be very limited. However, the uptake of water on or very near roots would result in the restoration of the water by capillary condensation due to the equilibration of the water vapor and liquid water. The resulting reduction of the water vapor could produce an isothermal gradient causing vapor flow from other areas of the soil, which would create most water vapor in other parts of the soil to maintain the balance between liquid water and water vapor. The net result is the transport of water to the roots that does not rely on capillary flow. Whether this could significantly contribute to the reduction of soil water during the summer is unknown.

### *Potential Consequences*

The slow loss of a substantial proportion of the winter precipitation throughout summer at low $\Psi$ would alter expected nutrient uptake by plants relative to expectations of the majority of water being removed by evapotranspiration when the soil is moderately wet. The greater prominence of vapor flow at very low $\Psi$ during the summer may cause an inaccessibility of many soil nutrients to plants. For example, if 20% of the winter precipitation remains when the $\Psi$ drops below -500kPa and vapor flow is predominantly responsible for the subsequent reduction of this water through evaporation or capillary condensation near roots, many nutrients dissolved in this water would be left in the soil throughout summer. Subsequent rains may dilute nutrients in the soil and provide some availability to plants, but could also leach a portion down the soil. This could be a contributing factor to the accumulation of nitrate in the deep root zones in deserts throughout the Holocene (Hartsough et al., 2001; Marion et al., 2008; Walvoord et al., 2003). The effect of the substantial removal of winter precipitation at very low $\Psi$ during the summer on nutrients and chemicals in soils requires additional study.

### *Future Research*

The reason hypothesized in this analysis that the flow of liquid water during the growing season in deserts cannot be modeled using HYDRUS-1D is that significant water reduction in the very dry region during summer cannot be accounted for in the VGM model. HYDRUS-1D cannot reproduce MPS-1 data in moderately wet soil because it overestimates the portion of the precipitation that contributes to raising the MPS-1 measurements above -500kPa. Although this hypothesis is an extension of known issues of the VGM model and is supported by a reduction in neutron probe counts throughout the summer, further research is needed. Alterations to the HYDRUS-1D model to allow the model to fit the data are necessary to support the hypothesis. Allowing the $\theta$ at the beginning of the growing season to be set below $\theta_r$ to account for water loss during the summer might improve the model by better estimating the portion of water contributing to sensor measurements above -500kPa. Improving the shape of the water retention curve used by HYDRUS-1D by implementing a soil hydraulic property model that better represents the dry region could also allow better simulation.

The inability of the HYDRUS-1D model to fit the MPS-1 data resulted in little potential for analysis of how root uptake by annuals affects water flow. The decline in the MPS-1 readings below the root zones of the annuals in close temporal proximity to the decline in MPS-1 readings in the annuals root zones suggests a relationship between creosote bush water uptake and the uptake of winter annuals that should be examined.

## 2.5 Conclusions

The inability of HYDRUS-1D to replicate the MPS-1 measurements may result from significant water flow below the lowest $\Psi$ that can be measured by the MPS-1s, which could not be accounted for in the model due to known inaccuracies of the van Genuchten-Mualem functions at very low $\theta$. Because the VGM model seemingly underestimates the increase in water content necessary to raise the $\Psi$ from highly negative values to moderately negative values, it overestimates the amount of water that must be removed subsequently to reduce the soil back to a highly negative $\Psi$. This was the most likely cause of the HYDRUS-1D models underestimating the timing of the decline in $\Psi$. This hypothesis is supported by field observations and neutron probe data that indicated that a substantial amount of water continued to be depleted throughout the dry summer after the measured $\Psi$ had declined despite the water retention curves predicting that this was not possible.

Additional research is needed to determine the extent to which vapor flow causes the loss of water throughout the summer. The possibility that condensed vapor water can provide a source of water to desert shrubs throughout the summer (Garcia et al., 2011) should be further examined, particularly since vapor transport dominates when matric potentials are low. A significant proportion of the annual water loss occurring over the dry summer due to vapor flow alters expectations for nutrient uptake, with nutrients presumably left in the soil and condensed when vapor flow dominates. Further investigation is needed to determine if this contributes to high concentrations of nitrate often measured in the deep root zones in deserts.

## References

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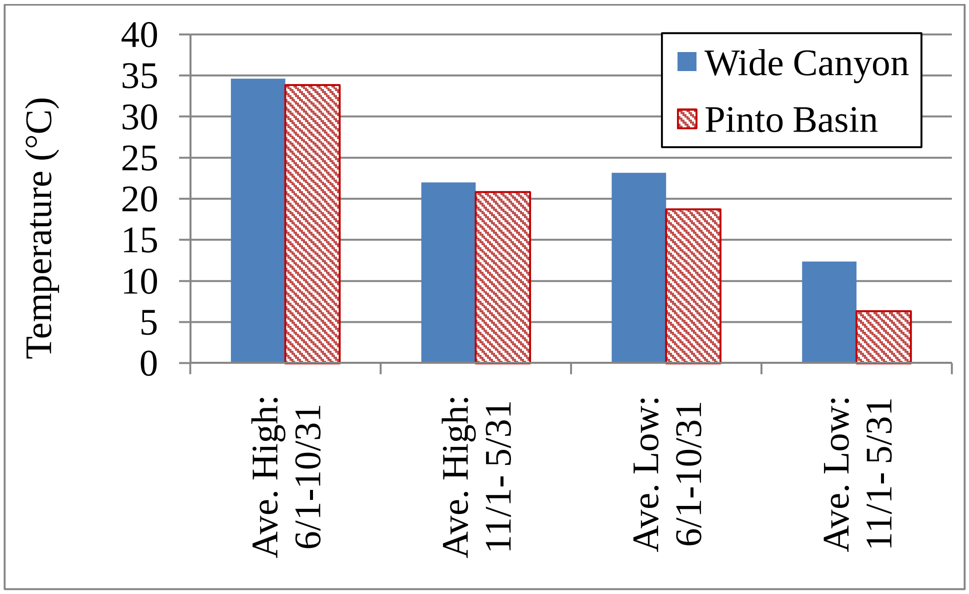
**Figure 1.1** Study site locations.

**Figure 1.2** Average temperatures and annual winter precipitation from 1/6/2005 to 5/31/2010 at WC and PB. Measured precipitation data is compared to estimated average precipitation from November to May from the NWS stations at Palm Springs (WC) and the Hayfield Pump Plant (PB).



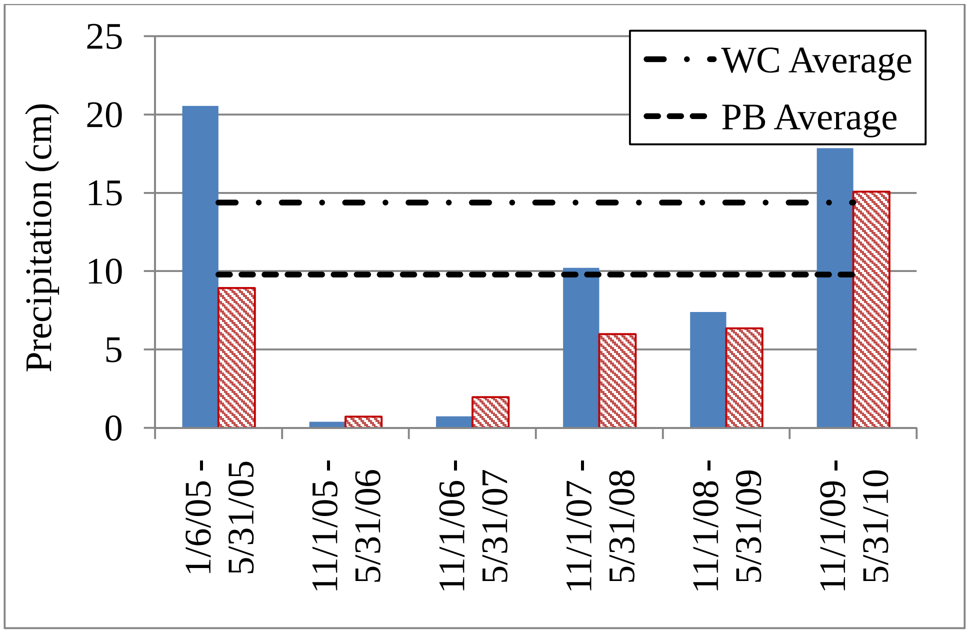


**Figure 1.3** Daily precipitation between 11/1/2008 and 5/31/2010 at WC and PB.

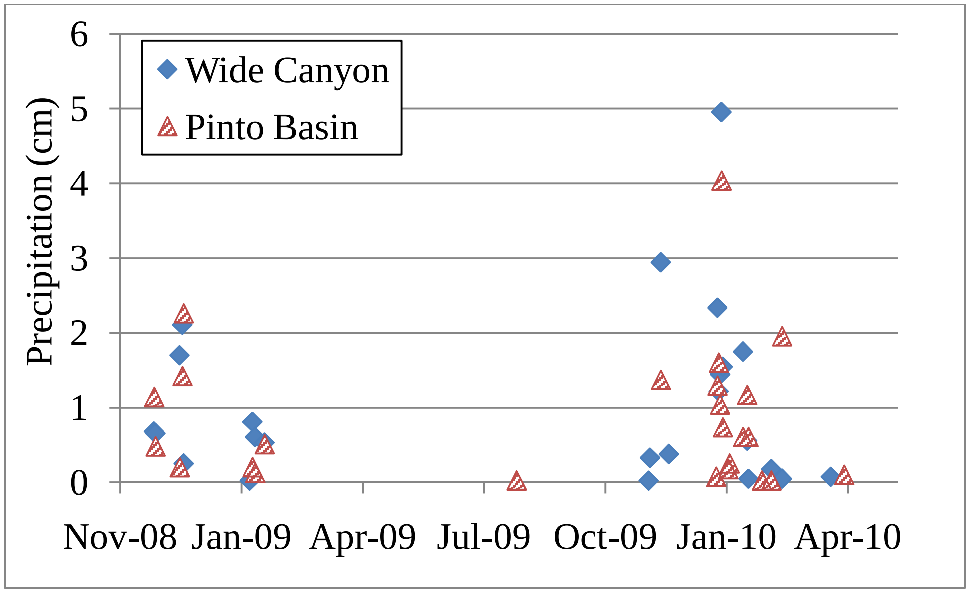


**Table 1.1** Measured particle size distribution and estimated soil hydraulic parameters determined by ROSETTA.

| Site | % Sand | % Silt | % Clay | $\theta_r$ | $\theta_s$ | $\alpha$ | $n$ | $K_s$ |
|---|---|---|---|---|---|---|---|---|
| WC | 87.3 | 8.8 | 3.9 | 0.0453 | 0.382 | 0.0379 | 2.25 | 227 |
| PB | 85.6 | 10.2 | 4.2 | 0.0437 | 0.383 | 0.0390 | 2.08 | 180 |

**Figure 1.4** Initial estimate for the root distribution of the creosote bushes at the sites. The input root distribution in normalized by the model HYDRUS-1D.

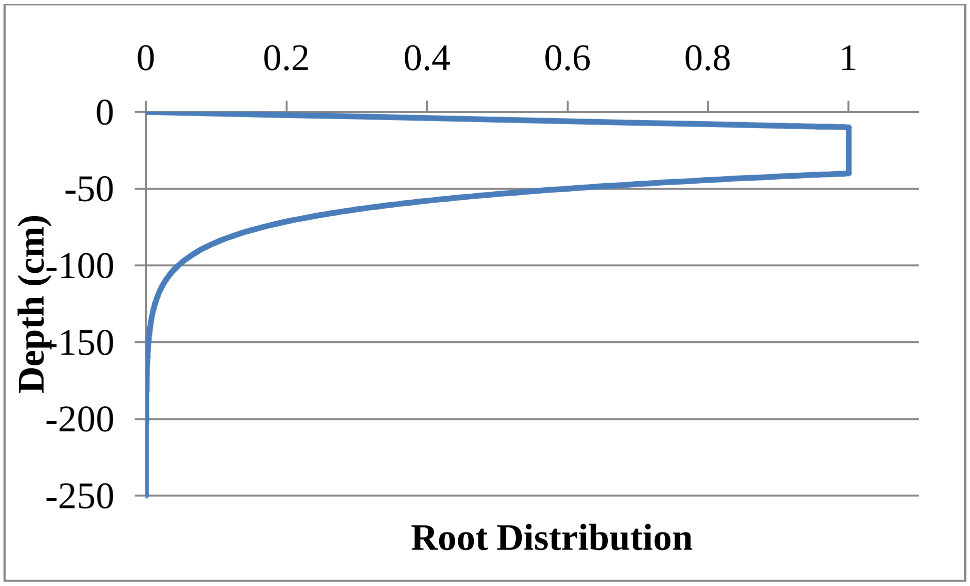
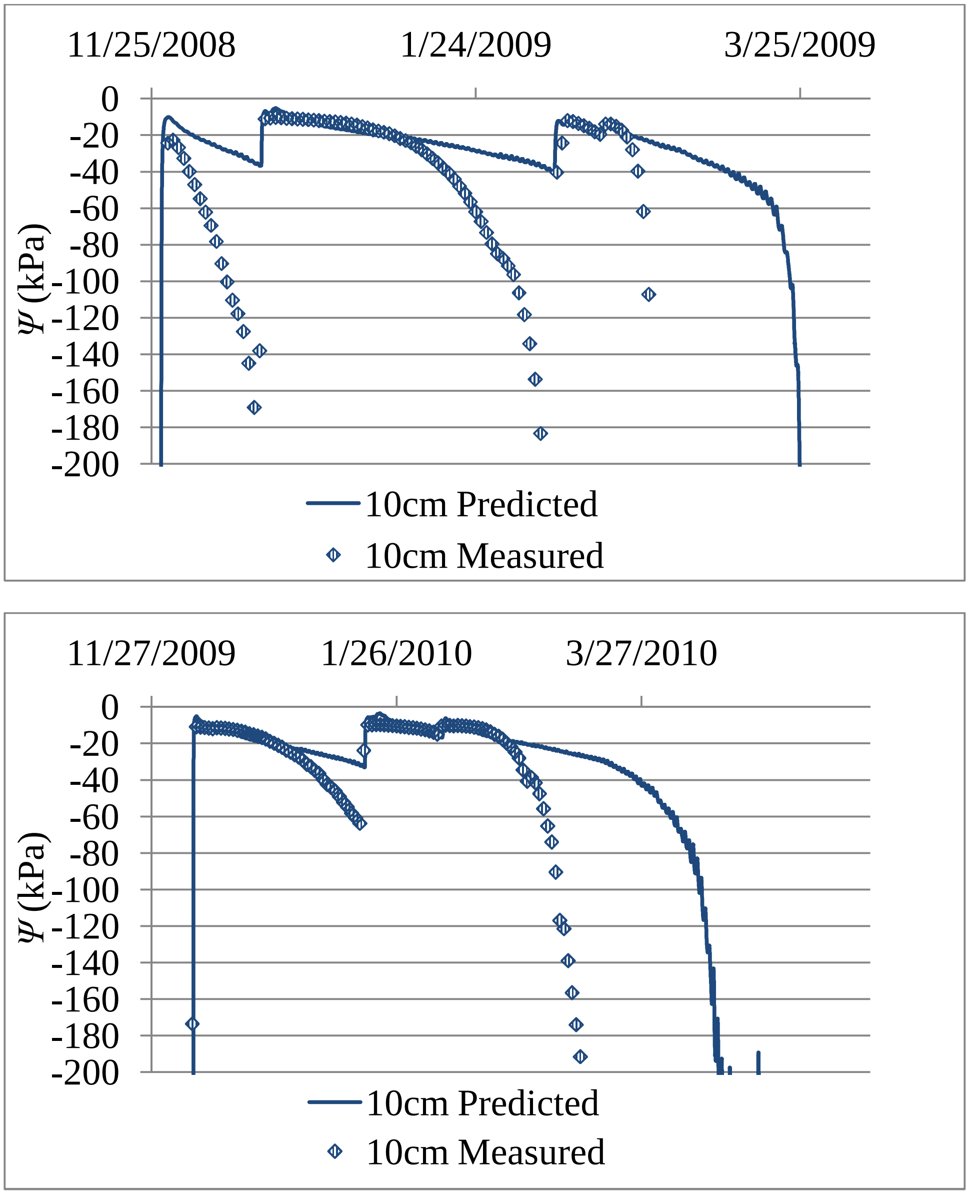
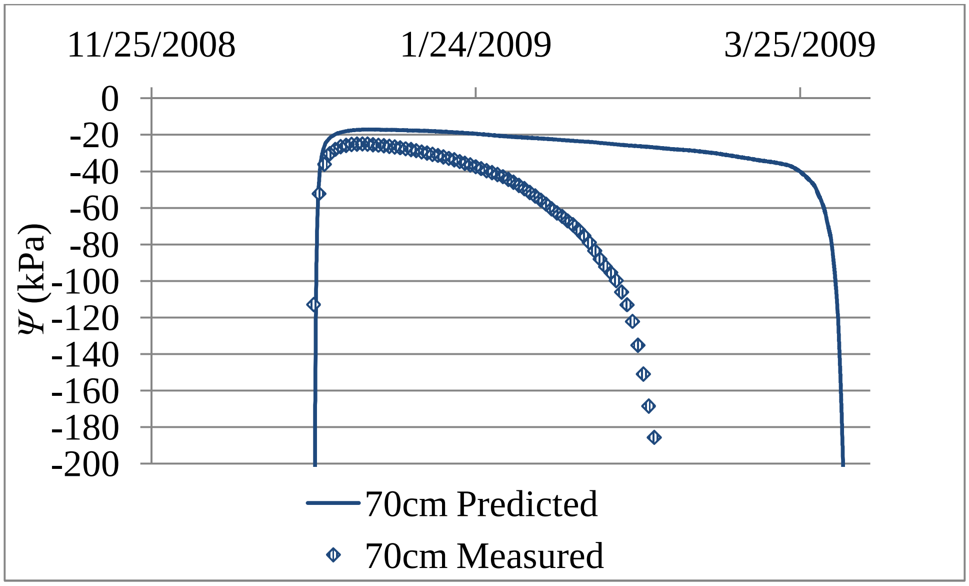


**Figure 1.5** Comparison between measured and predicted Ψ at 10cm and 70cm depth in the WC control plot during the winters of 2008-2009 and 2009-2010. The underestimation of the timing of the decline in Ψ by the model is representative of the model's predictions for all sensors at all depths at both sites. Graphs are displayed only between 0 and -200kPa to improve the clarity of trends.




11/25/2008
1/24/2009
3/25/2009
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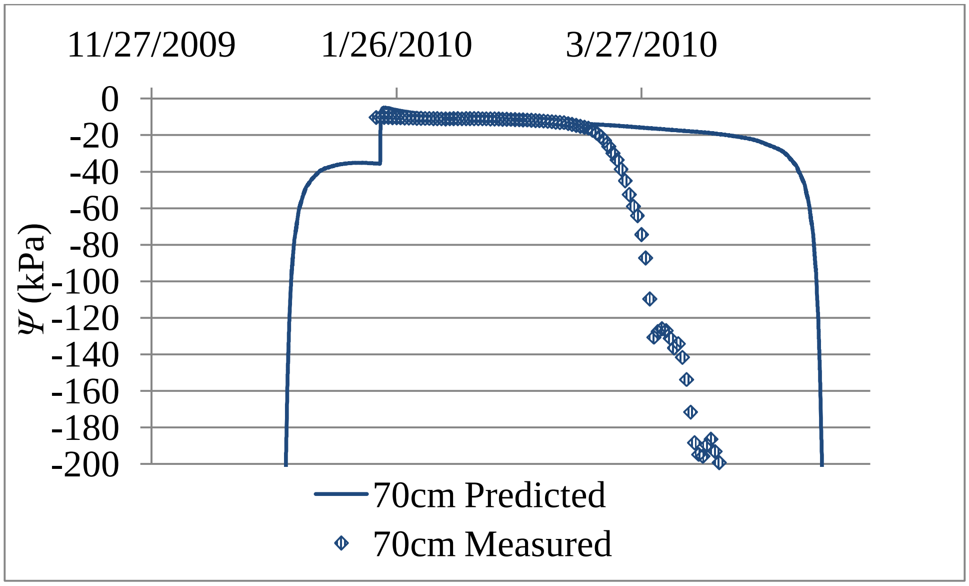
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Ψ (kPa)
70cm Predicted
70cm Measured


11/27/2009
1/26/2010
3/27/2010
0
-20
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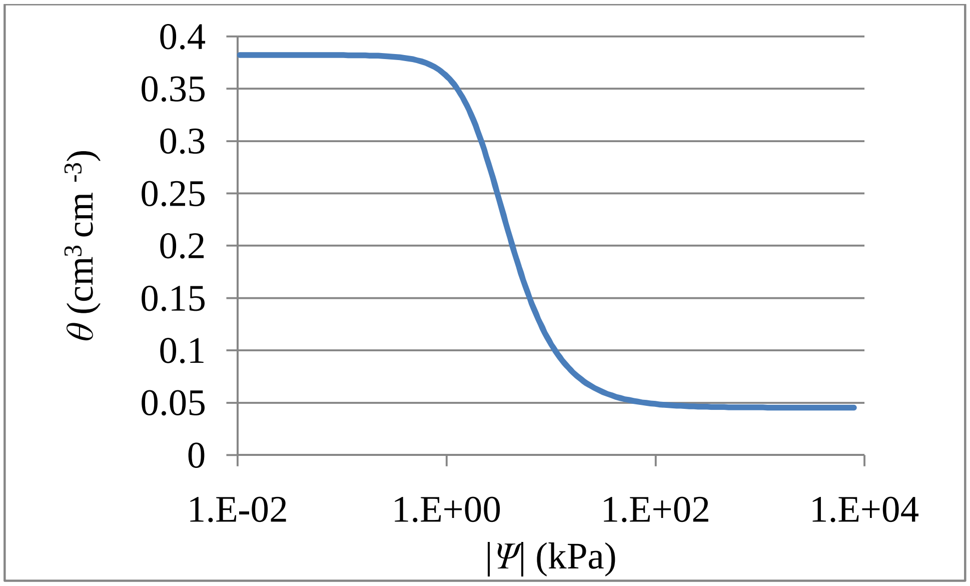
-60
-80
-100
-120
-140
-160
-180
-200
Ψ (kPa)
70cm Predicted
70cm Measured

**Figure 1.6** Predicted water retention curve and unsaturated hydraulic conductivity curves for the soils at WC. The retention and hydraulic conductivity curves for PB are similar.



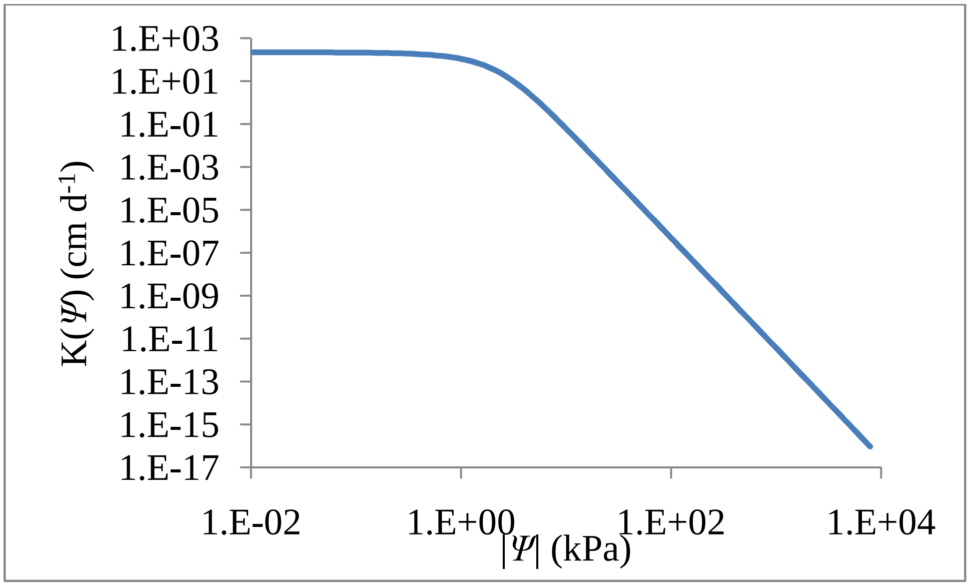
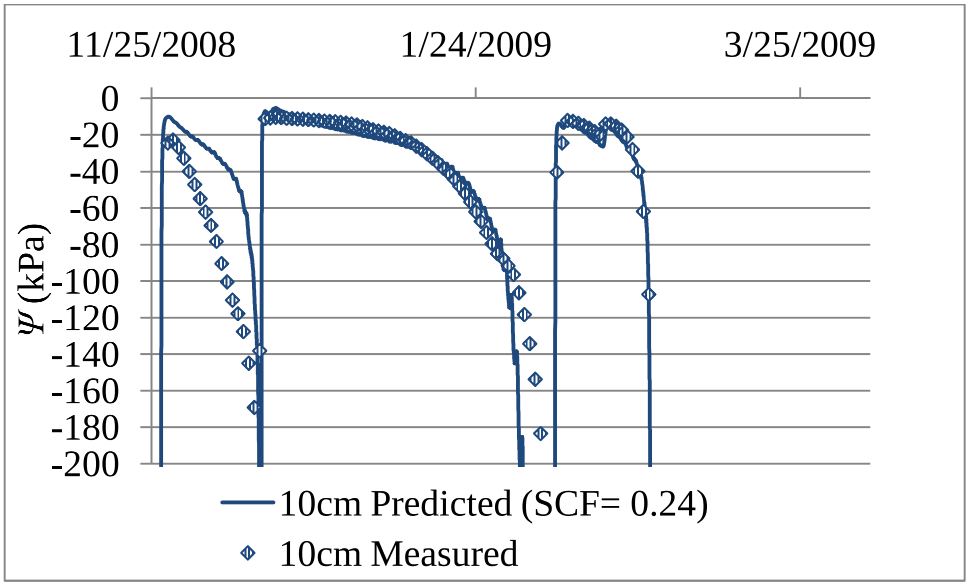
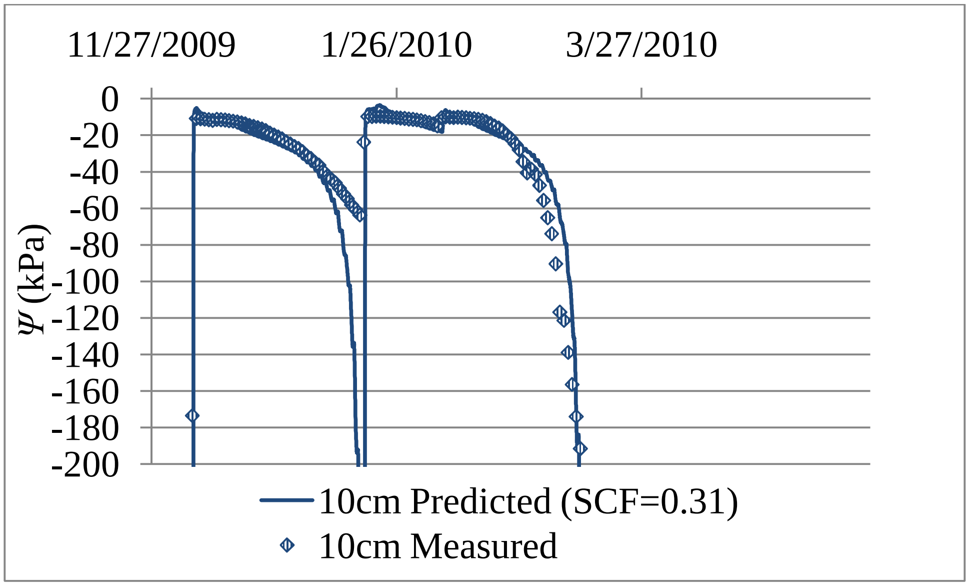
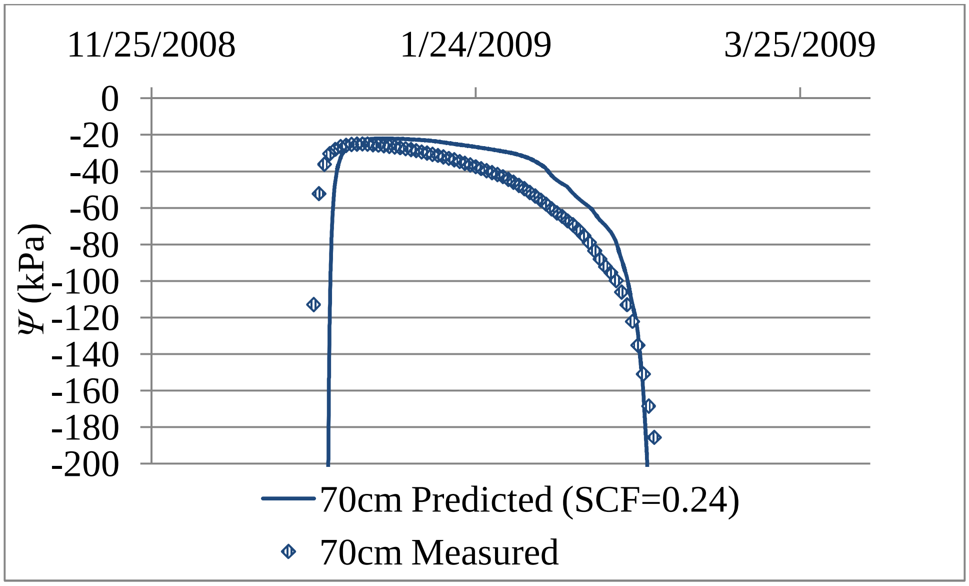
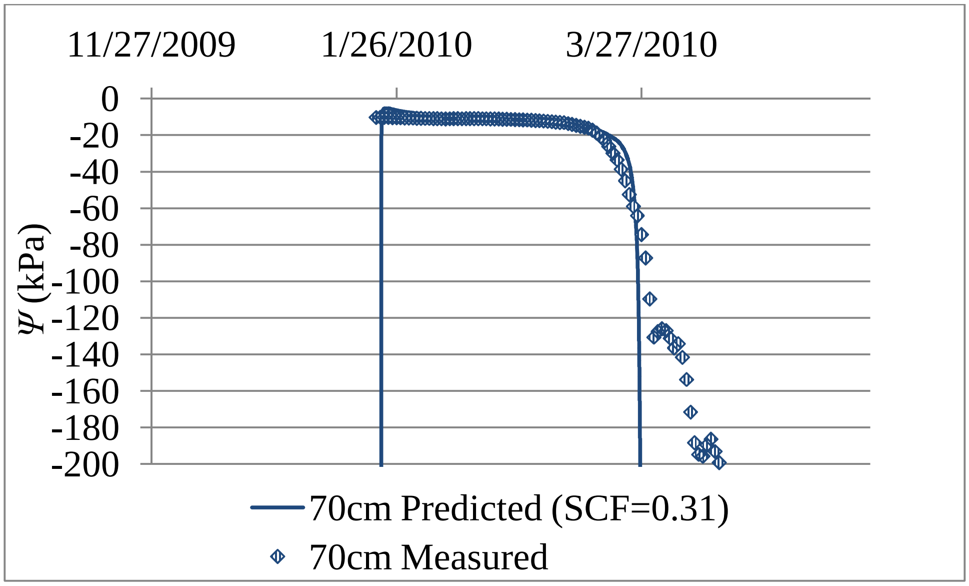


**Figure 1.7** Water potential predicted by HYDRUS-1D at 10cm and 70cm for the WC control plots when the surface cover fraction is raised. Similar improvements were found raising the SCF for all models.






11/25/2008
1/24/2009
3/25/2009
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Ψ (kPa)
70cm Predicted (SCF=0.24)
70cm Measured


11/27/2009
1/26/2010
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0
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-200
Ψ (kPa)
70cm Predicted (SCF=0.31)
70cm Measured

**Table 1.2** Surface cover fraction percentages producing the best fits of the data in HYDRUS-1D.

| Site | Plot Type | Year | % Surface Cover Estimated for Best Fit | Estimated % Shrub Leaf Cover |
|---|---|---|---|---|
| WC | Control | 2008-2009 | 24% | 11.8% ± 2.5% |
| | | 2009-2010 | 31% | 11.8% ± 2.5% |
| | Fertilized | 2008-2009 | 24% | 11.8% ± 2.5% |
| | | 2009-2010 | 32% | 11.8% ± 2.5% |
| PB | Control | 2008-2009 | 15% | 6.2% ± 1.8% |
| | | 2009-2010 | 35% | 6.2% ± 1.8% |
| | Fertilized | 2008-2009 | 13% | 6.2% ± 1.8% |
| | | 2009-2010 | 35% | 6.2% ± 1.8% |

**Figure 1.8** Predicted fit of the model to the data with 15% cover by annuals. Results from the WC control plot in the first year that are shown are typical of all results, with improved fit in the root zone not significantly improving the fit below the top 20cm.

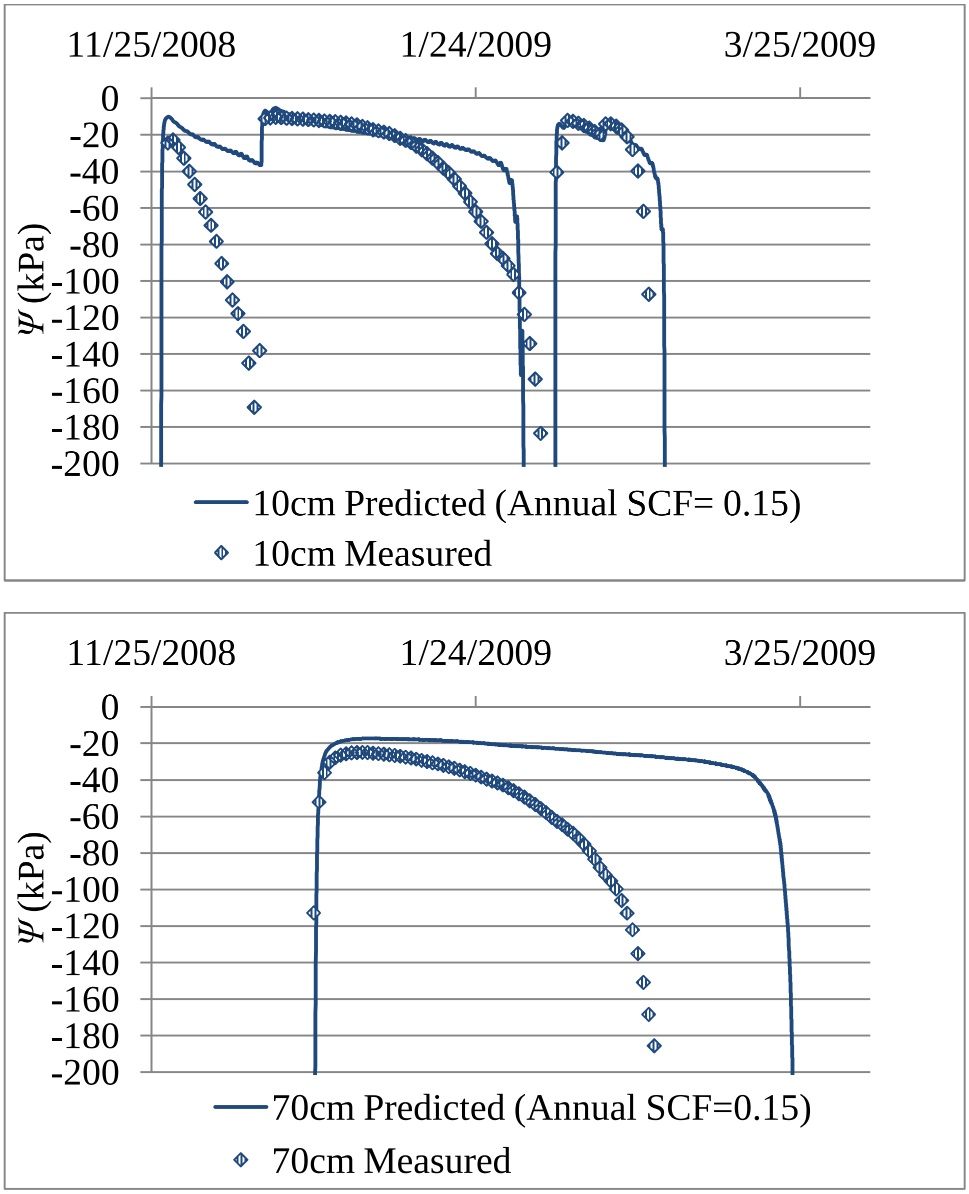
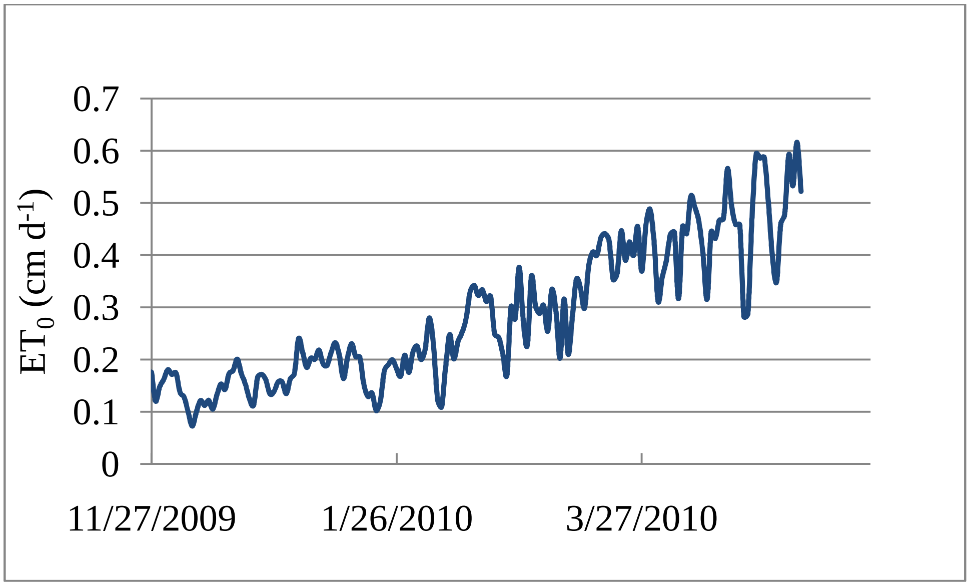


**Figure 1.9** Potential evapotranspiration and cumulative potential transpiration by deep-rooted shrubs at Wide Canyon (SCF=11.8) during the winter of 2009-2010.



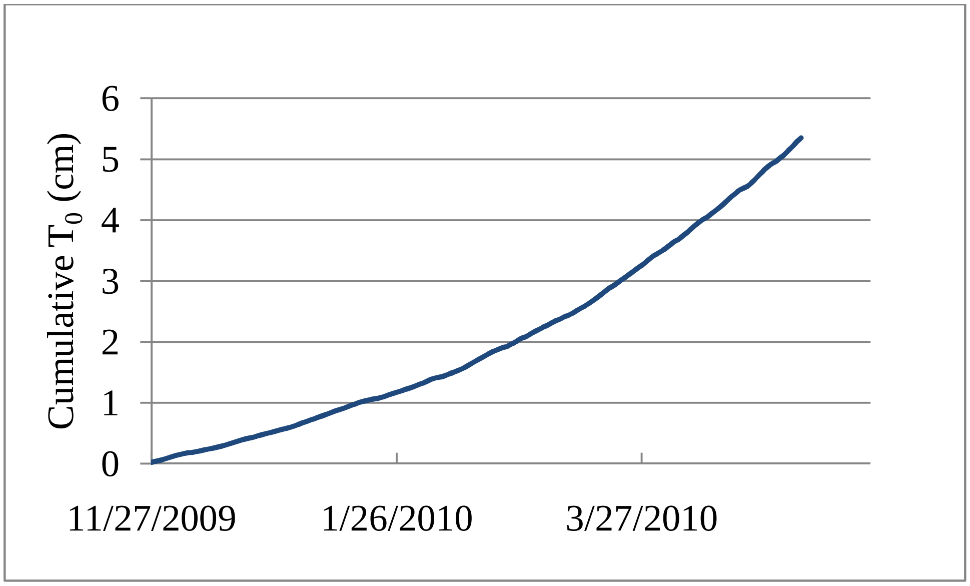


**Figure 1.10** Mean water contents estimated from neutron probe readings in 9 plots at both WC and PB.

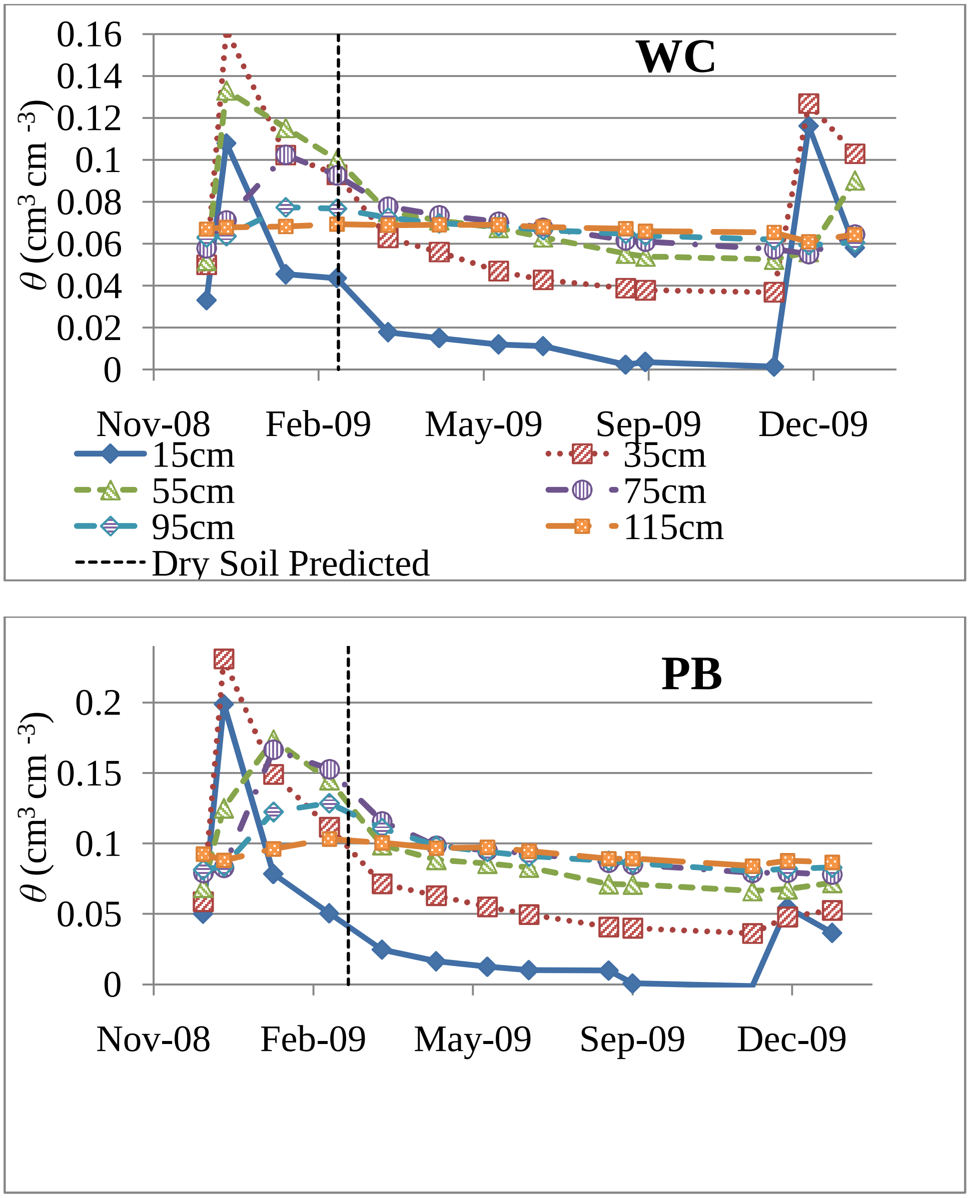
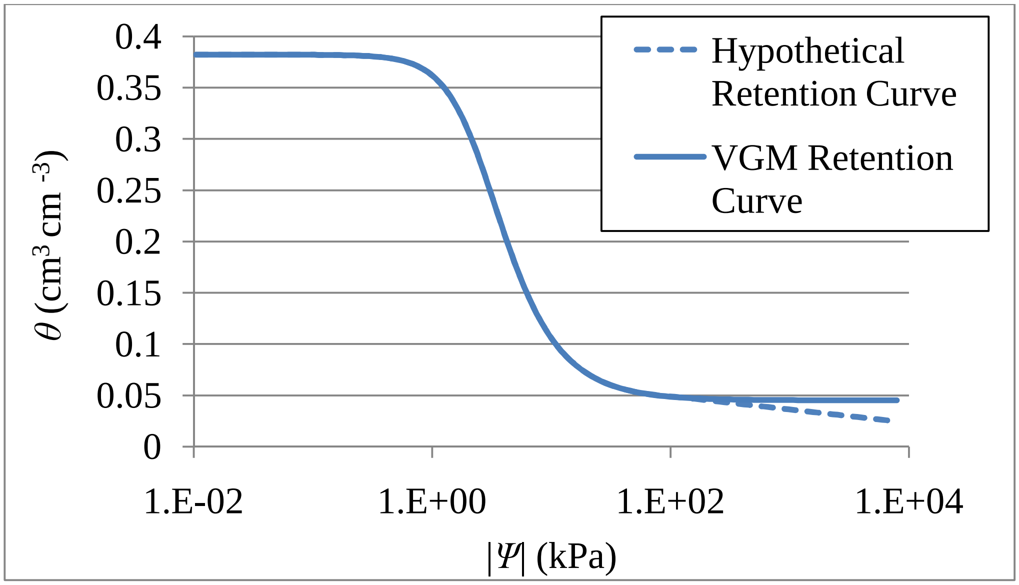


**Table 1.3** Estimated means and standard errors of $\theta$ from neutron probe measurements at different depths in late spring and late fall 2009.

| Site | Depth (cm) | Mean $\theta$ and Std.Error | Mean $\theta$ and Std. Error |
|---|---|---|---|
| PB | | 3/31/2009 | 11/18/2009 |
| | 15 | 0.0247 ± 0.0033 | 0.0012 ± 0.0028 |
| | 35 | 0.0715 ± 0.0018 | 0.0361 ± 0.0042 |
| | 55 | 0.0989 ± 0.0014 | 0.0663 ± 0.0018 |
| | 75 | 0.1157 ± 0.0017 | 0.0792 ± 0.0022 |
| | 95 | 0.1108 ± 0.0053 | 0.0805 ± 0.0039 |
| | 115 | 0.1006 ± 0.0046 | 0.0840 ± 0.0024 |
| | | | |
| WC | | 3/30/2009 | 11/19/2009 |
| | 15 | 0.0178±0.0031 | 0.00138±0.0008 |
| | 35 | 0.0627±0.0039 | 0.0369±0.0014 |
| | 55 | 0.0751±0.0028 | 0.0524±0.0011 |
| | 75 | 0.0776±0.0018 | 0.0573±0.0012 |
| | 95 | 0.0724±0.0018 | 0.0619±0.0012 |
| | 115 | 0.0689±0.0009 | 0.0654±0.0014 |

**Figure 1.11** Hypothetical retention curve for WC compared to the VGM model.



# **Chapter 2** Analysis of the effects of precipitation on nitrate concentrations in sandy desert soils in southern California

## Abstract

Nitrate ($NO_3$) concentration throughout the top100cm of soil in plots at two creosote bush-dominated sites in the Sonoran Desert were measured monthly for over a year. Fertilization with 30 kg N $ha^{-1}$ ammonium nitrate was done in four of the plots at each site to simulate the effects of anthropogenic nitrogen (N) deposition accumulating in the ecosystems. Measurement patterns indicate that $NO_3$ concentrations in soil are strongly dependent on rain. The rapid production of $NO_3$ following the first rains in both fertilized and unfertilized plots at both study sites eclipses estimates of anthropogenic $NO_3$ deposition on the soil surface throughout the summer, reducing the likelihood that dry deposition significantly affects the vegetation on an annual basis. However, the maintenance of higher concentrations of $NO_3$ in the soil throughout summer after the soil dries and the greater production of $NO_3$ following the first rains in the fertilized plots indicate a potential for buildup and long-term effects of deposition. Rapid leaching of $NO_3$ with significant rain events limited the uptake of $NO_3$ by shallow-rooted annual plants. The deep-rooted creosote bushes did not take up the entirety of the $NO_3$ below the root zones of the annuals, leaving much of the $NO_3$ from fertilizer to accumulate deep in root zone. The leaching of $NO_3$ and accumulation in the deep root zone may mitigate

the effects of N deposition on vegetation, but the N cycle at desert sites may still be vulnerable to disruption by N deposition, particularly in conjunction with climate change and the spread of invasive species.

## Introduction

Southern California is among the many regions throughout the world where consequences have been observed from the anthropogenic increase of biologically-available nitrogen (N) in the environment (Adams, 2003; Smith et al., 1999; Vitousek et al., 1997). An annual atmospheric release of approximately 0.36 Tg of $NO_x$ into southern California's South Coast Air Basin was estimated in 2002, with over 90% of it originating from fossil fuel combustion by motor vehicles (SCAQMD, 2007). $NO_x$, along with ammonia ($NH_3$) mainly from agricultural sources, results in many coniferous forests and shrublands in the South Coast Air Basin receiving an annual deposition of 20-45 kg $ha^{-1}$ (Fenn et al., 2003b). Because of the accumulation of $NO_x$ in the atmosphere during summer due to the infrequency of precipitation and atmospheric temperature inversions, much of the N enters ecosystems as dry deposition over the summer months (Bytnerowicz and Fenn, 1996; Fenn et al., 2003b; Padgett and Bytnerowicz, 2001; Riggan et al., 1985).

### *Effects of Increased Nitrogen Deposition*

Increases in reactive N in soil have been observed to change many processes of the terrestrial N cycle in many varied ecosystems, including nitrification (Fenn et al., 2003a; Fenn et al., 1996; Magill et al., 1997), N mineralization (Fenn et al., 2003a; Fenn et al., 1996; Magill et al., 1997; Vourlitis and Zorba, 2007), and denitrification (Hanson et al., 1994). Elevated tissue concentrations measured in plants demonstrate increased assimilation (Magill et al., 2004; Padgett and Allen, 1999; Rueth and Baron, 2002; Vourlitis et al., 2009) and declines in the abundance of mycorrhizae with N fertilization in some studies (Egerton-Warburton and Allen, 2000; Lilleskov et al., 2011; Treseder, 2004) indicate a potential for N deposition to alter how water and nutrients are absorbed. Nitrogen-fixation rates could also change since many lichens are sensitive to disturbances (Evans and Belnap, 1999). Both increased and decreased rates of decomposition have been observed in different ecosystems with increased biologically-available N in soil (Hobbie, 2005; Knorr et al., 2005).

These changes in the N cycle have correlated with changes in vegetation. N is a limiting nutrient in many ecosystems throughout the world (LeBauer and Treseder, 2008; Vitousek and Howarth, 1991), including many in southern California (Fenn et al., 2003a). An increase in N availability can not only increase productivity but can give nitrophilic species a competitive advantage, which can result in the competitive exclusion of other species and lead to a decrease in biodiversity (Bobbink et al., 2010; Tilman, 1987).

## *Nitrogen Deposition and Invasive Species in the Deserts of Southern California*

The invasion of exotic grasses and forbs in the deserts of southern California has been shown to result in a decline in the abundance and diversity of native species (Allen et al., 2009; Barrows et al., 2009; Brooks, 2000; DeFalco et al., 2007; Steers and Allen, 2010) and to add to the fuel load for wildfires (Brooks et al., 2004; Brooks and Minnich, 2006; Brown and Minnich, 1986). Because of the potential for invasive species to adversely affect native vegetation (Mack et al., 2000), the deposition of anthropogenic N into ecosystems threatened by a nitrophilic invasive species can be especially detrimental.

In many arid regions, both N and water limit productivity (Gutierrez and Whitford, 1987; Hooper and Johnson, 1999; Yahdjian et al., 2011). In the deserts of southern California, fertilization with N has been observed to increase productivity of both native and invasive annuals plants (DeFalco et al., 2003; Rao and Allen, 2010; Salo et al., 2005). However, when grown in competition, invasive annuals have frequently responded more positively to N fertilization than the natives (Allen et al., 2009; Brooks, 2003; DeFalco et al., 2003). This demonstrates a potential for anthropogenic N to facilitate the spread of invasive species.

Increased productivity of both native species and invasive species has resulted from N fertilization at some sites (Rao et al., 2010), which can create a fuel load above the threshold necessary to spread fire (Brooks, 2003; Rao et al., 2010). Many desert shrubs are poorly adapted to fire (Brown and Minnich, 1986) due to fires having been historically rare in many arid ecosystems (Brooks and Matchett, 2006), which can lead to severe, long-term consequences of fires that can reinforce shifts in vegetation.

Although most deserts in California receive significantly less deposition than ecosystems in closer proximity to urban centers (Fenn et al., 2003b), a small amount of deposited N may have a relatively larger effect in deserts due to the naturally low N availability. With all precipitation generally observed to be removed quickly from vegetated soils (Andraski, 1997; Kemp et al., 1997; Sandvig and Phillips, 2006), leaching below the root zones has been expected to be negligible (Peterjohn and Schlesinger, 1990). Therefore, there may be a considerable potential for N to accumulate in desert soils. In grasslands, decades of low level deposition have caused decreased diversity (Clark and Tilman, 2008), supporting the possibility that the deposition of low levels of N in the desert could have a similar effect over time.

### *Intent of the Analysis*

Precipitation is a major determinant in the relative success of annual natives and exotics in the arid regions of southern California (Brooks, 2003; Rao and Allen, 2010) and strongly affects the size and frequency of wildfires (Brown and Minnich, 1986). With its great influence on soil microbial processes (Austin et al., 2004; Schwinning and Sala, 2004; Stark and Firestone, 1995), assimilation, and leaching in deserts, the relationship between the N cycle and the hydrological cycle is critical for ascertaining the fate of deposited nitrate ($NO_3$) and determining its potential to cause shifts in vegetation and alter ecosystems. This analysis will be an examination of how concentrations of $NO_3$ vary throughout a desert soil at different depths following variable amounts of rain for the purpose of advancing the comprehension of the N cycle in desert soils and establishing the extent of its dependence on the weather. Although deposited ammonium ($NH_4$) is also of concern, this analysis focuses primarily on $NO_3$, with $NH_4$ only discussed in its relationship to $NO_3$.

## Materials and Methods

### *Two Study Sites in the Sonoran Desert*

The study sites, Wide Canyon (WC) and Pinto Basin (PB), are dominated by creosote bush (*Larrea tridentata*) and are located in the Sonoran desert in the southern part of Joshua Tree National Park (JOTR) in southern California (Figure 1.1). WC (33.943°N; 116.395°W; 501m above sea level) is downwind of numerous sources of pollution at approximately 20 km northeast of Palm Springs and 160 km of Los Angeles. PB (33.832°N; 115.758°W; 744m above sea level) is located in central JOTR approximately 100km east of WC. According to measurements taken between November 2004 and December 2005, WC receives about 2.13 kg $N\text{-}NO_3\ ha^{-1}$ and 3.11 kg $N\text{-}NH_4\ ha^{-1}$ bulk deposition annually, while PB receives approximately 1.62 kg $N\text{-}NO_3\ ha^{-1}$ and 1.73 kg $N\text{-}NH_4\ ha^{-1}$ (M. Fenn, personal communication). Having been collected in the open, these measurements underestimate deposition beneath the canopies of shrubs since canopy throughfall is expected to contribute to total deposition, though because the leaf area index of creosote bush is estimated to be < 1, the underestimation of deposition is unlikely to be large. Higher concentrations of nitric acid in the atmosphere of JOTR were measured in July than in February (Allen et al., 2009), which is expected to result in greater dry deposition of $NO_3$ during the summer than in the winter.

The soils at WC and PB are derived from a granitic parent material common in Joshua Tree National Park (Rao and Allen, 2010) and are dominated by sand (Table 2.1). Particle size distribution for 90 samples at each site taken from 9 plots representing 10 depths throughout the top 100cm of the soil was determined using the hydrometer method. There was no consistent pattern of variation with depth. Gravel composed 31% and 20% of the soil by weight at WC and PB respectively and the surface and subsurface of the soil of WC contain significantly more rocks than that of PB. Because of the sandiness of the soil at both sites, the hydraulic conductivity and retention curves of the soils are very steep (Figure 1.6). Therefore, the flow of water is fast when the soil is wet, but rapidly slows as the soil dries. The measured pH of the soil was 7.9 at PB and 7.1 at WC (Rao and Allen, 2010).

### *Dominant Vegetation at Wide Canyon and Pinto Basin*

The most prominent plant species at both sites is creosote bush, a flowering evergreen that covers vast expanses of the Mojave, Sonoran, and Chihuahua Deserts. Similar to many other desert plants, reproduction and growth of creosote bush depend strongly on both the timing and the amount of rainfall (Cunningham et al., 1979). Some studies have determined creosote bush to be limited by both water and N (Lajtha and Whitford, 1989;

Lightfoot and Whitford, 1987). Others have found N to be limiting to creosote bush growth only under particular conditions, such as when precipitation is sufficient for growth and after successive wet years have caused a depletion of soil nutrients (Sharifi et al., 1988). In a recent study in the Sonoran Desert, there was no response by creosote bush to N fertilization even during wet years (Hall et al., 2011).

Live shrub cover was estimated to be 9.5% +/- 2.7% at PB and 18.1% +/- 3.8% at WC (Rao and Allen, 2010). While a few other perennial bushes and cacti may grow between the creosote bushes, most of the desert floor is left uncovered. However, creosote bush is expected to have complex systems of lateral roots extending well beyond the canopy, underlying the interspaces throughout sites (Gibbens and Lenz, 2001). Root biomass declines with depth but many creosote bushes have roots reaching depths of 3 meters or more, some of which spread horizontally before bending into the soil (Gibbens and Lenz, 2001). The horizontal and vertical spread of the roots allows creosote bush to be very effective at withdrawing water, which has resulted in all precipitation being removed annually by evapotranspiration from soils covered by creosote bush at many desert sites (Andraski, 1997; Kemp et al., 1997; Sandvig and Phillips, 2006).

Higher levels of nutrients are found beneath creosote bush canopies relative to the interspaces (Garner and Steinberger, 1989; Reynolds et al., 1999; Schade and Hobbie, 2005; Schlesinger and Pilmanis, 1998; Schlesinger et al., 1996), correlating with the growth of annual plants predominantly under and around the creosote bushes. At WC and PB, more annuals grew on the north sides of the shrubs on average than on the south sides (Allen et al., 2009). The forbs *Chaenactis fremontii* and *Malacothrix glabrata* were the most abundant native plants at both sites during the study, with *Chaenactis* being more abundant at PB and *Malacothrix* more abundant at WC. The Mediterranean grass *Schismus barbatus*, which has spread extensively throughout the Californian deserts, was the most common invasive plant at both sites (Allen et al., 2009). N fertilization has been observed in previous studies to increase the productivity of *Schismus* species in the desert (Allen et al., 2009; Brooks, 2003), but native forbs at the sites were also more productive with N fertilization during some years. However, in 2004, species richness in fertilized plots was significantly reduced at PB, which had greater nonnative grass despite having lower deposition (Allen et al., 2009).

A severe drought in southern California during the winters of 2005-2006 and 2006-2007 resulted in no germination at WC during 2006-2007 and at PB during either winter (Rao and Allen, 2010). The abundance of invasive grasses *Schismus barbatus and S. arabicus* were diminished for several years following the drought relative to what had been observed in prior years (Schneider, 2010). This change did not appear to be sustained in the long term at PB and WC, with a significant amount of *Schismus* returning by the spring of 2011 (personal observation). Although many creosote bushes lost leaves and branches as a result of the drought, there was substantial growth at the bases of the bushes in the years following the drought.

### *The Flow of Water*

Weather stations have been measuring temperature and precipitation hourly at PB and WC since 2005. Temperatures were similar at WC and PB and varied little between years (Figure 1.2). High temperatures averaged 35.9°C and 16.1°C at PB and 36.6°C and 19.6°C at WC during summer and winter, respectively. Average low temperatures were 18.8°C during the summer and 6.4°C during the winter at PB and 23.1°C during summer and 12.4°C during the winter at WC.

Most precipitation occurs in the winter and early spring at both sites and the growth of annual plants generally begins with the first significant rainfalls and peaks in March or April. PB typically peaks a week or two after WC. WC often has a slightly higher annual rainfall than PB (Figure 1.2). Below average precipitation fell during the winter of 2008-2009, with 7.4cm of rain received at WC and 6.4cm at PB. During the winter of 2009-2010, precipitation at both sites was above average, with 17.9cm and 15.1cm of rain falling at WC and PB, respectively. Summer rain is generally infrequent at WC, but more is usually received at PB since the summer precipitation gradient increases eastward across JOTR (Rao et al., 2011). During the years of study in 2009 and 2010, summer precipitation was very low, with less than one centimeter of rain received by either site between May 1 and October 31.

MPS-1 dielectric water potential sensors (MPS-1, 2008) measured the matric potential of the soil water between November 2008 and December 2010. Using a solid matrix equilibration technique, the ceramic disks of the sensors reach hydraulic equilibrium with the soil after which the dielectric permittivity is measured to determine the amount of water in the sensors (Malazian et al., 2011). The sensors were installed approximately 0.5m from the edge of the canopy of two creosote bushes at each site at the depths of 5cm, 10cm, 15cm, 20cm, 25cm, 50cm, and 70cm. Measurements from these sensors are used for estimating the depth of water percolation on sampling dates, but are not discussed in detail. Based on MPS-1 measurements during the years of study, water most likely did not flow below 100cm at PB prior to the winter of 2009-2010 since the winter of 2004-2005. Therefore, between 2005 and 2010, no leaching of $NO_3$ below 100cm likely occurred at PB. The 10.1cm of water received at WC in 2007-2008 probably did result in some leaching below 100cm.

### *The Collection of Samples*

Soil samples were collected from nine plots spread over slightly less than 1 hectare at both PB and WC (Figure 2.1) between November 2008 and May 2010. Each plot was centered on a creosote bush and measured 6 meters by 6 meters (Rao and Allen, 2010), with other perennials seldom found within the plots. The lateral roots of the creosote bushes most likely underlie the entirety of the plots. Four of the plots at each site were fertilized with 30kg N/ha ammonium nitrate ($NH_4NO_3$) from December 2002 to December 2005 and in December 2008 and 2009. Plots with a relatively large amount of N added were chosen to make it easier to measure changes in N cycle. Although fertilization was intended to be done before the first rains to mimic the leaching of $NO_3$ accumulated on the soil surface over the summer into the soil, the fertilization closely followed the first rains in both 2008 and 2009.

An unfertilized control plot was located 7 to 30 meters from each fertilized plot, with one additional unfertilized plot at each site with no corresponding fertilized plot. Although the percent cover of annual plants had not increased in 2003 and 2004 after the first two applications of N (Allen et al. 2009), there appeared to be significantly more cover of annuals in fertilized plots than in unfertilized plots in the spring of 2010. In the survey at WC conducted in March 2010, the annual plants in the fertilized plots were estimated to cover 26% of the surface while in the unfertilized plots they averaged approximately 17% coverage. Similarly, when PB was surveyed in April 2010, the fertilized plots had 32% coverage by the annuals compared to 24% in the unfertilized plots.

Between November 2008 and May 2010, soil coring was done monthly near the edge of the creosote bush canopies in all nine plots at each site. The cores were taken in sections of 5cm to a depth of 25cm, with the top 5cm taken in two parts from 0-2cm and 2-5cm. In June and September of 2009 and in four months in early 2010, the cores were extended to a depth of 100cm and samples were taken from 35-40cm, 50-55cm, 75-80cm, and 95-100cm. Fewer samples at less frequent intervals were taken at these depths due to the expectation of less variation than in the top of the soil. Figure 2.2 shows the dates the coring was done at PB and WC during the winter of 2009-2010 in relation to the dates of rainfall and fertilization.

In late October and early November 2010, after the completion of regular coring, two cores were taken at each site to a depth of between 330cm and 345cm for the purpose of learning more about the $NO_3$ deep in the soil. One of the cores was taken in a fertilized plot and one in an unfertilized plot at each site, with soil from every depth collected in 5cm increments.

Extraction of N was done using a 1M KCl solution and the concentration of $NO_3$ in the soil was measured colorimetrically (Technicon Instruments Corp., Tarrytown, NY).

### *A Simple Column Experiment*

Several columns were run to establish some basic properties of $NO_3$ flow in the desert soils. Water was dripped at approximately 0.955cm $hr^{-1}$ on three columns filled with soil from PB that had been fertilized with 10.5 kg N $ha^{-1}$ of $NH_4NO_3$ and three more columns without fertilizer for 2, 4, or 8 hours. The columns were then cut open immediately after the water stopped and the soil was removed for analysis in 2cm increments. Due to limited repetitions, discussion and analysis of these columns will be limited to their demonstration of very elementary properties of $NO_3$ movement through the soil.

### *Methods of Analysis*

The variability of the distribution of N in desert soils makes the analysis of the desert N cycle difficult (Hunter et al., 1982). Because both very high measurements and very low measurements are representative of the soil, the calculations generally assume that the variations observed between the samples are representative of the spatial variations in the processes of the soil at the distance from the creosote where the samples were taken. Numerous samples are required for statistical significance. Calculated means are generally skewed by measurements of very high concentrations of $NO_3$.

Although two rainy seasons of data were taken, the fewer useable samples taken in the winter of 2008-2009 make trends far less apparent. Therefore, analysis focuses on the summer of 2009 and the winter of 2009-2010.

## Results

The average $NO_3$ concentrations in the fertilized plots were higher than in the unfertilized plots throughout the year. Figure 2.3 shows the mean concentrations measured between 0-2cm and 20-25cm, but higher mean concentrations were observed in fertilized plots at all depths. Similar trends were observed at the two sites throughout the year.

Average $NO_3$ concentrations were fairly constant between April and November of 2009, during which 0.025cm of rain fell at PB and no rain fell at WC. Figure 2.4 shows the mean concentrations during the summer at PB. Fewer samples taken below 25cm result in greater uncertainty at greater depths but the difference in mean concentrations between the fertilized and unfertilized plots was statistically significant at all depths except from 95-100cm at both sites. Estimates suggest the top 25cm of the fertilized plots contained an average of 2.8 kg-N $ha^{-1}$ and 4.7 kg-N $ha^{-1}$ more $NO_3$ throughout the summer than the control plots at PB and WC, respectively. Below 25cm, the data indicates that there is an even greater increase in the fertilized plots relative to the control plots, but too little data was taken to allow accurate calculations. Two anomalously large data points were removed from the control plots at WC in the calculation of the mean to prevent the appearance of trends that were not otherwise present. Deep cores taken in fall 2010 indicated that concentrations in fertilized plots remained higher than unfertilized plots below 100cm to a depth of 250cm at both sites (Figure 2.5), below which there were some high concentrations of $NO_3$ measured in both fertilized and unfertilized plots that could not be accounted for by fertilization. Because coring was done at only two plots at each site and natural variation is substantial, there is significant uncertainty in the observed concentrations.

Although differences in the summer means were statistically significant at most depths, high variability in measurements was typical, particularly in fertilized plots near the surface. The variability of the measurements throughout summer is shown in Figure 2.6. In spite of the variation observed, 80.3% of the samples from the fertilized plots taken during the summer at PB had higher concentrations than samples taken from the corresponding unfertilized plots at the same depth when 422 samples were compared. Similarly, at WC, the percentage of higher samples in fertilized relative to corresponding unfertilized plots was 80%, with 430 samples compared. As a result, despite natural variability, it is quite certain that a significant amount of N from fertilizer remains in the plots as $NO_3$ throughout the summer months.

Although dry deposition of $NO_3$ can accumulate on soil surfaces during summer (Padgett et al., 1999), the increase observed in the top 2cm of the sites was small relative to estimates of deposition.  Based on increases in the top 2cm of the control plots, approximately 0.6 kg N-$NO_3$ $ha^{-1}$ was deposited at WC and 0.4kg N-$NO_3$ $ha^{-1}$ was deposited at PB.

Samples the day after the first significant winter rains fell at PB and WC in December 2009 showed that $NO_3$ concentrations in fertilized and unfertilized plots at both sites were elevated relative to the median measured summer concentrations (Figure 2.7).  PB and WC had received 1.37cm and 2.95cm precipitation, respectively, on December 7, 2009.  The wetting front at PB was between 15cm and 20cm at the time of coring, while the wetting front at WC was between 25cm and 50cm, according to MPS-1 measurements.  Variation was exceptionally high in measurements of $NO_3$ concentration in the top 2cm on 12/8/09, with both concentrations higher than any that had been measured during summer and concentrations lower than any measured during summer. $NO_3$ concentration at WC increased relative to the summer median in almost all measurements from 2-25cm at WC in both fertilized and unfertilized plots, with the greatest increases observed near the surface (Figure 2.7).  At PB, $NO_3$ concentration increased between 2cm and 10cm in both the fertilized and unfertilized plots (Figure 2.7). Increases in the fertilized plots were greater on average than increases in the unfertilized plots at both sites.  The average increase in $NO_3$ between 2cm and 10cm in the control plots at PB would have required the addition of approximately 2.4 kg-N $ha^{-1}$ and the increase from 2-25cm in the control plots at WC would have required about

2.6 kg-N ha$^{-1}$. Ignoring anomalously high measurements, average increases for the same depths of the fertilized plots at PB and WC would have required the addition of 6.4 kg-N ha$^{-1}$ and 6.1 kg-N ha$^{-1}$, respectively.

$NO_3$ concentrations in the plots at both sites remained high relative to the median summer concentrations when the cores were taken in January 2010 (Figure 2.8), despite that MPS-1 data indicated that the soil at PB had become quite dry. Between the fertilization of PB and WC on 12/9/09 and 12/11/09, respectively, and coring in January, there was no rain at PB and 0.381cm of rain on 12/13/09 at WC. $NO_3$ from the fertilizer at WC spread with the small rains to a depth of 10-15cm. Concentrations in the top 2cm of the control plots were less variable than in December, with every plot measuring high concentrations relative to the summer averages but no extremely high measurements that had been observed in some plots in November. Despite the lack of spread of the fertilizer at PB, the concentration of $NO_3$ in the fertilized plots averaged 9.5kg-N ha$^{-1}$ greater than their summer medians while the unfertilized plots were on average 3.4kg-N ha$^{-1}$ higher than their summer medians.

Very low $NO_3$ concentrations were measured in the top 2cm of most plots in February following the majority of the rains of the winter of 2009-2010. Measurements in both the fertilized plots and unfertilized plots were below the previous summer's medians at both sites and there was no evidence of the fertilizer added in December, though the average concentrations of the fertilized plots remained higher than the unfertilized plots (Figure 2.9). Below 25cm, the $NO_3$ concentrations decreased considerably relative to the previous summer, more so in the fertilized plots than the unfertilized plots. The wetting front was below 1m when the samples were taken in February and column experiments indicated the potential for $NO_3$ to be rapidly leached from the soil, moving largely with the wetting front through a dry soil (Figure 2.10).

$NO_3$ concentrations appeared to change little between February and late spring despite the removal of most moisture. Cores taken in April and May, after the soil had dried, showed that concentrations were near the previous summer medians in the top 25cm but below the averages from 35-100cm at both sites (Figure 2.11).

## Discussion

### *Potential for Nitrogen Accumulation*

Higher $NO_3$ measurements in the fertilized plots than in the unfertilized plots throughout the summer of 2009 and in the late spring of 2010 demonstrate that alterations to the amount of extractable N present in soil resulting from fertilization can remain even after numerous rain events. It is unclear how much of the $NO_3$ remaining in the soil throughout the summer of 2009 was the result of fertilization in December 2008 and how much was the result of fertilizer added from 2002 to 2005. Although the decrease in soil $NO_3$ concentrations in February 2010 following large rains shows the potential for precipitation to result in the depletion of $NO_3$, the greater increase in $NO_3$ concentration in fertilized plots relative to unfertilized plots with the first rains of December 2009 demonstrates the potential for fertilizer N previously assimilated by plants to affect $NO_3$ concentrations when mineralized and nitrified in subsequent years.

The small amount of the $NO_3$ that appeared to accumulate in the top 2cm over summer 2009 indicates that the dry deposition to the soil surface throughout summer is likely negligible on an annual basis. Summer dry deposition to the soil surface appears to comprise about 28% and 25% of the estimated annual bulk $NO_3$ deposition. The sandy texture of the soils of PB and WC most likely influenced the apparent low deposition due to sand having less potential for the adsorption of $HNO_3^-$ vapor than clay and silt (Padgett and Bytnerowicz, 2001). Dry deposition on plant leaves might be greater at these sites, but canopy deposition measurements were not done and it is expected to have little effect on measured soil $NO_3$ concentrations since coring was not done directly beneath the canopies.

Although measured anthropogenic deposition of N is low, the potential for accumulation over years that was demonstrated by the fertilization experiment results in the deposition being a conceivable long-term threat to PB and WC. In grasslands, the addition of only 10 kg-N $ha^{-1}$ annually caused reductions in diversity over 23 years of study (Clark and Tilman, 2008). This amount is almost double the total annual deposition measured at WC; however, the low natural N input in deserts, as well as the potential for N to accumulate in the soil and biomass, could promote alterations to the vegetation over decades with less N than was observed to alter grasslands.

### *The Production of Nitrate*

Mineralization and nitrification appeared to begin rapidly following the first rains, which likely renders summer dry deposition of $NO_3$ negligible on an annual basis. Neither the localized high $NO_3$ concentrations amassed in the top 2cm nor the fairly consistent increase below the soil surface observed a day after the rains in December 2009 were likely to have resulted from deposition. The high variation in the soil surface between cores, the far greater amount of $NO_3$ in the surface relative to below in many locations, the larger increase in $NO_3$ in the fertilized plots relative to unfertilized plots, and the larger increase in $NO_3$ concentrations than any deposition estimates suggest that processes other than deposition account for much of the increase in $NO_3$ concentration. A contribution of deposited $NO_3$ to measured concentrations cannot be ruled out since wet deposition and the lateral spread in the soil of $NO_3$ that had been dry deposited on nearby creosote bushes may have enhanced measured $NO_3$ increases, but the extent of this influence is not clear from the measurements.

Although $NH_4$ concentrations in the surfaces of many plots declined in December 2009 (Chapter 3), decreases in $NH_4$ were not great enough to account fully for the increases in $NO_3$. The greater increase in $NO_3$ in the fertilized plots than in the unfertilized plots in December 2009 despite no fertilization done prior to the coring suggests that some N from fertilization in previous years became available after the first rains. The mineralization of organic matter from organisms that assimilated the $NO_3$ and $NH_4$ from the fertilizer in previous year, coupled with efficient nitrification, would explain a greater increase in $NO_3$ in fertilized plots than in unfertilized plots. The uneven distribution and variable rates of decay of organic matter could also explain the extreme variation in $NO_3$ measurements in the top 2cm of the December samples. A slight decrease in $NH_4$ following the first rains suggests more rapid nitrification than mineralization, which commonly occurs in Californian soils (Fenn et al., 2003a). The influence of N-fixation and denitrification on the $NO_3$ measurements is not known, but observed trends suggest the importance of mineralization and nitrification in determining $NO_3$ distribution.

Seemingly counter to the observation of a greater increase in $NO_3$ in fertilized than in unfertilized plots, Rao et al. (2009) did not find mineralization rates to have increased with deposition in a laboratory incubation experiment with soils from sixteen sites in the Sonoran desert that included WC and PB, though total mineralization increased with deposition. The differences in deposition at the sites studied by Rao et al. (2009) are much smaller than the differences in N added to the fertilized and unfertilized plots, making it plausible that the greater effects of elevated N were manifested in this study. While the study of Rao et al. (2009) was not focused on pulses of water or on mineralization occurring immediately following precipitation, concentrations measured at later dates do not indicate that there was rapid mineralization in the days following the application of water. Although the fast mineralization and nitrification necessary to produce the $NO_3$ increases immediately following precipitation was not supported by the experiments of Rao et al. (2009), many experiments have found that wet-dry cycles in arid and semiarid soils can result in significant N mineralization within one day of incubation (Austin et al., 2004). The stimulation of biological activity in desert ecosystems by pulses of water following dry periods has long been recognized (Noy-Meir, 1973), which includes the stimulation of microbial activity (Austin et al., 2004; Fisher et al., 1987; Schwinning and Sala, 2004). Evidence of rapid $NO_3$ increases may not have been observed by Rao et al. (2009) in weekly measurements because an increase in $NO_3$ following a water pulse may last only a few days, with immobilization resulting in a decline in the created $NO_3$ (Cui and Caldwell, 1997).

Exotic grass cover and total annual cover were both significantly greater in fertilized plots during the wet winter of 2005 (E. Allen, unpublished), so the greater creation of $NO_3$ in fertilized plots may have been a result of greater N content in organic matter. Statistically significant differences of total carbon and total N in the soil of fertilized and unfertilized plots were not observed in measurements possibly because of high spatial variability, limited samples, and the inclusion of organic matter with low turnover rates. However, alteration of the N in organic matter with high turnover rates remains a plausible explanation for the greater increase in $NO_3$ in the fertilized plots. Increased N in plant tissues has been observed following fertilization in many desert plants (DeFalco et al., 2003; Schneider, 2010), which can result in greater N in the litter after the plants die. In other studies, lower C:N ratios in litter and soil organic matter have correlated to greater N mineralization (Currie, 1999; Fenn et al., 1996; Vourlitis and Zorba, 2007; Vourlitis et al., 2007). Although another study in the Sonoran desert found that the addition of inorganic N increased nitrification more than N mineralization (Hall et al., 2011), too few measurements were taken at WC and PB in December to estimate the relative rates of nitrification and N mineralization between fertilized and unfertilized plots.

High levels of $NO_3$ were maintained in all plots in January, despite the probable removal of some $NO_3$ by assimilation as the soil became drier. This suggests a continuation of $NO_3$ creation by mineralization, N-fixation, and nitrification following coring in December. However, universally low measurements of $NO_3$ measured in the top 2cm of soil at both sites in February 2010 potentially suggest slower $NO_3$ creation late in the season, since samples taken two days after previous rains did not show spikes in $NO_3$ analogous to those observed one day after the first rains in December 2009. Because the soil had remained continually wet for a month prior to February 2010 due to frequent large precipitation events, a pulse of biological activity similar to that observed in December 2009 would not be expected in response to the rains prior to coring in February. The substantially greater amount of extractable N created by the pulse of microbial activity following the first rains of the wet season than was created after rains later in the wet season suggests that temporal asynchrony may be a factor in N limitation in annuals. Rather than temporal asynchrony due to the increase in N mineralization late in the season after most plant growth that can occur in semiarid and arid ecosystems (Augustine and McNaughton, 2004), temporal asynchrony at WC and PB may result from an initial high availability of $NO_3$ when seeds are germinating that is not available during subsequent growth due to diminished rates of $NO_3$ creation. Whether there is also greater mineralization and nitrification late in the growing season at PB and WC is not clear from the data.

### *Loss of Nitrate*

The potential for $NO_3$ to be leached below the root zones of annuals and other short-rooted plants is apparent, but measurements suggest that some $NO_3$ may also be lost to creosote bush in the deep root zone. Previous measurements at PB and WC indicated that $NO_3$ moves similarly to chloride (Rao, personal communication), which is often useful as a tracer in semiarid and arid soils (Allison et al., 1994; Phillips, 1994). In the column experiment with soils from PB, this was corroborated by the movement of $NO_3$ primarily with the wetting front (Figure 2.10). The rapid percolation of water through sandy soils when sufficiently wet due to high saturated hydraulic conductivities may result in the rapid leaching of $NO_3$ through the desert soils. Because only approximately 2cm of the 12cm of precipitation was estimated by HYDRUS-1D to have been removed from the soil by transpiration prior to the February 2010 measurements, plant uptake alone would not explain the decrease in $NO_3$ in the top 1m. Immobilization by microorganisms may have accounted for some of the decline in $NO_3$. With the wetting front estimated by the model HYDRUS-1D to be significantly below 1m at WC and PB in February 2010, leaching is likely a factor in the low $NO_3$ concentrations measured after the major rains.

The potential for rapid leaching to limit $NO_3$ availability to short-rooted plants has been shown in other studies in arid and semi-arid ecosystems. A model by Marion et al. (2008a) predicted that the vast majority of atmospherically deposited $NO_3$ would leach below 1m even when only a little rainfall percolated past 1m at a Mojave Desert site, which would cause the majority of $NO_3$ to be below the root-zones of annuals plants. In a semiarid coastal sage scrub ecosystem, Michalski et al. (2004) found that the majority of $NO_3$ that had accumulated on the surface was leached into the shallow groundwater without undergoing biotic or abiotic processes at the beginning of the rainy season.

Although the potential for $NO_3$ to leach below the root zones of the short-rooted annuals is clear, the reason for the incomplete uptake of $NO_3$ in the soil by the creosote bush is uncertain. Because the rooting depth of creosote bush has been measured to be about 3 to 5m (Gibbens and Lenz, 2001) and can be limited by maximum depth of water percolation when not growth is not otherwise inhibited (Wallace and Romney, 1972), it is unlikely that any $NO_3$ was leached below the creosote bush root zones anytime following fertilization. The substantial amount of $NO_3$ remaining within the root zone of fertilized plots after the soil dried in the summer of 2009 and the spring of 2010 suggest incomplete uptake of $NO_3$ by the creosote bushes. With the higher concentration of $NO_3$ remaining in the fertilized plots relative to the unfertilized plots to a depth of 2.3m in the cores taken in the fall of 2010, $NO_3$ from the fertilizer may be left spread throughout the soil. The difference between the top 2.3m of the fertilized and unfertilized plots measured at WC would have required the addition of about 90 kg N ha$^{-1}$, approximately half of the N applied by fertilizer during six years of fertilization. The effect of the fertilizer at PB may be less apparent due to the control plot having deep $NO_3$ concentrations found naturally in the soil nearer the surface than the fertilized plot, but the higher concentrations of $NO_3$ in the fertilized plot are still observed to a depth of about 2.3m, with a difference similar in scale to that of WC. Although too few repetitions were done to be certain that this difference is representative of the sites, it advances the possibility that a substantial amount of the fertilizer remains spread throughout the soil. Because N and water are the limiting factors in most arid ecosystems (Gutierrez and Whitford, 1987; Hooper and Johnson, 1999; Yahdjian et al., 2011) and all precipitation in many arid environments is removed from vegetated soils annually by evapotranspiration (Andraski, 1997; Kemp et al., 1997; Sandvig and Phillips, 2006), it is unexpected that so much $NO_3$ would remain in the soil. High concentrations of $NO_3$ found below about 230cm in both fertilized and unfertilized plots could not be accounted for by fertilization, but is consistent with other studies that have found high concentrations of $NO_3$ that has accumulated a few meters below the surface throughout the Holocene in desert soils (Hartsough et al., 2001; Marion et al., 2008b; Walvoord et al., 2003).

Increased leaching is a symptom of N saturation (Aber et al., 1989), which is a possible reason much $NO_3$ is left behind in the soil. The response of annuals to the fertilization in December 2009 indicated that they were N limited, but creosote bush may not be. If the leaching of $NO_3$ is a prominent factor in causing N-limitation in short-rooted desert plants, deeper-rooted plants in the same ecosystems may not be N-limited since leaching beyond their root zones does not occur. Hall et al. (2011) observed that while winter annuals responded to N and P fertilization in the Sonoran Desert near Phoenix, Arizona, creosote bush did not during a four year study, supporting the idea that creosote bush may not always be N-limited when annuals are. Uptake of the $NO_3$ from the fertilizer may have been incomplete due to the N saturation of the creosote bushes.

The possible role of N saturation in creosote bush at WC and PB in causing the incomplete uptake of $NO_3$ is unclear, but other symptoms have not been observed. Leaching into the deep soil may be the result in a natural inefficiency in the uptake of $NO_3$ by creosote bush, since it has been widely-observed that $NO_3$ has been accumulating in the deep root zones of arid regions in the southwestern US throughout the Holocene (Hartsough et al., 2001; Marion et al., 2008b; Walvoord et al., 2003). Since creosote bush has been found to be N limited in some studies (Lajtha and Whitford, 1989; Lightfoot and Whitford, 1987), it is unclear why so much $NO_3$ remains in the soil when it dries. A potential reason for nutrients being left in the soil annually may be the continuation of water removal by vapor flow processes throughout the dry season after capillary flow has become negligible (Chapter 1). Regardless of the cause, the substantial amount of $NO_3$ left behind by creosote bush may be lost to the desert N cycle, with possible future uptake by creosote bush required for its return to the surface.

Both PB and WC had higher average $NO_3$ concentrations from 35-100cm than were observed above those depths during the summer of 2009, which were not observed in the spring of 2010. At PB, precipitation patterns suggest that water was not likely to have percolated below 1m prior to the winter of 2009-2010 since the winter of 2004-2005, while at WC, there may have been some leaching below 1m in 2007-2008. This may have resulted in a substantial amount of $NO_3$ remaining in the root-zone throughout the summer of 2009 that was leached further into the soil with the greater rains of the winter of 2009-2010.

Excluding the bulge from 35-100cm during the summer of 2009, most $NO_3$ present in the soils at the sites appears widely spread in both the fertilized and unfertilized plots at WC and PB. The higher $NO_3$ concentrations in the fertilized plots than unfertilized plots have been observed throughout all depths of the soil. While $NO_3$ did spread significantly in the soil column experiments, the highest concentrations remained near the wetting front. Additionally, following the application of 7.6cm of water over 8 hours, $NO_3$ was below measureable amounts between 7cm and 21cm in the control column, which was never observed in the desert. The greater uniformity in the desert could partially result from the continual creation of $NO_3$ in wet soil, as well as from the leaching often being driven by repeated small rain events rather than the large continuous one simulated in the column experiment.

Although $NO_3$ soil storage that may ultimately result in the accumulation of $NO_3$ in the deep root zone appears to account for a substantial loss of N at WC and PB, gaseous loss may also be important. DayCent modeling of the soils at PB and WC predicted nitric oxide (NO) to be the primary gaseous loss, which was expected to be created via the nitrification pathway (Rao et al., 2010). Denitrification in deserts has not been extensively studied (Seitzinger et al., 2006) and its contribution to the pattern of $NO_3$ concentrations measured at WC and PB is unknown. The apparent soil storage and leaching of $NO_3$ at WC and PB suggests that gaseous loss is less significant at these sites than was predicted by Peterjohn and Schlesinger (1990) due to their assumption of little $NO_3$ storage in the deep soil. The potential for high soil surface temperatures during the summer to cause substantial gaseous nitrogen loss in soils in the Mojave Desert (McCalley and Sparks, 2009) could account for the relatively small accumulation of $NO_3$ and $NH_4$ observed on the soil surface at both sites during the summer of 2009. Deposition during the summer may be compensating for gaseous losses, resulting in only small increases being observed in the soil surface.

### *Nitrogen Limitation Resulting from Precipitation*

The hydrological cycle appears to be closely linked to the N cycle at PB and WC. The precipitation facilitating the creation of $NO_3$ can also leach the mobile $NO_3$ quickly through the highly-conductive sandy desert soil below the root zones of the annuals. $NO_3$ created in the wet soil following one precipitation event may only be available to short-rooted annual plants until the next significant rainfall, which may subsequently fuel the creation of more $NO_3$. If rapid production of $NO_3$ follows the first rainfall of the wet season but the production of $NO_3$ diminishes in the wet soil later in the season, as appeared to occur during the winter of 2009-2010 at WC and PB, a temporal asynchrony in $NO_3$ availability may result, with limited N available during annual plant growth due to leaching of most $NO_3$ available at germination. This suggests that the temporal pattern of rainfall is very important in determining the $NO_3$ availability to annual plants, with small to medium-sized intermittent rains offering the greatest opportunity for $NO_3$ uptake and the pattern of precipitation early in the season being especially important.

The timing of the precipitation in the winter of 2009-2010 would have restricted $NO_3$ uptake by annual plants. The dry month following the first rains in December would have allowed a significant period of uptake by the few budding annuals that germinated with the rains, but additional rain events may have fueled the production of more $NO_3$ and allowed for more uptake than occurred in the dry soils. The relatively large, frequent rains in January and early February that resulted in the depletion of $NO_3$ from the soil by the February measurements were likely inopportune for $NO_3$ uptake by annuals, with any $NO_3$ created in the wet soil often being leached within days by subsequent rains. The excessive leaching of $NO_3$ due to rainfall patterns, combined with an abundance of water to allow increased productivity, could have been responsible for the significantly greater cover of annuals in fertilized plots relative to unfertilized plots that was not clearly observed in previous dry years. Other desert studies have also observed that the increase in productivity of desert annuals with the addition of N is greater in years with higher rainfall (Hall et al., 2011; Hooper and Johnson, 1999). This reflects the tendency of N to restrict growth when water does not, but N limitations in years of high rainfall could also be exacerbated by increased leaching.

### *Disruption of the Nitrogen Cycle*

The balance within the N cycle may be very tenuous, with anthropogenic N inputs, invasive species, and climate change likely to have already disrupted that balance. The high concentration of nutrients beneath shrubs frequently observed in the desert soils (Garner and Steinberger, 1989; Reynolds et al., 1999; Schade and Hobbie, 2005; Schlesinger and Pilmanis, 1998; Schlesinger et al., 1996), suggests the importance of cycling by deep-rooted perennials in retaining N near the surface. With a proportion of $NO_3$ leached into the soil seemingly not being taken up by the creosote bushes, input from N-fixation and N deposition are necessary for offsetting the loss of $NO_3$ to the deep soil if the system is in balance.

If a loss of $NO_3$ into a generally-inaccessible pool deep within the soil occurs naturally in desert ecosystems, the potential for disruption with the presence of invasive species and with climate change is great. Because invasive species can change nutrient cycling by varying from native plants in biomass, productivity, and tissue chemistry (Ehrenfeld, 2003), they could alter the average amount of $NO_3$ leached into deep pools and change the amount of N available to future annuals when they decay. Since desert invasives have often responded more favorably to increased N availability than desert natives when grown in competition (Allen et al., 2009; Brooks, 2003; DeFalco et al., 2003), the current presence of invasives may improve the conditions for future invasives by preventing $NO_3$ leaching if more N is taken up by annual plants than would be in the absence of the invasives. A shift in the timing and amount of precipitation due to climate change could similarly alter the long-term average $NO_3$ leached to the deep pools, in addition to influencing many other chemical and biological processes in desert ecosystems.

## Conclusions

$NO_3$ deposition is not likely to have much effect on an annual basis because a much larger amount of $NO_3$ is created after the first rains relative to the amount deposited. However, deposited $NO_3$ may result in the accumulation of biologically-available N in the biomass and soil over time. The effects of fertilization in previous years were observed both in elevated concentrations of $NO_3$ that remained throughout the dry season, a greater production of $NO_3$ in the fertilized plots after the first rains, and increased surface cover of annual vegetation at the sites. The potential for deposited $NO_3$ that accumulates on the soil surface to affect vegetation on a yearly basis is limited because of rapid leaching due to the high saturated hydraulic conductivities of the sandy soil. $NO_3$ dry deposited during the summer, when the atmospheric concentrations of $NO_x$ are the highest, may be mostly leached below the root zones of the annuals with the rain required for germination. Although uptake by deep-rooted creosote bush is possible, a significant amount of $NO_3$ appears to be accumulating in the deep root zones of the fertilized plots. With the rapidity of $NO_3$ leaching, deposited $NH_4$ may be the greater cause of changes in the annual vegetation and in the mineralization and nitrification rates. Rapid leaching of $NO_3$ may be a major reason N is a limiting nutrient in deserts, since the same rains that drive the creation of $NO_3$ by mineralization and nitrification can also leach any $NO_3$ created previously below the root zones of the annuals. An apparent decline in the rates of mineralization and/or nitrification later in the rainy season may also be contributing factors.

The accumulation of N in the soil may be highly dependent on the timing and amount of precipitation, which heavily influence soil microbial processes, plant uptake, and leaching. No additional $NO_3$ was observed in the top of the soil in spring 2010 despite fertilization in December 2009 and accumulation in previous years. Above average precipitation may have led to greater leaching and uptake by annuals, leading to elevated levels of $NO_3$ remaining in the soil near the surface of the fertilized plots but no additional $NO_3$ accumulation. The influence of precipitation on the ratio of $NO_3$ retained in the soil surface and taken up by the annuals leads to a high potential for climate change to disrupt the desert N cycle. With the presence of invasive species further disrupting nutrient cycling (Ehrenfeld, 2003), deposition of N is only one factor with the potential to produce alterations in the N cycle.

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**Table 2.1** Estimated particle-size distributions at Wide Canyon and Pinto Basin.

| Site | %Sand | | | %Silt | | | %Clay | | |
|---|---|---|---|---|---|---|---|---|---|
| | Max. | Min. | Ave. | Max. | Min. | Ave. | Max. | Min. | Ave. |
| WC | 92.2% | 72.8% | 85.6% | 22.2% | 2.0% | 10.9% | 5.0% | 2.0% | 3.5% |
| PB | 96.8% | 72.1% | 86.4% | 22.2% | 2.2% | 9.8% | 7.0% | 1.0% | 3.8% |

**Figure 2.1** Approximate distribution of plots at PB and WC. “H” plots were fertilized with 30kg N ha$^{-1}$, while “C” plots were controls.

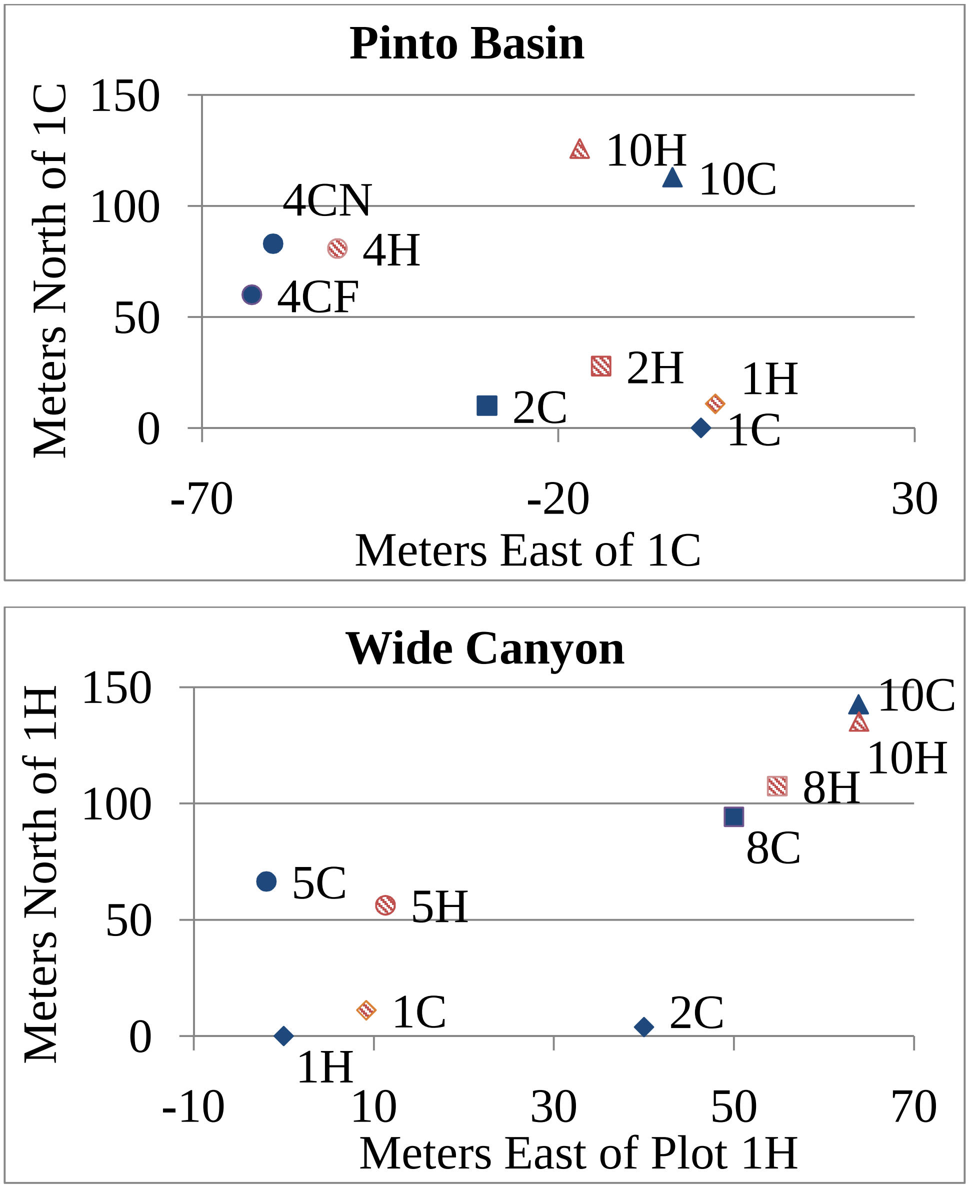


**Figure 2.2** Precipitation timing in relation to the dates of sampling and fertilization at PB and WC during winter 2009-2010.

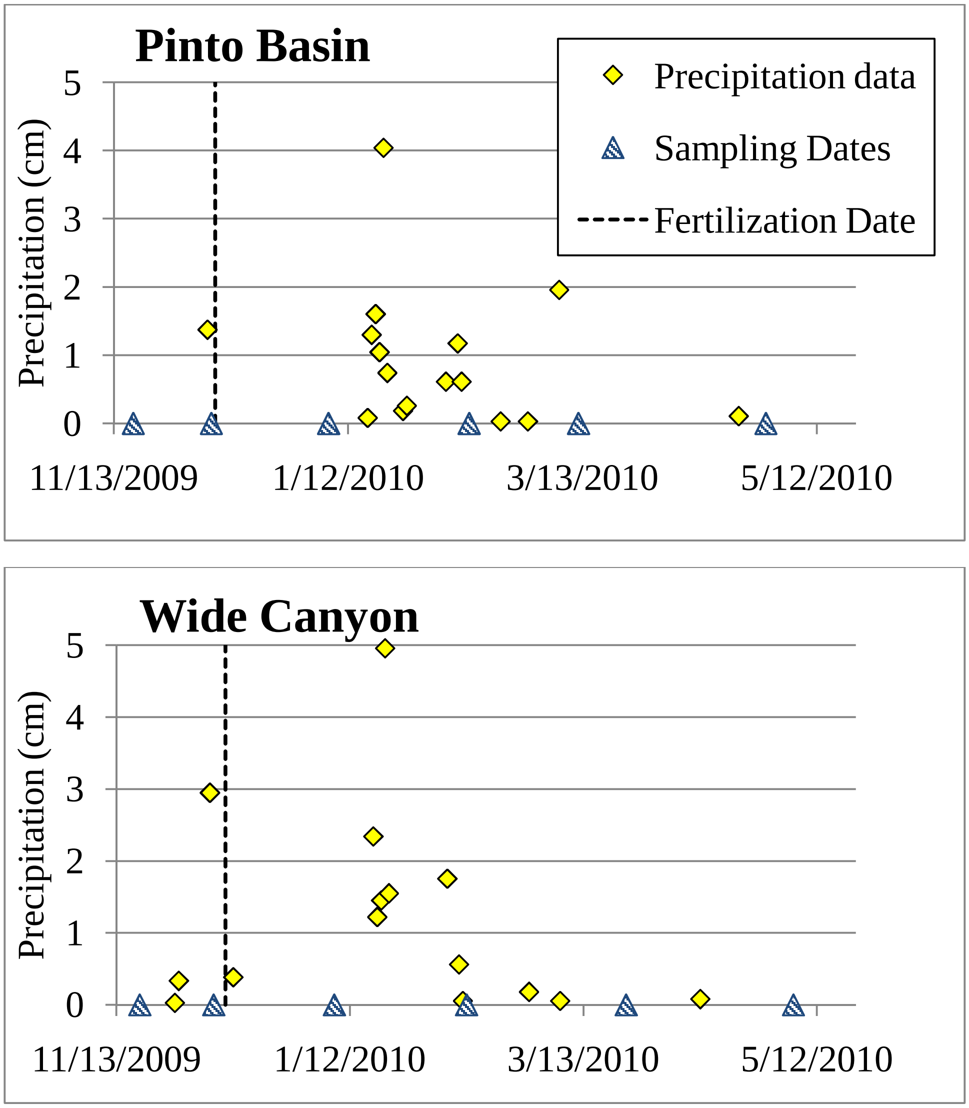
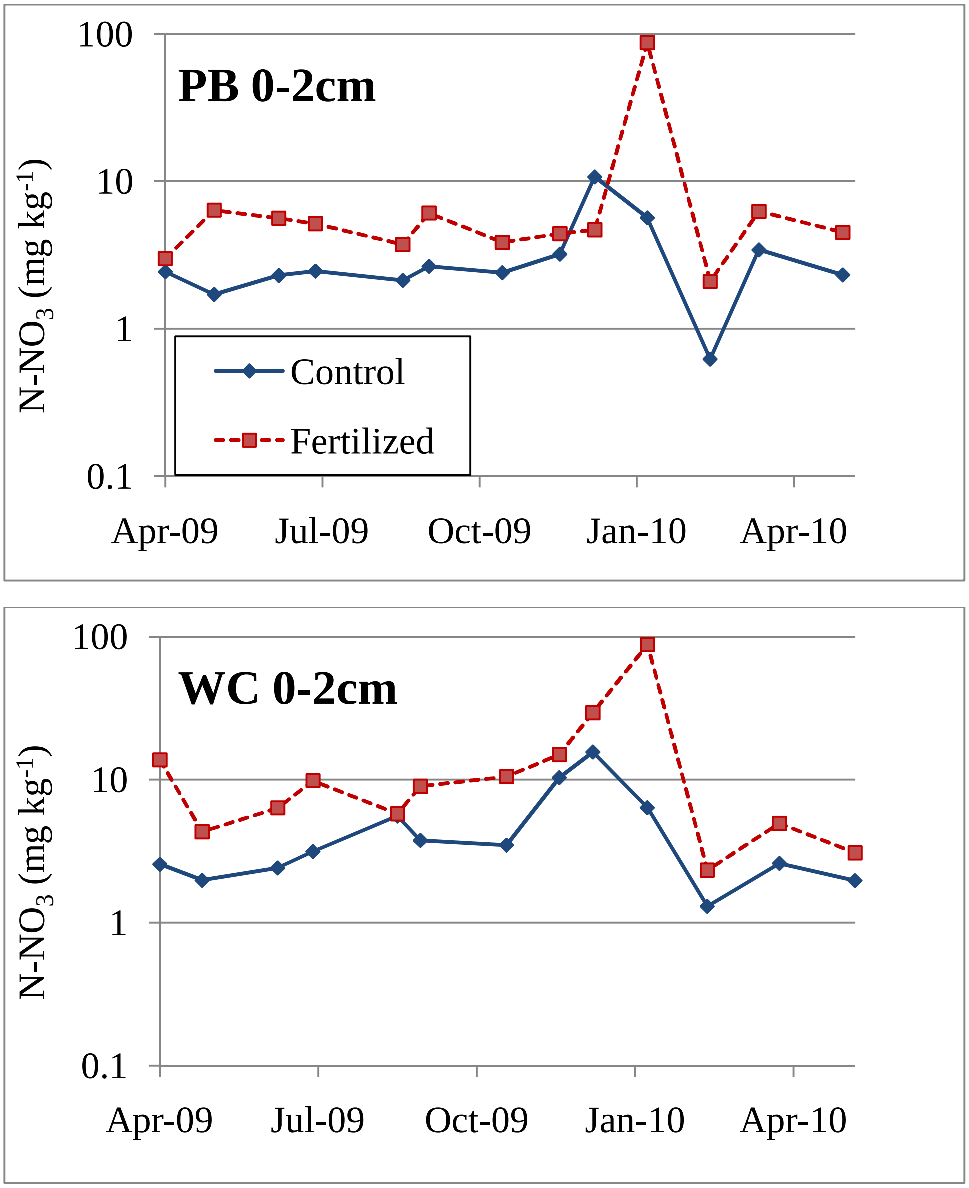
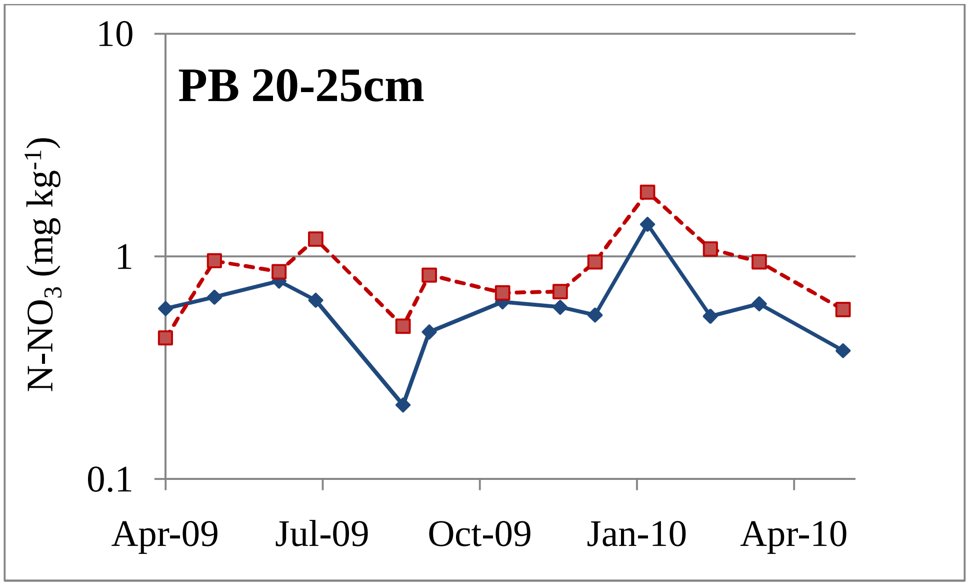


**Figure 2.3** Mean concentrations of $NO_3$ measured in the soils at PB and WC. Higher $NO_3$ measurements in the fertilized plots than in the unfertilized plots were typical of all depths.




PB 20-25cm
N-NO$_3$ (mg kg$^{-1}$)
10
1
0.1
Apr-09
Jul-09
Oct-09
Jan-10
Apr-10

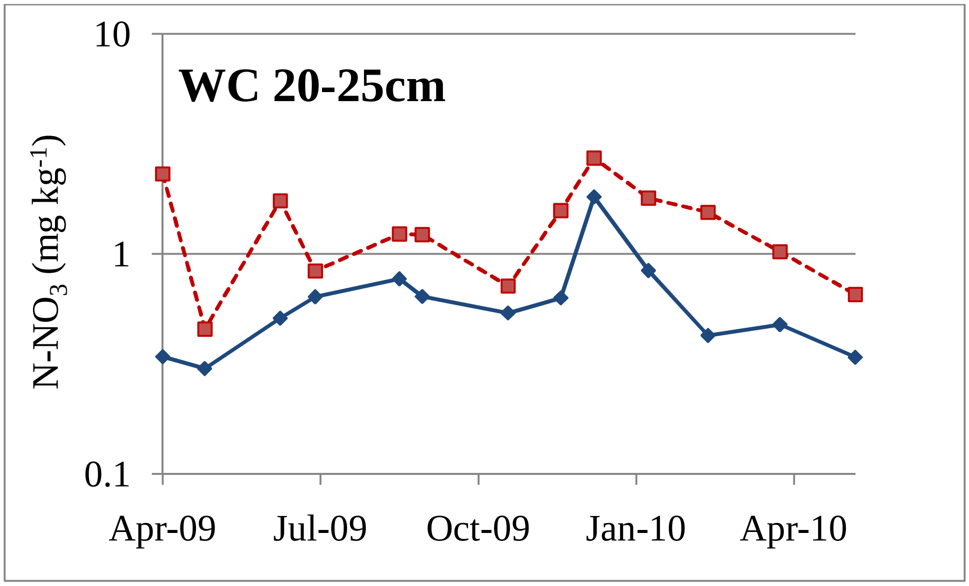

WC 20-25cm
N-NO$_3$ (mg kg$^{-1}$)
10
1
0.1
Apr-09
Jul-09
Oct-09
Jan-10
Apr-10

**Figure 2.4** Mean concentrations of $NO_3$ measured with depth in all plots from April to November 2009. Differences in the means between fertilized and control plots were statistically significant at all depths except 95-100cm.

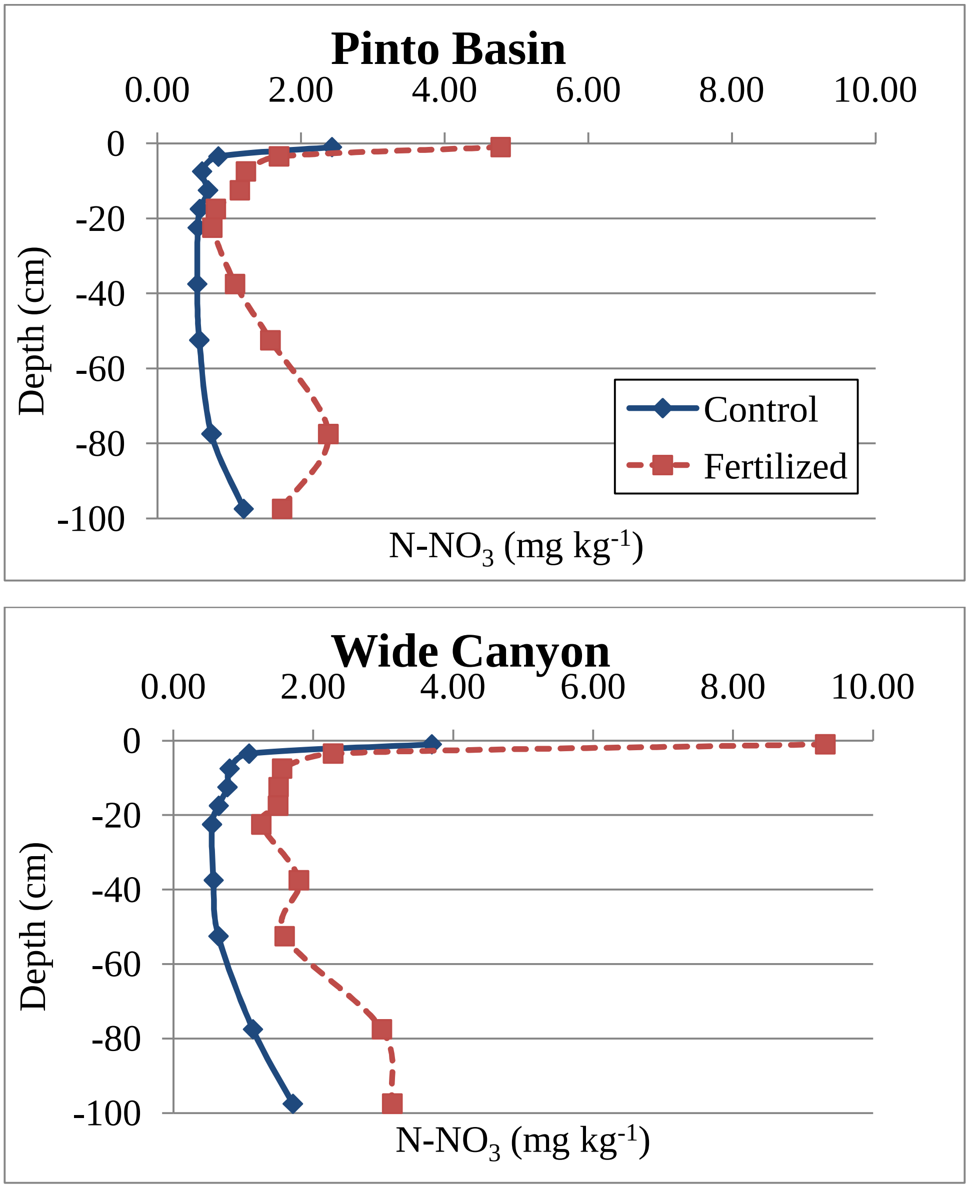
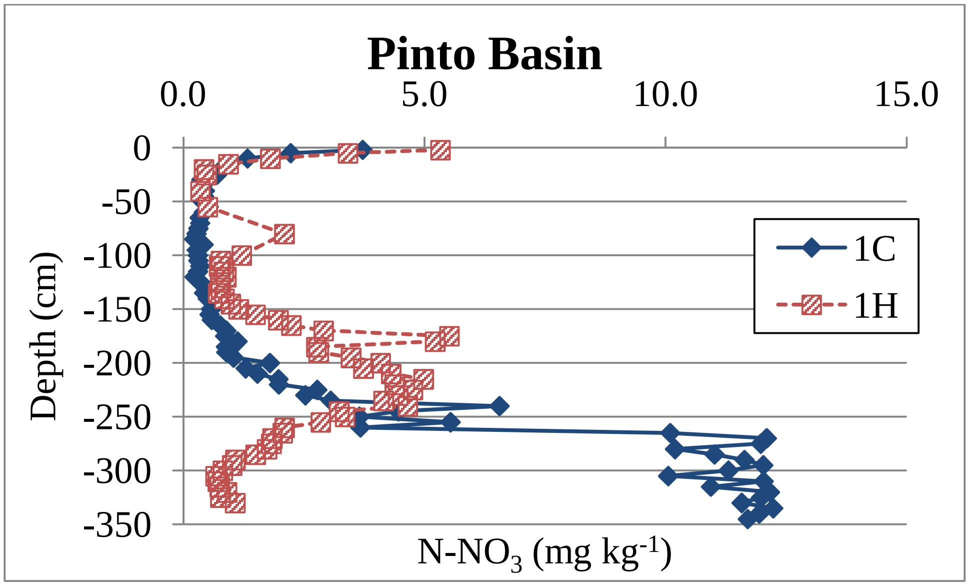


**Figure 2.5** $NO_3$ measurements in deep cores taken in two plots at both PB and WC in Fall 2010.



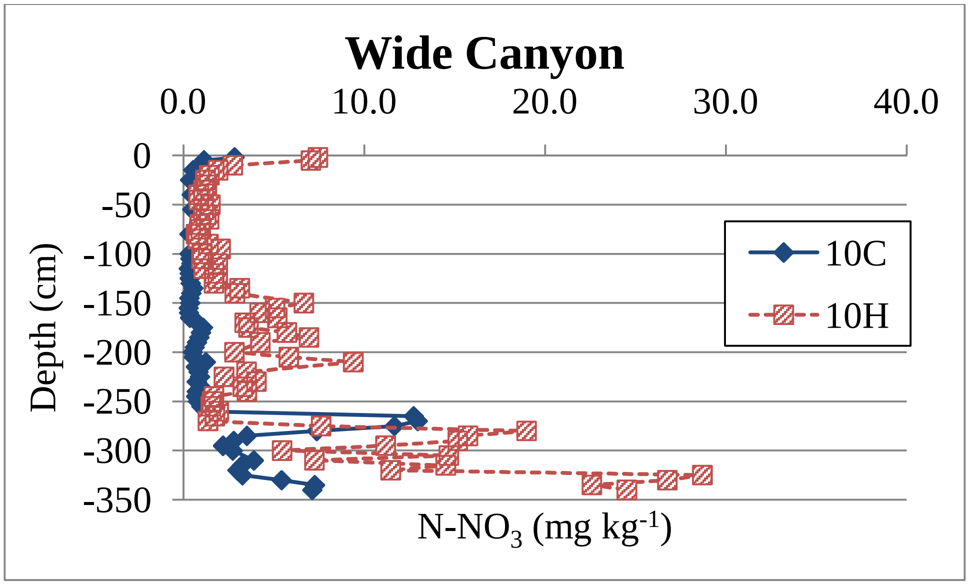


**Figure 2.6** Variability in measured concentrations of $NO_3$ between plots at two depths at PB. Greater variation was observed near the surface, particularly in the fertilized plots. Similar variability was observed at WC.

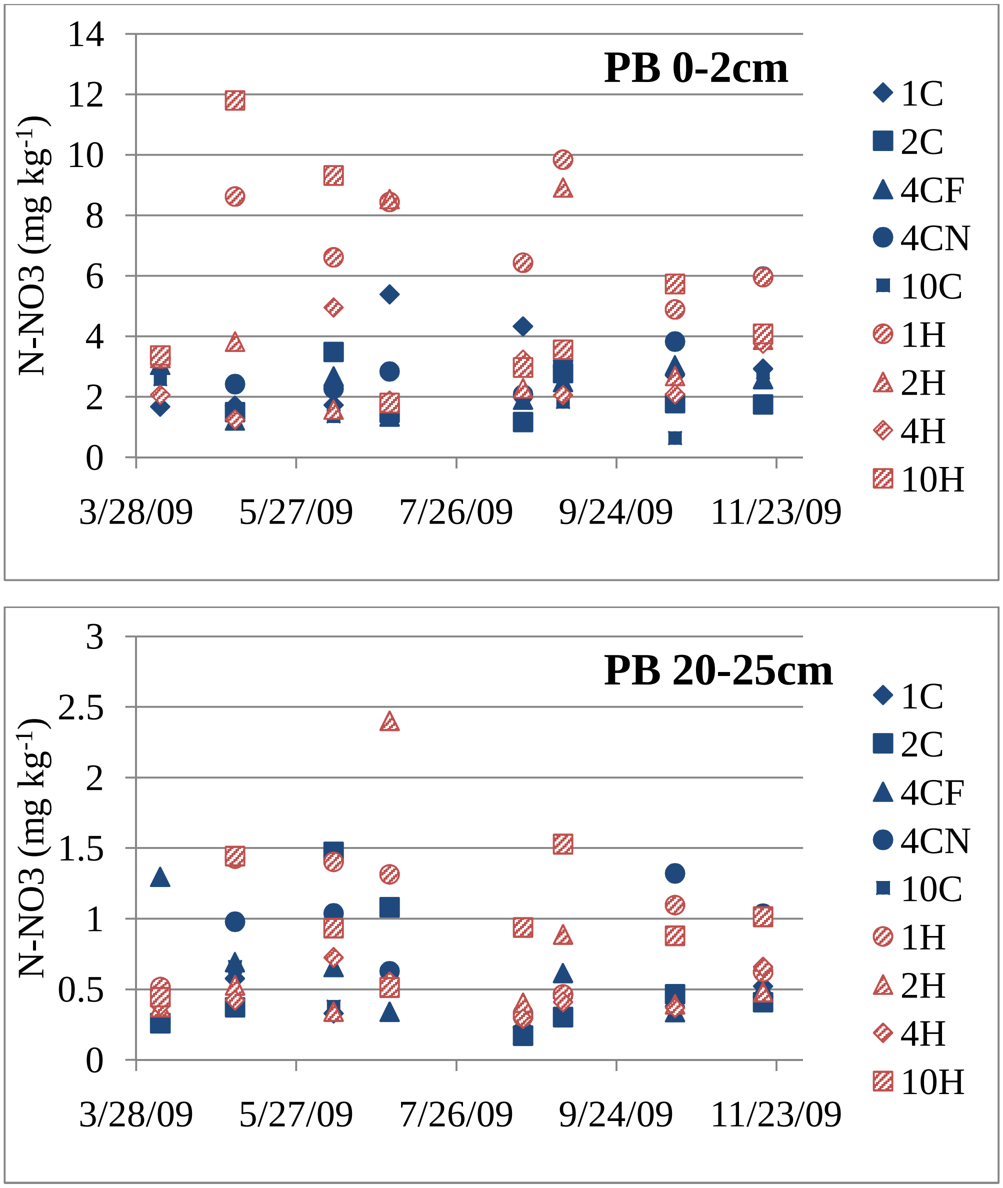


**Figure 2.7** Changes in $NO_3$ concentrations relative to the summer median for the same depth in samples taken 12/8/2009 at PB and WC. Three very large increases in $NO_3$ in the soil surface at WC and one at PB are not shown.

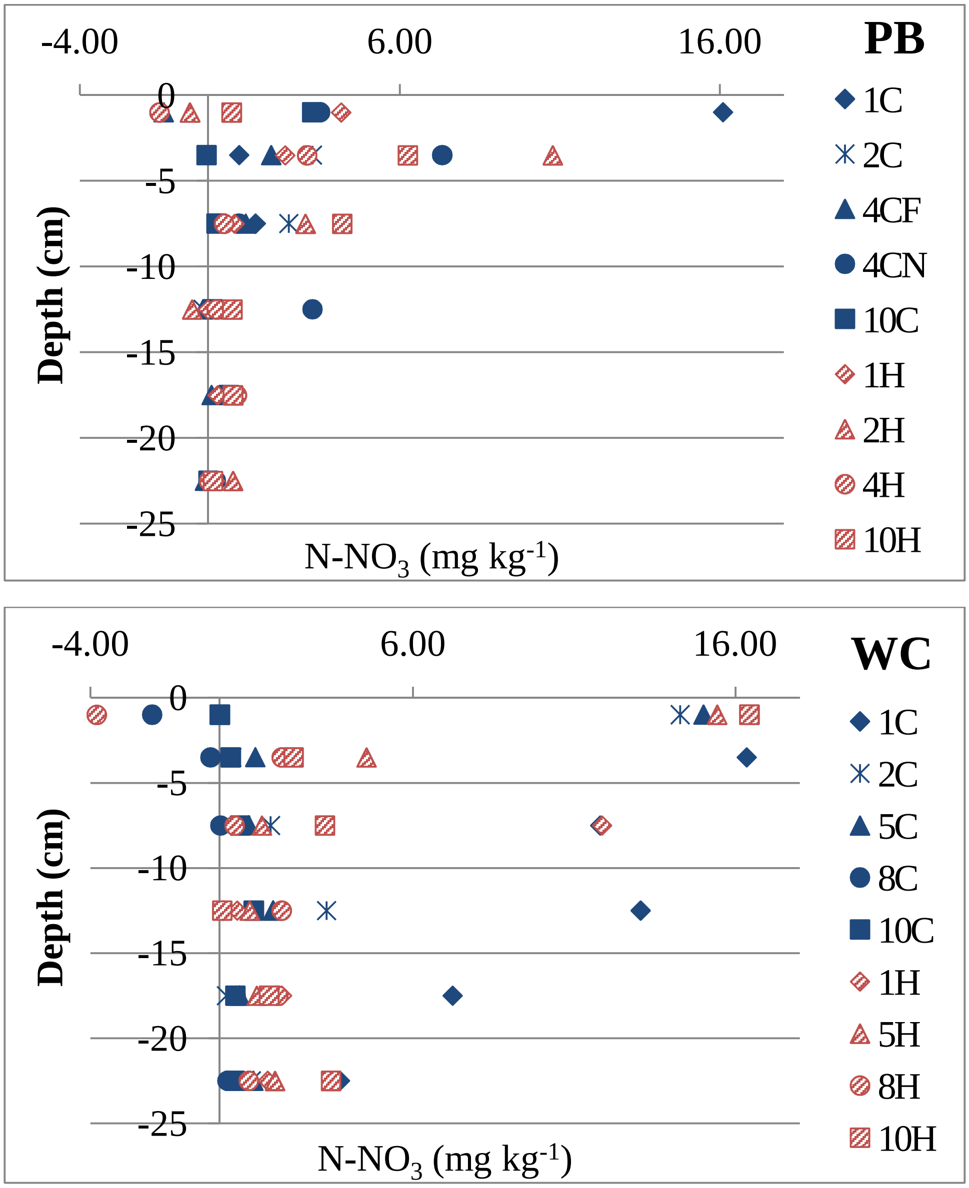


**Figure 2.8** Changes in $NO_3$ concentrations relative to the summer median for the same depth in samples taken 1/7/2010 at PB and 1/8/2010 at WC. Large increases in $NO_3$ in the top 2cm of the fertilized plots due to fertilization are not shown.

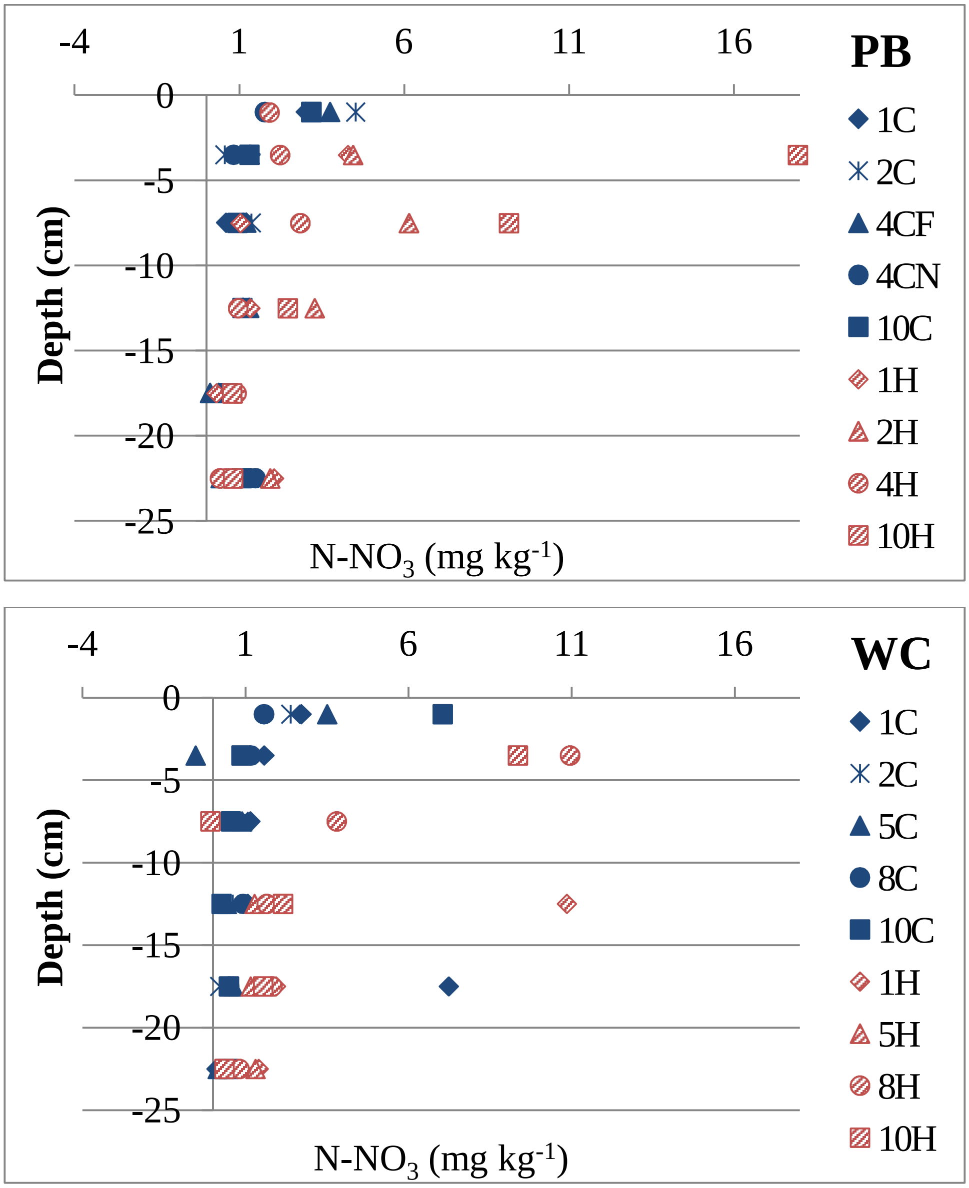
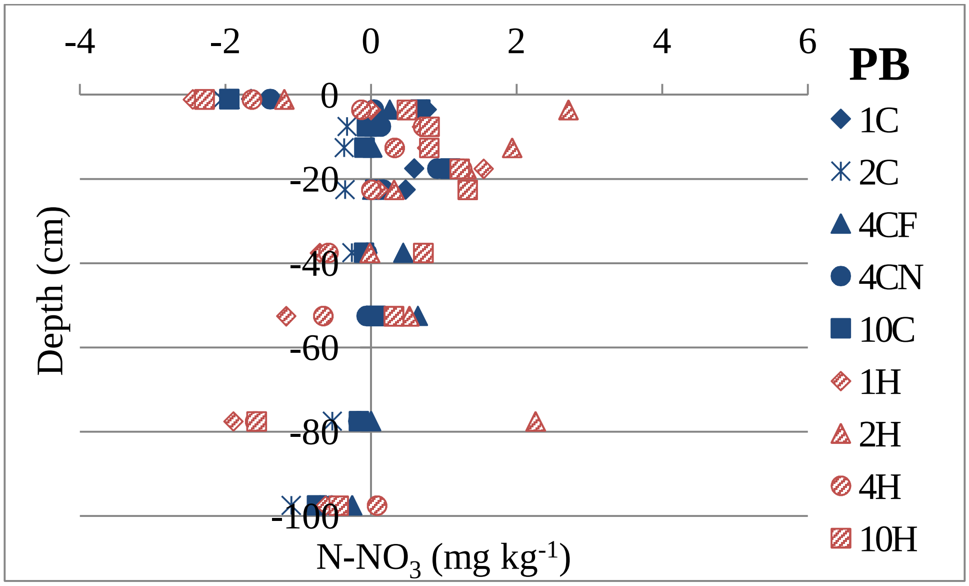


**Figure 2.9** Changes in $NO_3$ concentrations relative to the summer median for the same depth in samples taken 2/12/2010 at PB and 2/1/2010 at WC.



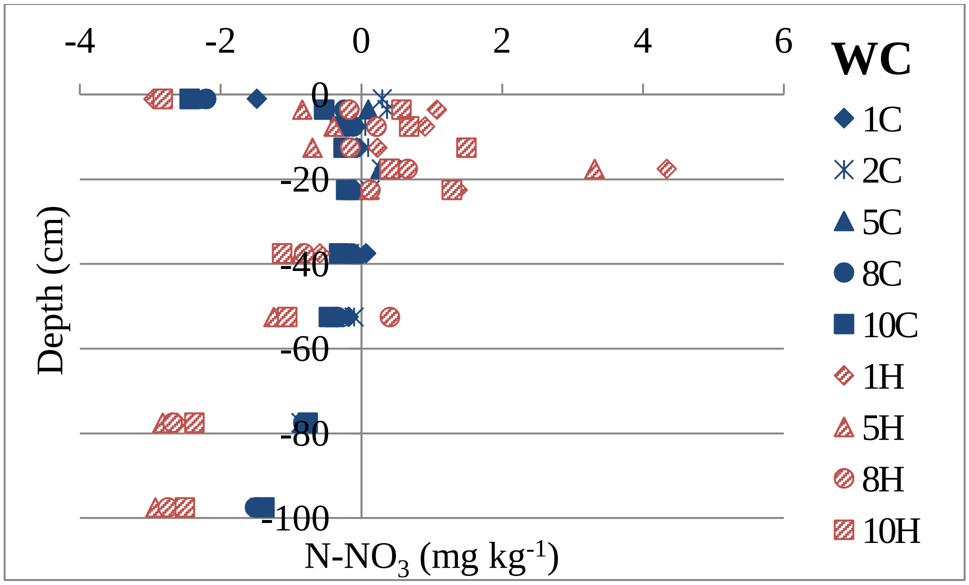


**Figure 2.10** $NO_3$ concentrations measured in soil columns after the application of water at 0.955cm $hr^{-1}$ for 2 hours and 8 hours.

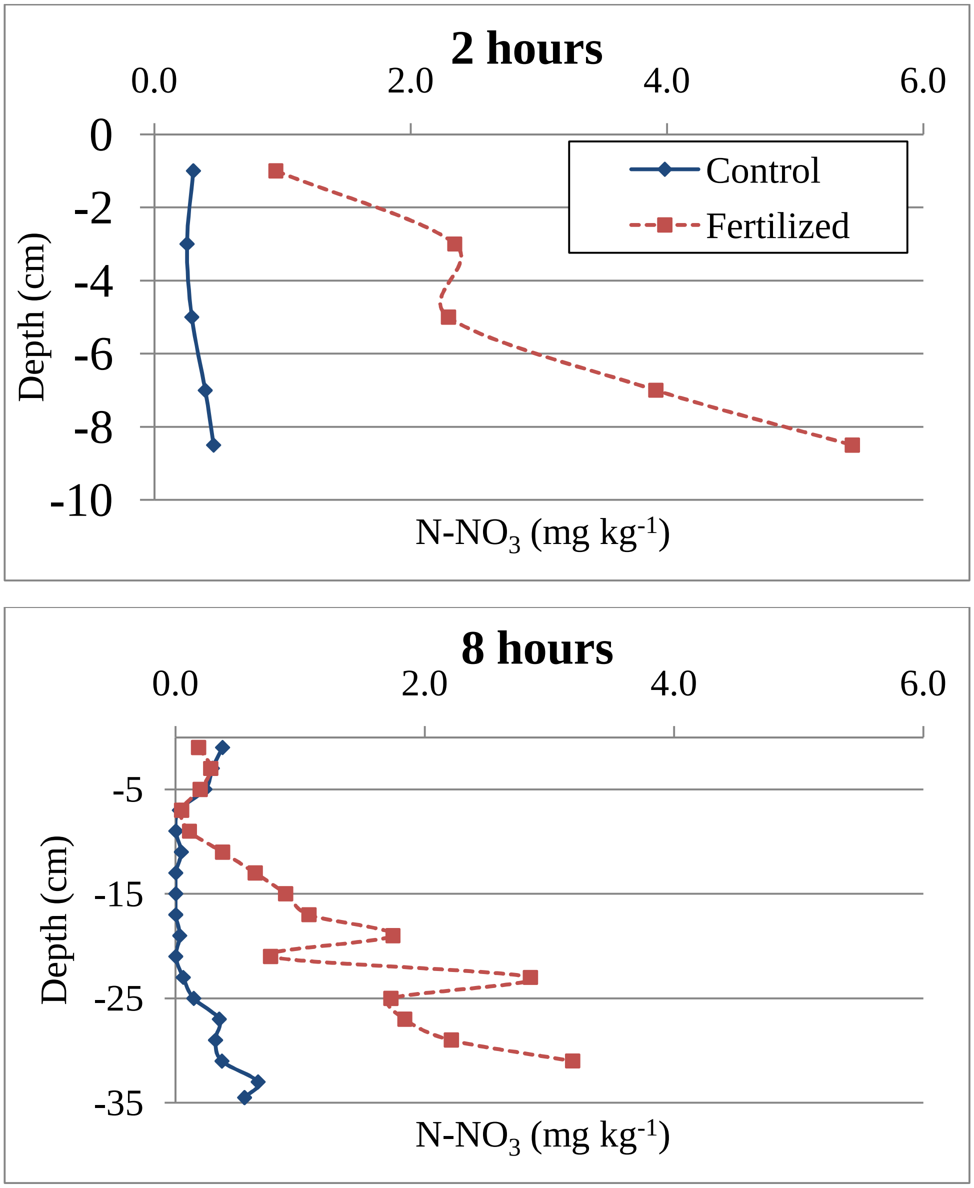
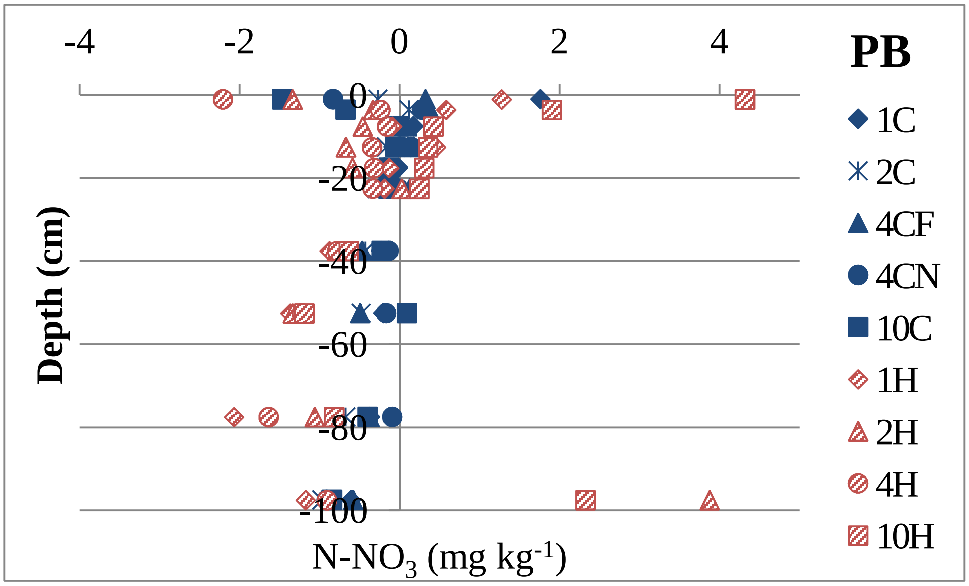
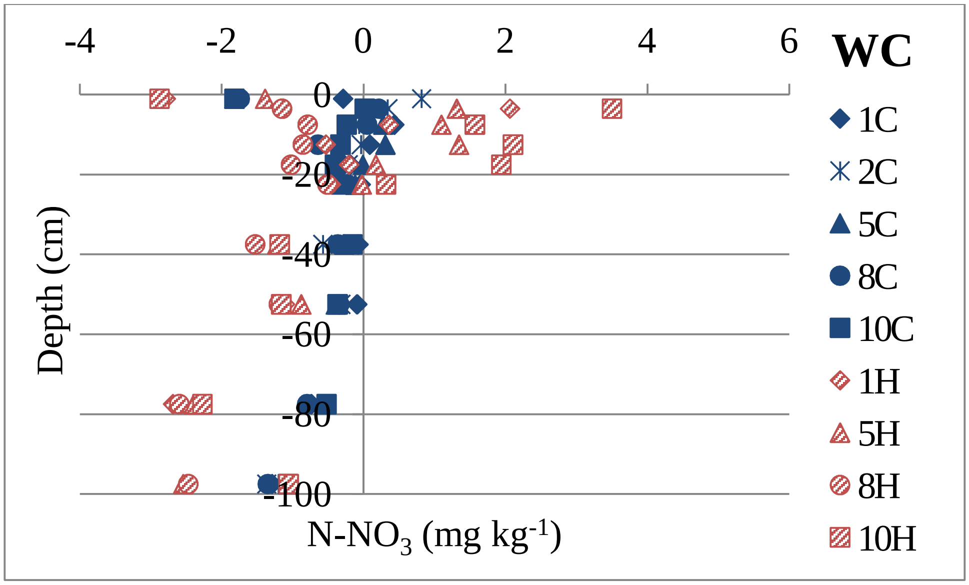


**Figure 2.11** Changes in $NO_3$ concentrations relative to the summer median for the same depth in samples taken 4/29/2010 at PB and 5/6/2010 at WC.





## **Chapter 3** Analysis of the effects of precipitation on ammonium concentrations in sandy desert soils in southern California

### Abstract

Eight plots were fertilized with 30 kg N $ha^{-1}$ ammonium nitrate at two creosote bush-dominated sites in the Sonoran Desert in order to determine the effects of the accumulation of biologically-available nitrogen (N) on the nitrogen cycle in desert ecosystems. The fertilizer was added in December to simulate an influx of N with early winter rains hypothesized to occur as a result of the buildup of dry deposited ammonium ($NH_4$) and nitrate ($NO_3$) throughout the summer. Concentrations of $NH_4$ and $NO_3$ were measured monthly in sections to the depth of 25cm. While much $NO_3$ was rapidly leached below the root zones of annual plants with rains, $NH_4$ was significantly retarded, causing a higher percentage of it to remain in the root zones for longer periods, potentially allowing for greater uptake by annuals. The extent of the retardation and the reason that it is relatively high despite low clay, organic matter, and silt is unknown. $NH_4$ in fertilized plots remained elevated throughout the year, indicating a potential for $NH_4$ to accumulate in the soil over time, but deposition does not appear likely to have significant annual effects due to the rapidity of the creation of extractable N following the first rains of the growing seasons. The addition of the fertilizer in December 2009 led to no additional accumulation of $NH_4$ in the soil after it dried, but it maintained the difference in concentrations between fertilized plots and unfertilized plots resulting from

fertilization in previous years. While the N cycle in the desert remains incompletely understood, the study of $NH_4$ concentrations in the soil suggests the strong dependence on precipitation, the importance of retardation in determining the extent of its availability to short-rooted plants, the potential for accumulation of biologically-available N in soil that may be partially mitigated by leaching, and the effects of fertilization on mineralization and nitrification in following years.

## Introduction

While the effects of nitrogen (N) deposition are widely studied, distinction is seldom made between the deposition of ammonium ($NH_4$) and the deposition of nitrate ($NO_3$). Although both can provide the nutrient N to plants and $NH_4$ can be readily converted into $NO_3$ through nitrification, the mobility of the two ions is very different in many soils. The soils of the deserts of southern California are frequently very sandy with high saturated hydraulic conductivities that cause rapid water flow when the soil is sufficiently wet. As a result, nutrients can be leached quickly below the root zones of annuals and other short-rooted plants with precipitation. While $NO_3$ is highly mobile in the sandy soils (Chapter 2), the cation $NH_4$ generally is retarded by adsorption, increasing the likelihood of a higher proportion of $NH_4$ remaining in the root zones of annuals.

Livestock, soil emissions, and fertilizer were responsible for the majority of the approximately 51,000 Mg of ammonia estimated to be released annually into the South Coast Air Basin (SCAB) in southern California as of 1997 (Chitjian et al., 2000). $NH_4$

emissions from motor vehicles can also be significant (Kean et al., 2000). Although the amount of $NO_x$ released primarily by fossil fuel combustion into the SCAB annually was estimated to be approximately seven times that amount as of 2002 (SCAQMD, 2007), $NH_4$ deposition in the deserts downwind of the SCAB can be greater than $NO_3$ deposition due to closer agricultural sources of ammonia supplementing the atmospheric pollution from distant urban centers. Dry deposition on soil surfaces, which enters into the soil with subsequent rains, is a major contributor to total deposition due to infrequent precipitation and atmospheric temperature inversions during the Mediterranean summers (Bytnerowicz and Fenn, 1996; Fenn et al., 2003b; Padgett and Bytnerowicz, 2001; Riggan et al., 1985).

### *Effects of Ammonium Deposition on the N Cycle*

Alterations to the N cycle resulting from the deposition of anthropogenic $NH_4$ are difficult to observe due to the complicated role of $NH_4$. In deserts and most other ecosystems, mineralization and N-fixation provide a substantial source of $NH_4$, in addition to deposition. Although $NH_4$ can be toxic to many plants if it is the primary source of N, it can still be directly taken up by plants or be lost to nitrification, volatilization, or leaching.

Many processes of the N cycle have been observed to be altered with the deposition of biologically-available N, including mineralization (Fenn et al., 2003a; Fenn et al., 1996; Magill et al., 1997; Vourlitis and Zorba, 2007), nitrification (Fenn et al., 2003a; Fenn et al., 1996; Magill et al., 1997), and denitrification (Hanson et al., 1994). Many lichens are sensitive to disturbance, making alterations to the rates of N-fixation also conceivable (Evans and Belnap, 1999). Assimilation can increase with increased soil N, with high N tissue concentrations having been observed in many plants (Magill et al., 2004; Padgett and Allen, 1999; Rueth and Baron, 2002; Vourlitis et al., 2009), but the effects on decomposition have varied between increased rates, decreased rates, and no change in rates in different ecosystems (Hobbie, 2005; Knorr et al., 2005). Although the richness of mycorrhizae has declined with N fertilization in some studies (Egerton-Warburton and Allen, 2000; Lilleskov et al., 2011; Treseder, 2004), in another study the addition of $NH_4$ resulted in increased growth of myccorhizae while $NO_3$ did not (Yoshida and Allen, 2001), demonstrating the potential for different effects from different forms of N.

### *Nitrogen Deposition and Invasive Species in the Deserts of Southern California*

Substantially less N deposition is typical in the deserts of southern California relative to environments closer to large urban centers (Fenn et al., 2003b); however, the naturally low amounts of N in arid ecosystems may result in greater effects from the deposited N. The expectation of negligible leaching below the root zones (Peterjohn and Schlesinger, 1990) may enhance the potential for N to accumulate in desert soils. Over time, low levels of deposition have decreased diversity in grasslands (Clark and Tilman, 2008), making it plausible that a similar effect may be observed in deserts.

N is commonly the main nutrient that limits productivity in many ecosystems around the world (LeBauer and Treseder, 2008; Vitousek and Howarth, 1991), which includes numerous southern Californian ecosystems (Fenn et al., 2003a). Both N and water commonly limit productivity in deserts (Gutierrez and Whitford, 1987; Hooper and Johnson, 1999; Yahdjian et al., 2011). As a limiting nutrient, N has a particularly great potential to instigate alterations in the abundance and composition of vegetation. The effects of increased biologically-available N have been observed in many ecosystems throughout the world (Adams, 2003; Smith et al., 1999; Vitousek et al., 1997). Among the problems caused by elevated N is the potential for diversity to decrease due to competitive exclusion by nitrophilic species, which may be given a competitive advantage by greater N availability (Bobbink et al., 1998; Tilman, 1987).

The native annual forbs and grasses in the deserts southern California are currently threatened by the spread of an invasive forbs and grasses (Barrows et al., 2009; Brooks, 2000; DeFalco et al., 2007) . Many native and invasive annual plants in the arid regions of southern California respond to N fertilization with increased productivity (DeFalco et al., 2003; Rao and Allen, 2010; Salo et al., 2005), but invasives have sometimes shown greater response than natives when grown in competition (Brooks, 2003; DeFalco et al., 2003). As a result, N deposition may accelerate the spread of invasives.

### *Intent of the Analysis*

Although anthropogenic N has been observed to alter vegetation in the Californian deserts (Allen et al., 2009; Brooks, 2003; DeFalco et al., 2003), the extent to which deposited N is taken up by the annual plants is not clear. Much of the deposited $NO_3$ appears to be lost to the annuals by rapid leaching below their root zones (Chapter 2), but the adsorption of $NH_4$ could allow a longer period of retention near the soil surfaces.

This analysis is meant to assess the potential for annual plants to take up the N from deposited $NH_4$ by examining how field measurements of $NH_4$ concentration throughout different depths of desert soils vary in relation to precipitation events. While the field measurements cannot conclusively demonstrate the relative importance of different processes of the N cycle, they can illuminate patterns of variation of $NH_4$ concentration in the soil and provide a basis for future research.

## Materials and Methods

### *The Study Sites*

Pinto Basin (33.832°N; 115.758°W; 744m above sea level) and Wide Canyon (33.943°N; 116.395°W; 501m above sea level) are located in the Colorado Desert part of the Sonoran Desert in California (Figure 1.1). The dominant vegetation at both sites is creosote scrub (*Larrea tridentata*), a long-lived flowering evergreen shrub that is common throughout the deserts of the American southwest. Wide Canyon (WC) is located at the western edge of Joshua Tree National Park (JOTR), approximately 160 kilometers east of Los Angeles and 20 miles northeast of Palm Springs. Pinto Basin (PB) is located in central JOTR, approximately 100km east of WC. Deposition is estimated to be greater at WC than at PB. Between November 2004 and December 2005, approximately 2.13 kg N-$NO_3$ $ha^{-1}$ and 3.11 kg N-$NH_4$ $ha^{-1}$ bulk deposition was measured at WC and 1.62 kg N-$NO_3$ $ha^{-1}$ and 1.73 kg N-$NH_4$ $ha^{-1}$ bulk deposition was measured at PB (M. Fenn, personal communication). These measurements do not include dry deposition on plant canopies, which is also expected to contribute.  Measurements in February and July 2004 at the sites indicated that atmospheric concentrations of ammonia in JOTR are higher in winter than in summer, contrasting $NO_3$ measurements for which the opposite was true (Allen et al., 2009).

The hydrometer method was used to determine the particle size distribution for 10 samples at depths throughout the top 100cm of the soil at nine plots at each site.  The soils at both sites were very sandy with no consistent variations at different depths (Table 2.1).  There were substantially more rocks at WC than at PB, which corresponded to a higher percent gravel in the soil at WC than at PB, averaging 31% and 20%, respectively. The soil pH was measured at 7.1 at WC and 7.9 at PB (Rao and Allen, 2010).  Both sites originated from a granitic parent material that is common in JOTR (Rao et al., 2011). The retention and hydraulic conductivity curves are very steep for the sandy soils at the sites (Figure 1.6), meaning a rapid rate of water flow when the soil is sufficiently wet that drops very quickly as the soil dries.

### *The Vegetation at the Study Sites*

Creosote bushes and other shrubs were estimated to cover approximately 9.5% +/- 2.7% at PB and 18.1% +/- 3.8% at WC (Rao and Allen, 2010), leaving large expanses of the desert floor without vegetation for most of the year.  Because the lateral roots of creosote bushes often spread well beyond the edge of the canopy (Brisson and Reynolds, 1994; Gibbens and Lenz, 2001; Wallace and Romney, 1972), as well as several meters deep into the soil (Gibbens and Lenz, 2001), the roots of the central creosote bush likely spread throughout the plots. At many creosote-dominated sites, all precipitation is removed annually by evapotranspiration (Andraski, 1997; Kemp et al., 1997; Sandvig and Phillips, 2006). Both the timing and amount of precipitation strongly affect the growth and reproduction of creosote bushes (Cunningham et al., 1979). Studies have varied in their assessments of whether creosotes bushes are N-limited. While some have found a limitation by both water and N similar to other desert vegetation (Lajtha and Whitford, 1989; Lightfoot and Whitford, 1987), a recent study found no effect on creosote bush from N fertilization on creosotes in the Sonoran Desert (Hall et al., 2011). Another study determined that successive wet years could result in a depletion of nutrients by extending plant growth, resulting in a N-limitation that was not distinctly observed otherwise (Sharifi et al., 1988).

Annual plants grew at greatest densities beneath the shrubs, with more growing on the north sides than the south sides (Allen et al., 2009), while the interspaces were sparsely vegetated. This corresponds to greater amounts of nutrients in the soils beneath canopies of desert perennials (Garner and Steinberger, 1989; Reynolds et al., 1999; Schade and Hobbie, 2005; Schlesinger and Pilmanis, 1998; Schlesinger et al., 1996).

The native forb *Chaenactis fremontii* was the most abundant plant at PB and the native forb *Malacothrix glabrata* dominated WC during the study from 2008 to 2010, though both were common at both sites. The most abundant invasive plant at both sites was the exotic grass *Schismus barbatus* (Allen et al., 2009). N fertilization has been observed to increase the productivity of Schismus species in the desert (Allen et al., 2009; Brooks, 2003). Although significant reductions in species richness and the cover of annual natives were observed in fertilized plots at PB in 2004 (Allen et al., 2009), fertilization appeared to result in increased growth of annual natives at both sites in the spring of 2010. In the March 2010 survey at WC, the annual plants in the fertilized plots were estimated to cover 26% of the surface while in the unfertilized plots averaged approximately 17% coverage. The April 2010 survey showed similar differences at PB, with the fertilized plots having 32% annual coverage compared to 24% in the unfertilized plots. This was less apparent in other years, such as during the first two years of fertilization that showed no increase in percent cover by the annuals (Allen et al., 2009).

There was no germination at PB during the winters of 2005-2006 and 2006-2007 and at WC in the winter of 2006-2007 due to severe droughts both years (Rao and Allen, 2010). The abundance of *Schismus barbatus*, as well as *S. arabicus*, was reduced after the drought relative to the years prior to the drought (Schneider, 2010), though it was in greater abundance by the spring of 2011 than in previous years following the drought (personal observation). Creosote bushes had also been adversely affected by the drought, having lost leaves and branches, but there was significant recovery following the drought, with most growth at the bases of the bushes.

### *Water in the Desert*

Rainfall and temperature were measured hourly by on-site weather stations at both sites beginning in 2005. Figure 1.2 shows the average temperatures and the annual precipitation measured at the sites from 2005-2010. The summers at both sites are hot and dry, with most rain falling in the winter and early spring. Annual plants generally begin growing following sizeable rainfalls and peak in March or April, with PB generally peaking one or two weeks later than WC. The rainfall was below average in the winter of 2008-2009 and above average in the winter of 2009-2010. WC generally receives slightly more rain than PB during the winter, with 7.4 cm falling at WC in the winter of 2008-2009 and 17.9cm in the winter of 2009-2010. PB received 6.4cm of rain in the winter of 2008-2009 and 15.1cm in the winter of 2009-2010. Little summer rain is common at WC, with more being common at PB due to an eastward increase in the summer precipitation gradient in JOTR (Rao et al., 2011). However, summer precipitation in 2009 and 2010 was exceptionally low, with under a centimeter of rain falling between May 1 and October 31 at either site.

PB and WC were similar in temperature and there was little variation between years. The average summer high temperatures were 35.9°C at PB and 36.6°C at WC, while the average winter highs were 16.1°C at PB and 19.6°C at WC during the years of study. Summer lows averaged 18.8°C at PB and 23.1°C at WC and winter lows averaged 6.4°C at PB and 12.4°C at WC.

To estimate the depth of water infiltration on dates when sampling was done, data from MPS-1 dielectric matric potential sensors (MPS-1, 2008) was analyzed. These used a solid matrix equilibration technique to measure the matric potential of the soil water from November 2008 to December 2010. Two sets of sensors were installed at each site at depths of 5cm, 10cm, 15cm, 20cm, 25cm, 50cm, and 70cm at approximately 0.5m from the edge of the canopies of the creosote bushes. From the measurements of the MPS-1s, it can be extrapolated that before the winter of 2009-2010, water likely had not percolated below 100cm at PB since the winter of 2004-2005, making $NO_3$ leaching below 100cm unlikely between 2005 and 2010. Some leaching below 100cm may have occurred at WC due to the 10.1cm of rain received in the winter of 2007-2008.

### *The Soil Cores*

Because comparisons between PB and WC were difficult due to variations in factors other than N deposition, 4 fertilized and 5 unfertilized plots spread over slightly less than 1 hectare at each site were studied in order to compare the effects on the soil of added $NH_4$ and $NO_3$ from the fertilizer to control conditions. Figure 2.1 shows approximately how the plots were spread. 30 kg N/ha of ammonium nitrate ($NH_4NO_3$) was added to four 6 x 6 meters plots each centered around a creosote bush at both WC and PB in December 2008 and December 2009 shortly after the first rains, though it was intended to be done prior to the first rains to mimic the leaching of N that had accumulated on the soil surface over summer. Prior to the study, the plots had been fertilized annually in December from 2002 to 2005 with the same amount of $NH_4NO_3$. Although 30 kg-N $ha^{-1}$ is far higher than any estimates of $NH_4$ or $NO_3$ deposition, a large amount of $NH_4NO_3$ was used to allow a clearer observation of the effects of N from the fertilizer against the natural variation in the desert sites. Measurements were also taken in corresponding control plots, located within 7 to 30 meters of each fertilized plot, with one extra control plot at each site with no corresponding fertilized plot.

From November 2008 and May 2010, monthly soil cores were taken to a depth of 25cm on the east side of the creosote bushes immediately outside the canopy in each of the nine plots at both sites. The cores were taken in increments of 5cm with the exception of the top 5cm, which was taken in two sections from 0 to 2cm and 2 to 5cm. The depth of cores was increased to 100cm in June and September of 2009 and in cores taken from January to May 2010, with samples also being taken from 35-40cm, 50-55cm, 75-80cm, and 95-100cm. The less frequent samples at greater depths reflected the expectation of less variation below the top of the soil. The dates of the coring at PB and WC during the winter of 2009-2010 are shown in Figure 2.2 in relation to precipitation and fertilization. Additionally, in October and November 2010, one core was taken in a fertilized plot and another in an unfertilized plot at each site to a depth of between 330cm and 345cm and collected at every depth in sections of 5cm for the purpose of examining the deep soil.

$NH_4$ was extracted with 1M KCl and measured colorimetrically (Technicon Instruments Corp., Tarrytown, NY).

### *The Soil Columns*

A very basic experiment was run with 6 soil columns in order to assess how the $NH_4$ adsorbs to the soils. All columns were filled with soil from PB and three of the columns were fertilized with 10.5 kg N $ha^{-1}$ $NH_4NO_3$, with the other three being used as controls. Soil from the top 2cm was not included in the columns due to the variably high concentrations of $NH_4$. Water was dripped on the columns at a rate of approximately 0.955cm $hr^{-1}$ for 2, 4, or 8 hours, after which the columns were immediately cut open to remove the soil in 2cm sections for an analysis of the extractable N. Too few repetitions make this experiment merely exploratory, but it is useful for the discussion of trends observed in the field samples

### *Methods of Analysis*

N concentrations are highly variable in desert soils (Hunter et al., 1982), complicating any analysis of the N cycle. Both the very high measurements and very low measurements are characteristic of the N cycle in the soils. Variations between samples are assumed to be demonstrative of the spatial distribution in the processes of the N cycle at the distance from the creosote bushes at which the samples were taken.

Although the experiment began in November 2008, the analysis will focus on the data taken between April 2009 and May 2010 because the conditions during that time resulted in a more complete data set that shows trends with greater clarity.

## Results

$NH_4$ concentrations remained higher in the top 2cm of the fertilized plots relative to the unfertilized plots throughout the year, but very little $NH_4$ appeared to move downward. Figure 3.1 shows the mean concentrations of $NH_4$ between April 2009 and May 2010 from 0-2cm and 20-25cm. Measurements showed that the concentration of $NH_4$ diminished with depth and differences between fertilized plots and unfertilized plots became less pronounced. Throughout the year, the $NH_4$ was remained highly concentrated in the top 2cm. This high surface concentration is most likely partially caused by the considerable retardation of $NH_4$ relative to the flow of water in the soils at the sites, which was observed in the column experiments. In Figure 3.2, the results of the column experiments after 2, 4, and 8 hours are shown. Even after 8 hours of water application and a wetting front that had moved to 35cm, no significant difference between the fertilized and unfertilized columns below the top 2cm was observed. Not all $NH_4$ added was accounted for in the column measurements, with the top 2cm of the fertilized columns being 10.3-10.9 mg N-$NH_4$ $kg^{-1}$ higher when the fertilizer would have increased the concentration by 14.6 mg N-$NH_4$ $kg^{-1}$ if there was no loss. No extra $NO_3$ was observed to account for the decrease in $NH_4$ by nitrification.

Between April and November 2009, when 0.025cm of rain fell at PB and no rain fell at WC, fertilized plots had significantly higher $NH_4$ concentrations than unfertilized plots despite fertilizer not being applied since the beginning of the previous winter. Measurements were highly variable (Figure 3.3), with the top 2cm of fertilized plots being particularly disposed to large spikes in $NH_4$ concentration. At both WC and PB, concentrations, variability, and differences between the fertilized and unfertilized plots diminished quickly with depth. The means of all concentrations measured between April and November 2009 at a given depth in fertilized and unfertilized plots at PB and WC are shown in Figure 3.4. The differences between the means are statistically significant to 25cm. Despite the observed variability, 187 comparisons between measured concentrations at a given depth on a given day in corresponding plots at PB during the summer showed that concentrations in the fertilized plots were higher approximately

83% of the time in the top 25cm. At WC, 186 comparisons similarly established that fertilized plots had higher concentrations about 82% of the time. On average, the fertilized plots contained approximately 11.8 kg-N ha$^{-1}$ more $NH_4$ than the unfertilized plots at PB and 9.0 kg-N ha$^{-1}$ more $NH_4$ at WC during the summer of 2009. The top 2cm accounted for about 45% and 43% of that difference at PB and WC, respectively.

Some $NH_4$ deposition is expected to accumulate in the top 2cm of soil throughout the summer. The mean concentration of $NH_4$ in the top 2cm at WC appeared to increase by 2.5 kg-N ha$^{-1}$, mostly in the late spring and early summer. However, there was also a slight increase in measurements below the top 2cm that could not have been accounted for by deposition, as was observed at 20-25cm in Figure 3.1. The reason for this increase is unclear, though it may have simply resulted from chance. PB did not show a significant increase in the top 2cm or below.

$NH_4$ decreased in the top 2cm of most plots relative to median summer concentrations following the first significant precipitation in December 2009 (Figure 3.5). Below the top 2cm, $NH_4$ concentrations generally remained near the summer median concentration. The fertilized plots at PB were an exception, with $NH_4$ concentration appearing to decline throughout the top 15cm. Samples were taken the day after the rains. Whereas the wetting front at PB was at approximately 15-20cm, the wetting front at WC had moved beyond the 25cm depth that was sampled due to greater rain. Large increases in $NO_3$ were measured at both sites in these cores (Chapter 2), but $NH_4$ did not decrease sufficiently to fully account for this $NO_3$.

In January 2010, average $NH_4$ concentrations increased relative to the previous sampling and were higher than the median concentrations of the previous summer, with the exception of the fertilized plots at PB (Figure 3.6). WC had received 0.381cm of rain on 12/13/09 after fertilization on 12/11/09, but PB received no rain between fertilization and the January coring, leaving all fertilizer concentrated in the top 2cm. Below the top 2cm, the fertilized plots at PB were similar to the median concentrations the previous summer. Because the control plots at both sites had clearly increased in concentration relative to the previous summer while the fertilized plots at WC did not, the difference in concentration between the fertilized and unfertilized plots was reduced in the January cores. While most of the fertilizer remained in the surface at WC, elevated concentrations were observed in all plots from 2-5cm, with very high concentrations at 5-10cm observed in two plots.

There was no evidence of the $NH_4$ added in the fertilizer when the cores were taken in February 2010 after the majority of the season's rains (Figure 3.7). In the top 2cm of the fertilized and unfertilized plots at both sites, the concentrations of $NH_4$ were low relative to the median concentration of the previous summer, but the concentrations of $NH_4$ below the surface in the control plots were high. Despite the addition of the fertilizer, concentrations in the fertilized plots were near the mean the previous summer. While they remained higher than the unfertilized plots, the difference between the fertilized and unfertilized plots had decreased.

$NH_4$ concentrations in all plots were elevated relative to the summer of 2009 after the soil dried in the spring of 2010 (Figure 3.8). Unfertilized plots maintained approximately the same concentrations that were measured in February, but fertilized plots increased significantly.

## Discussion

### *A High Retardation Factor for a Sandy Soil*

$NH_4$ retardation in the soil from PB and WC appears to be high relative to estimates from the few studies done on $NH_4$ adsorption in sandy soils. The vast majority of extractable $NH_4$ remained in the top 2cm of the soil in all measurements at both sites during the study and the column experiments with soil from PB showed no statistically significant difference below the top 2cm of the soil column between the fertilized and unfertilized columns following 8 hours of water application when the wetting front was at 35cm. Since the plurality of $NO_3$ moved with the wetting front, the retardation factor (R) of $NH_4$ appears to be at least 17.5.

Considering the basic equation for the retardation,

$$R = 1 + \rho_b K_d/\theta_v$$

high bulk densities ($\rho_b$) and low volumetric water content ($\theta_v$) can contribute to a high retardation factor, in addition to a high distribution coefficient ($K_d$). $\rho_b$ is generally higher in sandy soils and water contents typically remain below saturation in the desert as a result of the slow rate of water application combined with the rapid percolation in sandy soils at high water contents. In the columns, the peak water content measured in the top 2cm was approximately 0.28 $cm^3$ $cm^{-3}$. With a bulk density of 1.63 g $cm^{-3}$ estimated for the soil at PB (Rao and Allen, 2010), the observed retardation in the soil columns would require the $K_d$ to be approximately 2.8 $cm^3$/g. Although this would not be close to many $K_d$ values for agricultural soils, for which $K_d$ in the range of 3-4 $cm^3$ $g^{-1}$ is typical (Hanson et al., 2006), the small fraction of clay, silt, and organic matter at PB was expected to result in a relatively low $K_d$.

Previous studies on $NH_4$ adsorption in sandy soils have been rare, but $NH_4$ adsorption in sandy soil has been found to be weak relative to silt and clay loams (Wang and Alva, 2000). In a sandy Tunisian soil, the highest measured $K_d$ was 0.82 $cm^3$/g (Jellali et al., 2010), which is significantly less than the minimum $K_d$ required to cause the lack of $NH_4$ leaching below 2cm in the soil column. A $K_d$ of 1.5 $cm^3$/g provided the best fit for measurements in a sandy soil in an early N model (Iskandar and Selim, 1981).

While the remainder of 12.3 to 13.1 mg N-$NH_4$ $kg^{-1}$ in the top 2cm of the soil columns indicates a high retardation relative to other studies in sandy soils, large variations observed in other studies suggest that the soil at PB is not necessarily exceptional. $NH_4$ adsorption in the sandy Tunisian soil studied by Jellali et al. (2010) varied between 1 to 30.7 mg $kg^{-1}$ with the application of solution of concentrations between 4.9 and 36.4 mg $L^{-1}$. Wang and Alva (2000) determined that $NH_4$ adsorption was primarily between 10.8 and 23.7 mg $kg^{-1}$ in the sandy soils of citrus groves in Florida after contact with a 140 mg

N-$NH_4$ $L^{-1}$ solution, with one soil sample from a depth of 90-100cm being observed to adsorb approximately 75 mg $kg^{-1}$ of $NH_4$. Although numerous soils in these studies had a physical capacity to adsorb the amount of $NH_4$ measured in the top 2cm of the columns, a significant amount of $NH_4$ remained that was not adsorbed in the experiments of Wang and Alva (2000) and Jellali et al. (2010), which was not evident in the PB soil columns.

The high concentration at which the $NH_4$ entered the PB soil columns is likely a contributing factor in the high retardation observed. Previous studies have observed that the increase in adsorption with the concentration of $NH_4$ in the applied solution holds true in sandy soils (Jellali et al., 2010; Wang and Alva, 2000). The $NH_4$ from the solid fertilizer applied to the PB columns presumably entered the soil at very high concentrations with the first few drops of water. The effects of high concentrations on $NH_4$ adsorption may also be important at field sites, both because solid fertilizer had been added in the study and because evaporation may cause $NH_4$ on the surface to become highly concentrated as the soil dries.

Although the initial high concentration may explain the initial adsorption, subsequent desorption would be expected with the continued application of water as the adsorbed $NH_4$ equilibrated with the low concentration in solution. In the PB soil columns and at the field sites, physical non-equilibrium could result in the slower leaching of $NH_4$, though this has not been explored. Preferential flow, which can occur even in largely homogeneous sandy soils, can be simulated using a dual-permeability model that assumes more rapid water flow in fractures than in the soil matrix pore system and the exchange of solutes between these regions (Gerke and Vangenuchten, 1993). With highly concentrated $NH_4$ entering dry soil and clean water applied subsequently entering a wet soil, $NH_4$ may have remained concentrated primarily in the less permeable matrix during the experiment. The dilution of the $NH_4$ in the soil matrix would depend on the solute exchange between the fractures and the matrix, with the rapid percolation of water near saturation in the sandy soil limiting time for the exchange. Future experiments are necessary to determine if these conditions of the PB soil column experiment resulted in greater retardation of $NH_4$ than is typical of a sandy soil and whether this could have affected $NH_4$ movement at the field sites.

The $NH_4$ distributions at PB and WC were very similar throughout the year, suggesting the properties of the soils are similar. Although at both sites the majority of $NH_4$ was found in the top 2cm throughout the year, the influence of nitrification, plant uptake, ammonia volatilization, mineralization, and other processes in maintaining the distribution at the sites makes it difficult to ascertain the importance of adsorption in retaining $NH_4$ in the soil surface. The 0.381cm of rain at WC on 12/13/09, three days after the application of fertilizer, produced significant increases in $NH_4$ from 2-5cm in all fertilized plots and from 5-10cm in two of the plots in the samples taken on 1/7/10. Although the majority of $NH_4$ remained in the top 2cm, the distribution of $NH_4$ resembled the distribution of the $NO_3$ from the fertilizer. The previous set of samples, which had been taken in December one day after the first winter rains, showed no evidence of downward flow of $NH_4$ in the soil surface at either site, more consistent with the columns. Dissimilar conditions appear to result in substantially different mobility.

Differences in conditions that could have influenced the apparent deeper movement of $NH_4$ in the January cores relative to the December cores include that soil had previously been wetted at the time of the fertilization prior to the January cores, the longer delay between the rains and the coring in January, and the higher concentration of $NH_4$ on the soil surface after fertilization. Although the hypothesis that preferential flow caused different distribution under different conditions is possible, the seemingly inconsistent behavior of $NH_4$ at these sites highlights the necessity for more studies of $NH_4$ movement in sandy soils.

Because of the granitic parent material at both sites (Rao et al., 2011), the potential importance $NH_4$ fixation should be investigated. $NH_4$ fixation refers to the sequestering of $NH_4$ in the interlayer of a 2:1 clay mineral. Significant $NH_4$ fixation occurs in many coarse-textured decomposed granite substrates in California (Rider et al., 2006; Rider et al., 2005). With very fine sands fixing the most $NH_4$ per unit weight and substantial fixation by coarse sand due to its high prevalence in the substrates (Rider et al., 2005), the $NH_4$-fixation observed in decomposed granites, which appears to be caused by interstratified biotite-vermiculite collapse (Rider et al., 2005), may be applicable in the coarse-textured granite-derived soils at PB and WC. However, the importance of $NH_4$ fixation at PB and WC is questionable since the soils at PB and WC are not newly exposed-substrates like the decomposed granites studied by Rider et al. (2006). Nevertheless, with little information available on the $NH_4$-fixation capacities of the soils at WC and PB and insufficiently explained measurements, further investigation is warranted. If $NH_4$ fixation at WC and PB was significant, the extraction with KCl could have resulted in an underestimation of the $NH_4$ measured in the soil since the addition of KCl can collapse the lattice structure and trap the $NH_4$ in the interlayer (Rider et al., 2005). This may be an explanation for the measurements of only 64-68% of $NH_4$ applied in the fertilized columns following extraction, though volatilization may also have been a factor.

Further research is necessary to ascertain why $NH_4$ is strongly retained in the soil surface at PB and WC and whether the retardation of $NH_4$ observed in the soil columns is typical of desert soils in southern California.

### *Consequences of Slower Leaching*

The retardation of $NH_4$ in the soils at WC and PB may affect nutrient availability by providing the annuals and other short-rooted plants a source of N after the highly mobile $NO_3$ is leached beyond their root zone. The initially rapid percolation of water during rains due to the high saturated hydraulic conductivities of the sandy soil can result in a substantial loss of $NO_3$ to annual plants with even moderate precipitation (Chapter 2). Additionally, with a substantial amount of $NO_3$ not being taken up by the creosote bushes (Chapter 2), $NO_3$ leaching may not only prevent $NO_3$ uptake by annuals but also result in a long-term loss of N to the desert N cycle, since leached $NO_3$ has been accumulating several meters below the soil surface at many desert sites throughout the Holocene (Hartsough et al., 2001; Marion et al., 2008; Walvoord et al., 2003). If deposited $NH_4$ remains in the root zones of the annual plants longer than the deposited $NO_3$, a higher proportion of the N from the deposited a $NH_4$ would likely be taken up by the annual plants and retained in the desert N cycle. This would mean a greater potential for accumulation of N from deposited $NH_4$ in plant tissue, litter, and soil over time relative to deposited $NO_3$. With N limitation in annual plants possibly frequently triggered by leaching (Chapter 2), $NH_4$ deposition may be more disruptive than $NO_3$ deposition. Additionally with atmospheric ammonia concentrations in JOTR being higher in winter than in summer (Allen et al., 2009), much of the $NH_4$ may be deposited as $NO_3$ is leached through the annual root zones by rains.

Although plants have the potential to take up $NH_4$ directly, nitrification may also allow for the potential restoration of $NO_3$ after rains leach previously present $NO_3$ below the root zones of annuals. Nitrification appears to have begun rapidly with the first rains at WC and PB. After the first rains in December, $NO_3$ at both sites increased between the depths of 2cm and 25cm by an average of approximately 2.5 kg-N $ha^{-1}$ and 6.35 kg-N $ha^{-1}$ relative to the summer averages in the unfertilized and fertilized plots respectively, with variable high spikes in $NO_3$ concentration in the top 2cm. Although a half-life of approximately 3.5 days for nitrification would be expected for rate coefficients typically estimated in literature, there is great variability in rate coefficients estimates in different soils (Hanson et al., 2006). While $NO_3$ creation may have continued briefly after the cores were taken during transport to the lab and as the oven drying began, $NO_3$ creation estimates at PB and WC remain fairly high relative to literature values. Nitrification is rapid in many soils in southern California (Fenn et al., 2003a; Vourlitis and Zorba, 2007), but at PB and WC, the extractable $NH_4$ concentration in the soil surface typically exceeded the $NO_3$ concentration by a ratio of more than 2:1.

Although adsorption could hinder nitrification, higher $NO_3$ concentrations below the surface suggest leaching diminishes the surface concentrations. Soil cores to 3.3-3.4m depth that were taken in the fall of 2010 generally had higher $NH_4$ than $NO_3$ concentrations to a depth of 110-160cm in the two fertilized plots sampled and to a depth of 215-260cm in two corresponding unfertilized plots, below which $NO_3$ was higher (Figure 3.9). The differences between the fertilized and unfertilized plots provide some support to the hypothesis that fertilization increased $NO_3$ concentrations in the deep soil but not $NH_4$ concentrations, resulting in higher $NO_3$ concentrations than $NH_4$ at lesser depths than would occur naturally.

The lowest ratios of $NH_4$ to $NO_3$ in the soil surface, approximately 1:1, were measured in December 2009 following the first rains and in January 2010 following a dry month after the first rains, suggesting high nitrification at the beginning of the rainy season. The highest ratios of $NH_4$ to $NO_3$ were measured in February 2010, after the majority of the winter rains, averaging 12:1 in the fertilized plots and 7:1 in the unfertilized plots. The leaching of $NO_3$ during the heavy rains of January and early February is likely responsible for much of the depletion of extractable N (Chapter 2). Although the $NH_4$ from the added fertilizer disappeared following the January-February rains, the $NH_4$ concentrations in the soil returned to approximately what they had been prior to fertilization, while the surface $NO_3$ measurements were exceptionally small. Nitrification appeared to occur more slowly in February than in December. The remainder of a significant, stable amount of $NH_4$ that does not undergo nitrification may indicate significant inhibition of nitrification by adsorption. New $NH_4$ from mineralization, N fixation, and fertilization may undergo nitrification rapidly, while $NH_4$ that is adsorbed to the soils when the rains begin is hindered. Some $NH_4$ from fertilization may have become part of the slower nitrifying pool since higher stable concentrations of $NH_4$ were measured in fertilized plots.

### *The Production of Ammonium*

Increased $NO_3$ concentrations at PB and WC after the rains in December 2009 likely resulted from nitrification (Chapter 2); however, the simultaneous production of $NH_4$ would have been necessary for the observed measurements since the increase in $NO_3$ was greater than the decrease in $NH_4$. The importance of deposition in increasing the extractable N in the soil is unknown, but the variable spikes in $NO_3$ concentration in the top 2cm would not likely be the result of deposition and the increase in $NO_3$ in the soil dwarfed estimates of deposition. N mineralization, followed by nitrification, could account for the greater increases in $NO_3$ observed in fertilized plots relative to unfertilized plots, since it would return previously assimilated N to the pool of extractable N. High mineralization and nitrification likely continues following the December sampling, since high levels of $NO_3$ remained in the January samples even as the soil became significantly drier and there was little loss of $NH_4$. The contribution of N-fixation and denitrification in determining the amount of $NO_3$ and $NH_4$ is uncertain. Rao et al. (2010) estimated no denitrification at PB or WC and an annual input from N fixation of 0.7 kg N/ha, which would be fairly small relative to the increases in N observed immediately following the first rains.

Although the greater production of $NO_3$ in fertilized plots relative to unfertilized plots would likely be due to greater mineralization, a laboratory incubation experiment with soils from sixteen Sonoran desert sites including WC and PB by Rao et al. (2009) showed an increase in total mineralization with deposition but not in mineralization rates. Mineralization rates may only significantly increase when the differences in N applied are large enough, since the differences between the fertilized and unfertilized plots at the sites are much greater than between the soils studied by Rao et al. (2009). Rao et al. (2009) did not focus on pulses of water or on mineralization occurring immediately after rains, but concentrations measured in the weeks after water application show no evidence of previous rapid mineralization. However, many other experiments have shown that wet-dry cycles in semiarid and arid soils can produce significant N mineralization within a single day of incubation (Austin et al., 2004). Pulses of water following dry periods are known to stimulate biological activity in desert ecosystems (Noy-Meir, 1973), including microbial activity (Austin et al., 2004; Fisher et al., 1987; Schwinning and Sala, 2004). Increased $NO_3$ created following a water pulse may last only a few days since it can be immobilized (Cui and Caldwell, 1997), potentially explaining why no evidence of this rapid increase was observed in the weekly measurements of Rao et al. (2009). Because surface cover of plants was not significantly higher in fertilized plots prior to 2010 (Allen et al., 2009), the greater increase in $NO_3$ in fertilized plots would have resulted from greater N in organic matter rather than more organic matter. If fertilization altered the amount of N in the organic matter with high turnover rates, greater increases in $NO_3$ in the fertilized plots after rains would be expected. Measurements did not show statistically significant differences between fertilized and unfertilized plots in total carbon (C) and total N (N), possibly due to limited samples, high spatial variability, and the inclusion of organic matter with low turnover rates. Fertilization can increase the N in the plant tissues of many desert plants (DeFalco et al., 2003; Schneider, 2010), which may increase the N in the litter in subsequent years. Lower C:N ratios in litter and soil organic matter have correlated to greater N mineralization in many ecosystems (Currie, 1999; Fenn et al., 1996; Vourlitis and Zorba, 2007; Vourlitis et al., 2007).

### *The Loss of Ammonium*

After the month of heavy rains in January and early February, there was no evidence of the $NH_4$ from the fertilizer on the top of the soil, but the amount of $NH_4$ remained elevated relative to $NO_3$. Although it was clear that nitrification was no longer creating $NO_3$ as rapidly prior to the February cores as it did following the first rains, the change in rates of mineralization is less clear because significant $NH_4$ remained in the soil in February that may have replaced previously nitrified $NH_4$. Below the surface, the unfertilized plots showed a significant increase in $NH_4$ relative to the summer average, but the fertilized plots did not, though the average concentrations remained high in the fertilized plots relative to the unfertilized plots. Therefore, the difference between the fertilized plots and unfertilized plots was reduced in February 2010 relative to the previous summer despite the added fertilizer. The disappearance of the $NH_4$ from fertilizer in February may be attributable largely to leaching following nitrification, since the soils have exhibited significant potential for nitrification, the wetting front was likely well below a meter at both sites in February, and $NO_3$ is highly mobile in the soils (Chapter 2). Differences between the 3.3-3.4 meter cores taken in the fall of 2010 suggest that roughly 50% of the fertilizer applied may have been leached as $NO_3$ (Chapter 2). A proportion of the fertilizer $NH_4$ would have been taken up as $NH_4$ or $NO_3$ by the plants and microbes as well, contributing to the decline in measureable extractable $NH_4$ in February 2010.

The application of the fertilizer subsequent to the first rains rather than prior may have severely limited plant uptake of the fertilizer in 2010. Whereas the first rains could have driven the fertilizer into the soil and allowed a month for potential nitrification reactions and uptake with the water, the rains that drove the fertilizer into the soil in January were followed closely by more rains. In conditions where significant rains occur in close temporal proximity, the potential for the leaching of both $NO_3$ previously present and $NO_3$ resulting from nitrification below the root zone of the annuals is particularly high.

Although some gaseous loss is also expected, it was not measured and the high proportion of applied N accounted for in the deep soil and likely in plant tissue and litter suggest that it is likely a more minor loss than deep root zone soil storage. DayCent modeling of the soils at PB and WC by Rao et al. (2010) estimated that the primary gaseous loss is by nitric oxide (NO) via the nitrification pathway. The lack of much accumulation of $NO_3$ and $NH_4$ on the soil surfaces at the sites during the summer of 2009 may have resulted from deposition balancing gaseous loss, which is expected to be substantial in summer due to high soil-surface temperatures (McCalley and Sparks, 2009).

### *The Ammonium Remaining in the Soil*

In April and May 2010, after the soil was dry, $NH_4$ was elevated in fertilized and unfertilized plots relative to the summer of 2009. $NH_4$ concentrations increased after February, as it was presumably restored by mineralization and N-fixation after some was lost during the January rains. The increase in the fertilized plots was greater than in the unfertilized plots, which had been higher than the summer measurements since January. The reasons for the differences between the fertilized and unfertilized plots are not known. One possibility is that because the fertilized plots are unnaturally elevated and would not be expected to be in equilibrium, the $NH_4$ in the system would be lost over time as balance is restored without the addition of more fertilizer. The differences between fertilized and unfertilized plots were reduced in December and January, before the fertilizer entered the soil, and in February after heavy rains were not favorable for the retention of the fertilizer in the top of the soil. As the soil dried in March and April, greater mineralization may have occurred in the fertilized plots due to the previous assimilation of fertilizer, restoring the differences between the fertilized and unfertilized plots to approximately the ratio observed the previous year.

The reason for the remainder of greater amount of $NH_4$ in the soil in both the fertilized plots and the unfertilized plots at both sites is unknown. One hypothesis is that differences in the timing and amount of precipitation relative to the previous year may have resulted in different rates of mineralization and nitrification. Whereas $NO_3$ concentrations appeared to return to levels similar to those observed previous summers in the top 25cm by April and May 2010, the concentration of $NH_4$ was elevated. Measurements in May showed more highly concentrated patches of both $NO_3$ and $NH_4$ on the surface of the soils, which had not been observed in February, suggesting the continuation of mineralization and nitrification on the surface as the soils dried. Although the soil was observed to be dry by the MPS-1 sensors in March 2010 (Chapter 1), much of the increase in $NH_4$ below the surface was observed between March 2010 and May 2010. Residual moisture is present in the soil even after the soil was too dry for capillary flow (Chapter 1), which may allow continued mineralization and nitrification in dry soil. Increases in $NH_4$ throughout the soils between March and May despite the apparent cessation of most capillary flow indicate that mineralization may be occurring at different depths in the late spring. Previous studies have suggested that decomposition and mineralization in the deep rhizosphere in the desert may occur similarly to in shallow layers (Canadell et al., 1996; Silva et al., 1989). With the production and decomposition of fine roots being related to fluctuations of water in the soil (Peek et al., 2005), N mineralization of dead roots, as well as dead microorganisms, could have caused the increase in $NH_4$ as the soils dried in the late spring 2010. Although this may have accounted for the creation of $NH_4$ in the late spring, it does not explain why $NH_4$

concentration was greater in the spring of 2010 than in 2009. The remainder of different amounts of $NH_4$ in the soils may reflect the substantial differences in timing and precipitation between the winters of 2008-2009 and 2009-2010, which appear to greatly affect the desert N cycle.

## Conclusions

The leaching of $NH_4$ in the soil is significantly retarded, which may lead to a longer period of availability for short-rooted annual plants of deposited $NH_4$ relative to deposited $NO_3$. Further research is required to determine the extent of the retardation, as well as the reason that it is as great as it is considering the small fraction of clay, silt, or organic matter in the soil. $NH_4$ deposited during summer is likely to have little effect annually, since it is small relative to the creation of $NO_3$ and $NH_4$ following the first rains. However, deposition of $NH_4$ during the winter, when atmospheric $NH_4$ concentrations were highest in JOTR (Allen et al., 2009) may provide a source of N to the annuals when mineralization and nitrification have slowed and extractable soil N has been assimilated or leached. High concentrations of $NH_4$ measured in fertilized plots throughout the year demonstrate its potential to accumulate in the soil, which had previously been demonstrated in the vicinity of JOTR in concentrations in soil correlated to N deposition gradients (Rao et al., 2011). While deposition currently remains low relative to the amount of fertilization necessary to produce changes, continuous low level deposition may accumulate over decades, resulting in similar effects on vegetation to those observed in the fertilized plots. However, the potential for $NH_4$ to buildup in the soil may be dependent on rainfall. Despite the addition of fertilizer, the differences between the fertilized and unfertilized plots after the soil dried in the spring of 2010 did not increase relative to the previous summer. The above average precipitation of the winter of 2009-2010 may have limited accumulation of $NH_4$ in the soils relative to previous years, with the fertilizer added merely maintaining the differences between the fertilized and unfertilized plots rather than increasing it. The combination of climate change, invasive species, and N deposition could strongly disrupt the N cycle in the American southwest, which could have serious repercussions for the vegetation.

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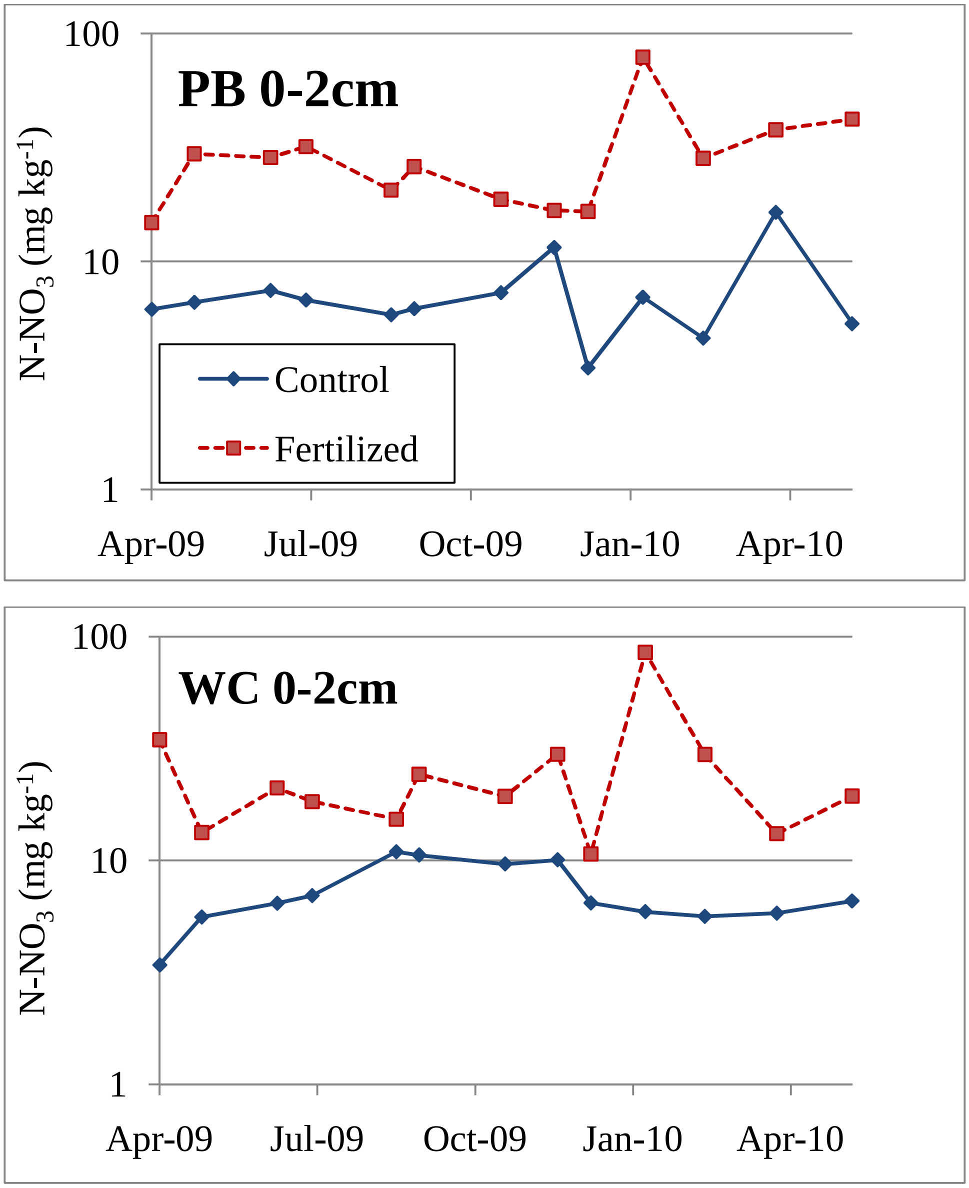
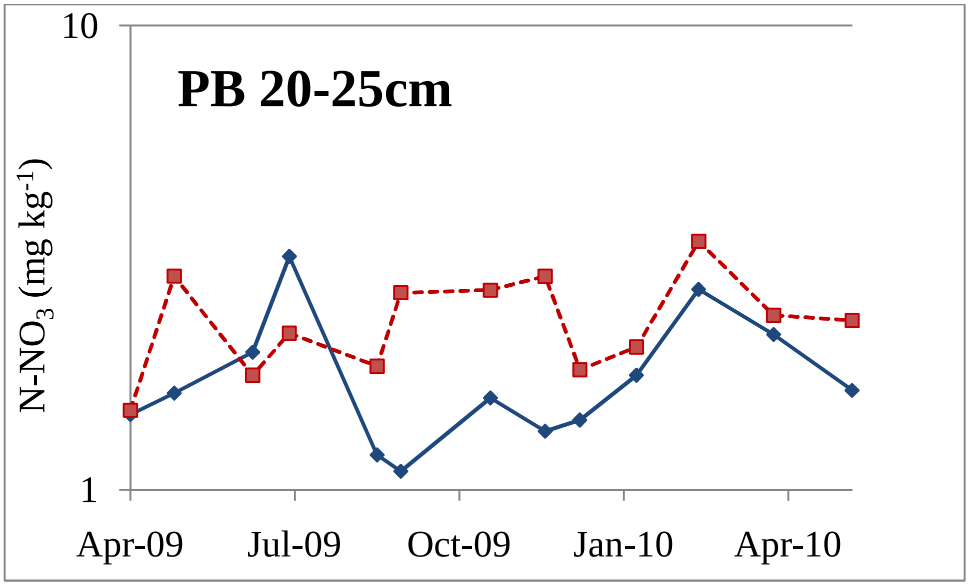
**Figure 3.1** Mean concentrations of $NH_4$ measured in the soils at PB and WC from 0-2cm and 20-25cm. Higher $NH_4$ measurements in the fertilized plots than in the unfertilized plots were observed near the soil surface but differences diminished with depth. $NH_4$ concentrations near the surface were greater throughout the year than with increasing depth.




10
PB 20-25cm
N-NO$_3$ (mg kg$^{-1}$)
1
Apr-09
Jul-09
Oct-09
Jan-10
Apr-10

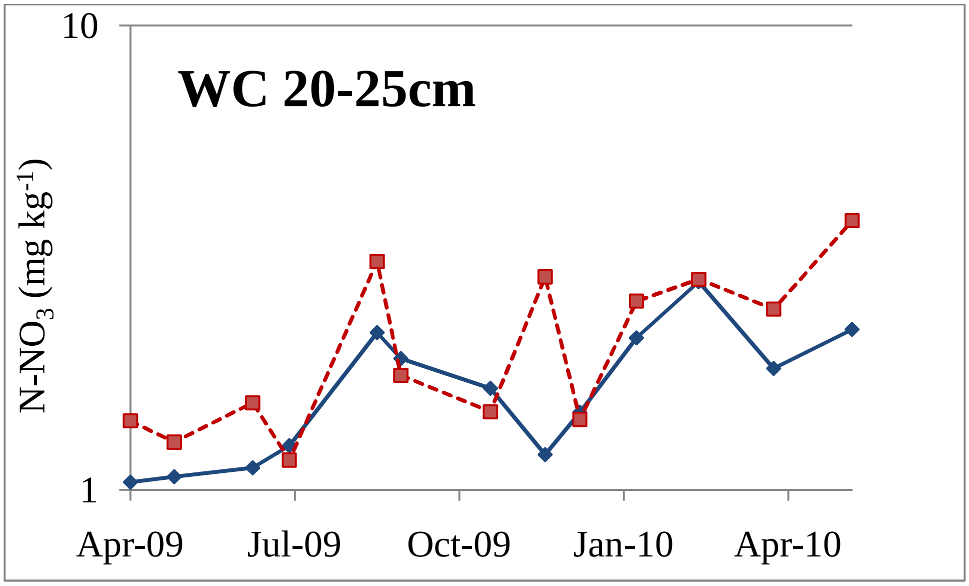
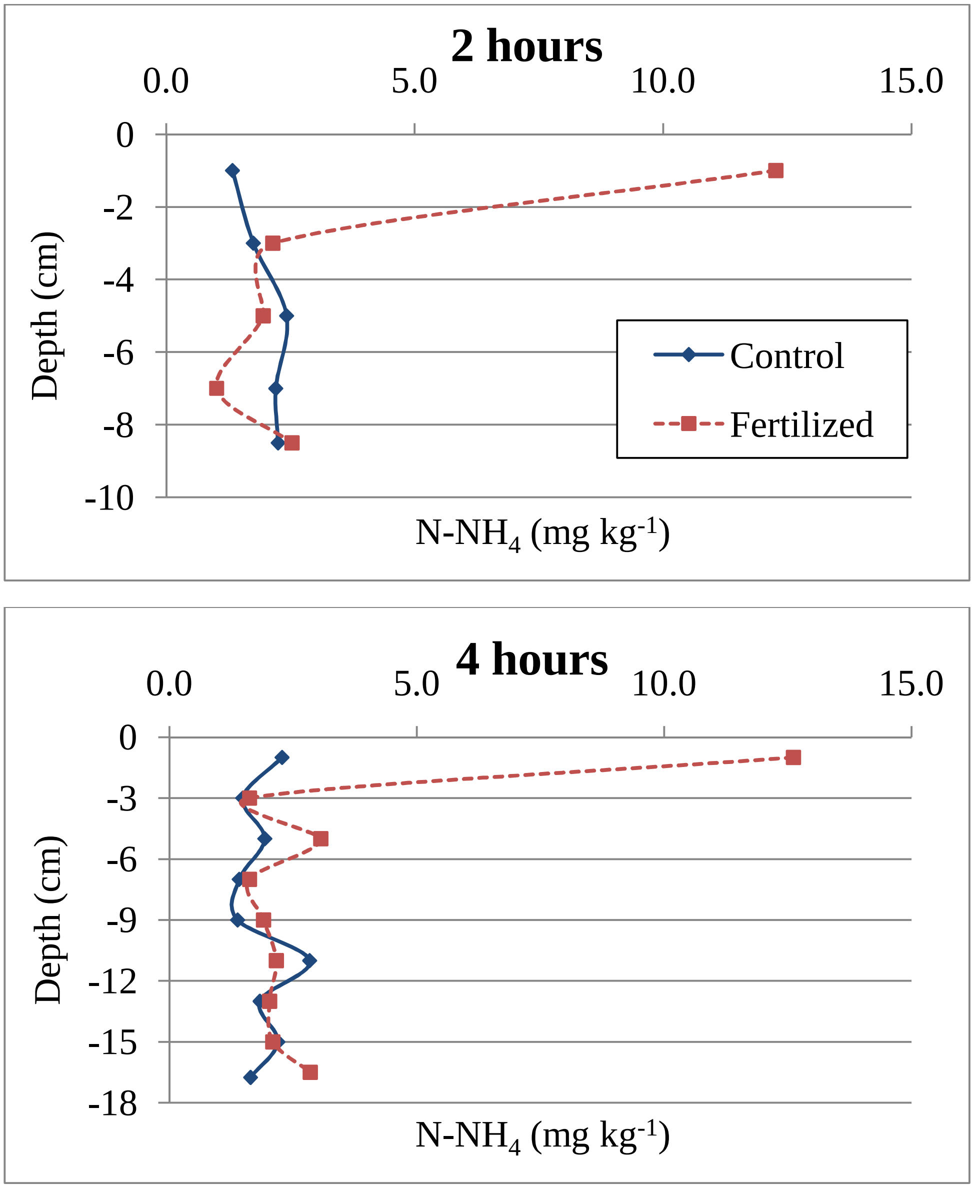

10
WC 20-25cm
N-NO$_3$ (mg kg$^{-1}$)
1
Apr-09
Jul-09
Oct-09
Jan-10
Apr-10

**Figure 3.2** $NH_4$ concentrations measured in soil columns after the application of water at 0.955cm $hr^{-1}$ for 2 hours, 4 hours, and 8 hours.



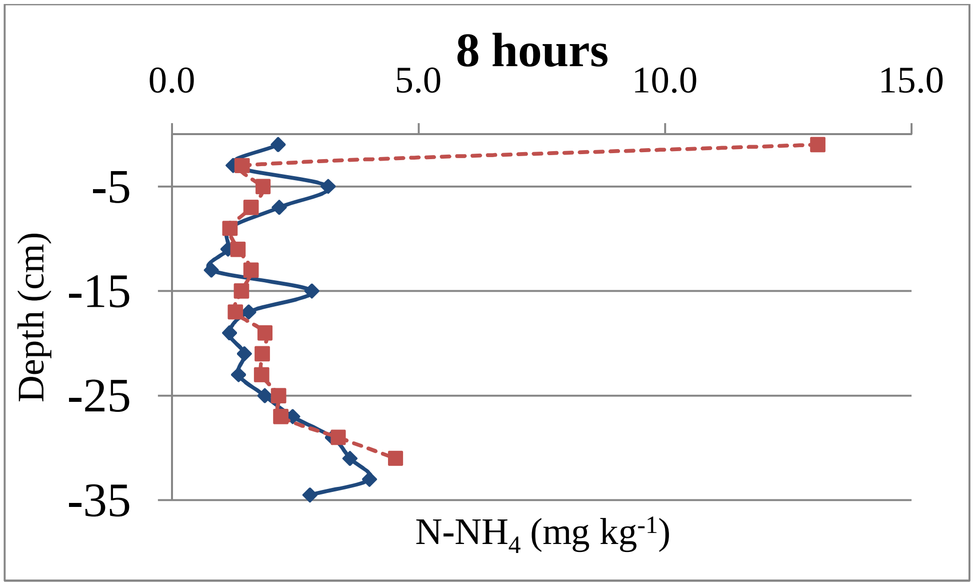
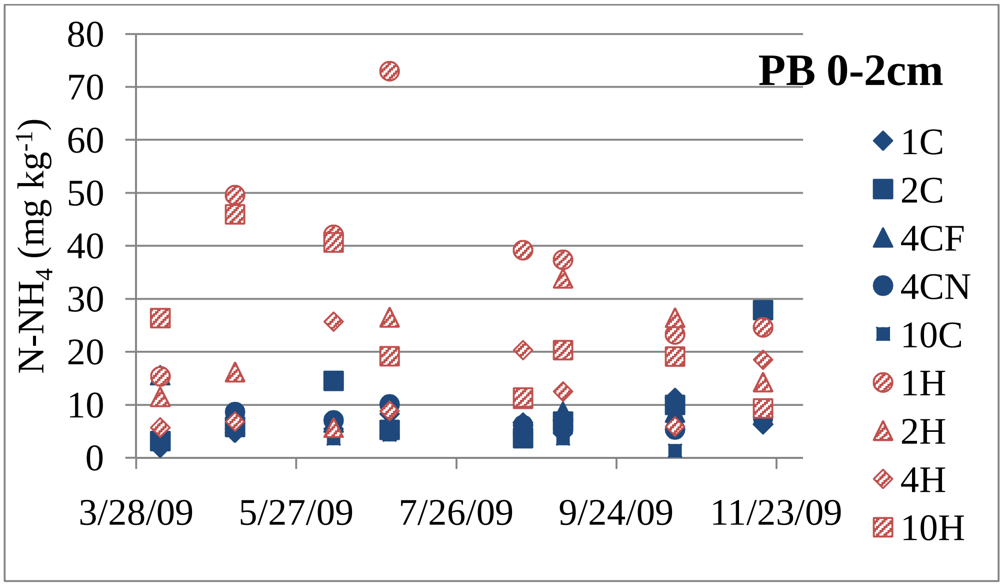

8 hours
0.0
5.0
10.0
15.0
-5
-15
-25
-35
Depth (cm)
N-NH4 (mg kg-1)

**Figure 3.3** Variability in measured concentrations of $NH_4$ between plots at two depths at PB. Concentrations in the top 2cm of fertilized plots were highly variable but less variability, lower concentrations, and less difference between fertilized and control plots was found with greater depth. Similar variability was observed at WC.



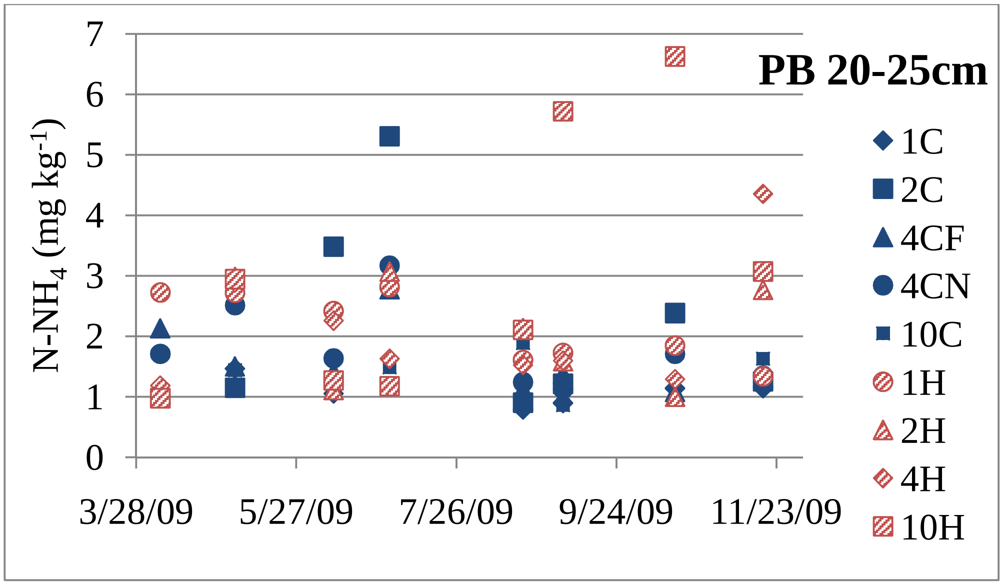


**Figure 3.4** Mean concentrations of $NH_4$ with depth measured in all plots from April to November 2009. Differences in the means between fertilized and control plots were statistically significant to the depth of 25cm at both sites.

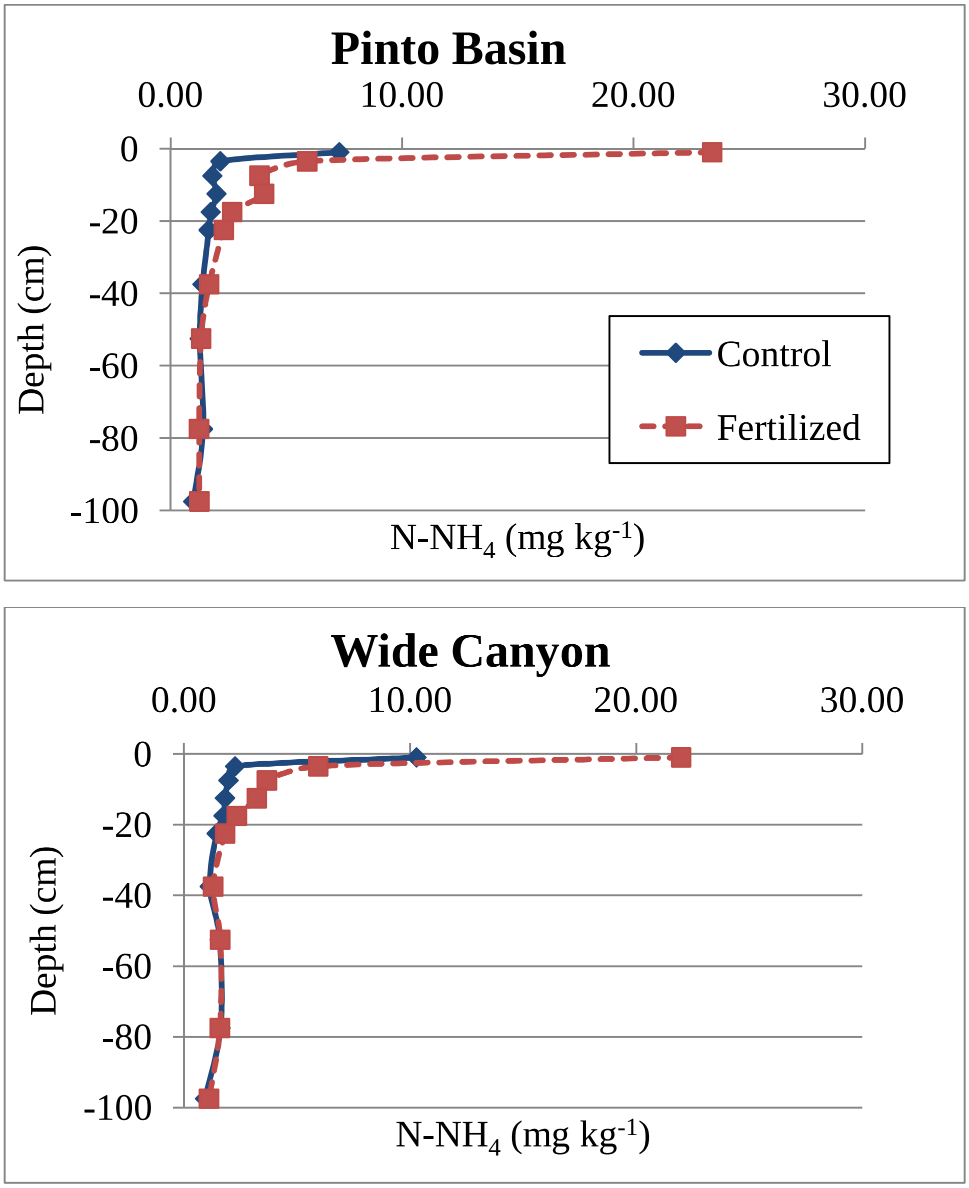
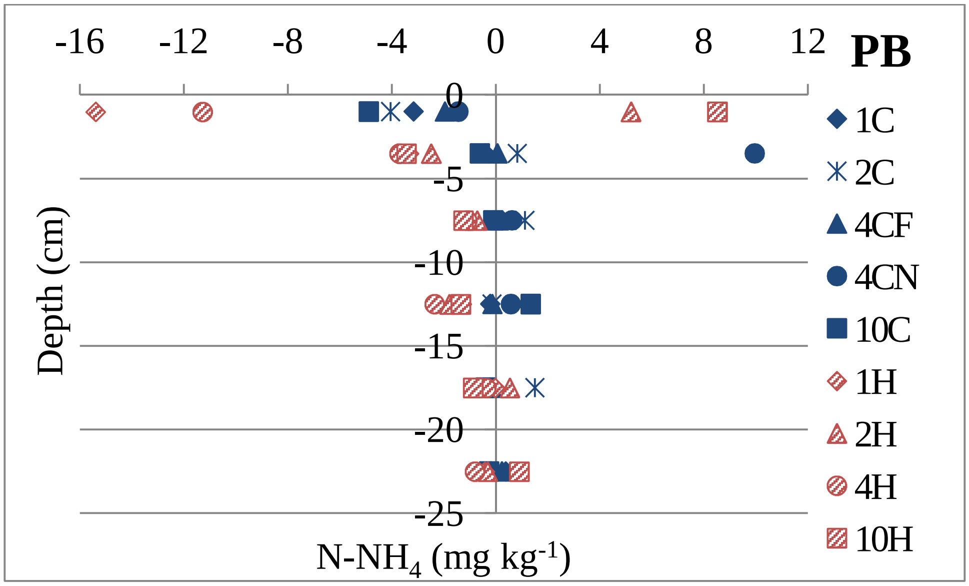


**Figure 3.5** Changes in $NH_4$ concentrations relative to the summer median for the same depth in samples taken 12/8/2009 at PB and WC.



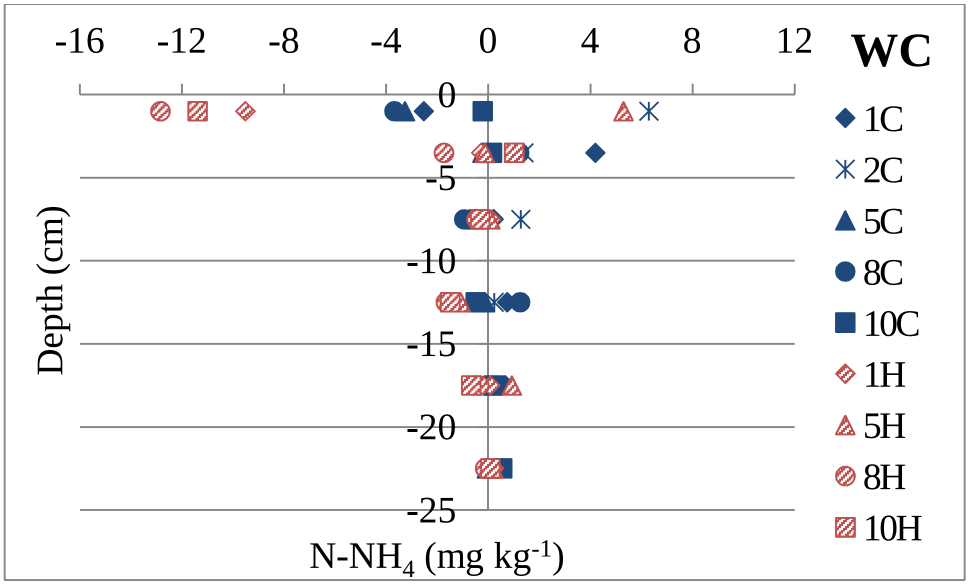


**Figure 3.6** Changes in $NH_4$ concentrations relative to the summer median for the same depth in samples taken 1/7/2010 at PB and 1/8/2010 at WC. Large increases in $NH_4$ in the top 2cm of the fertilized plots due to fertilization are not shown.

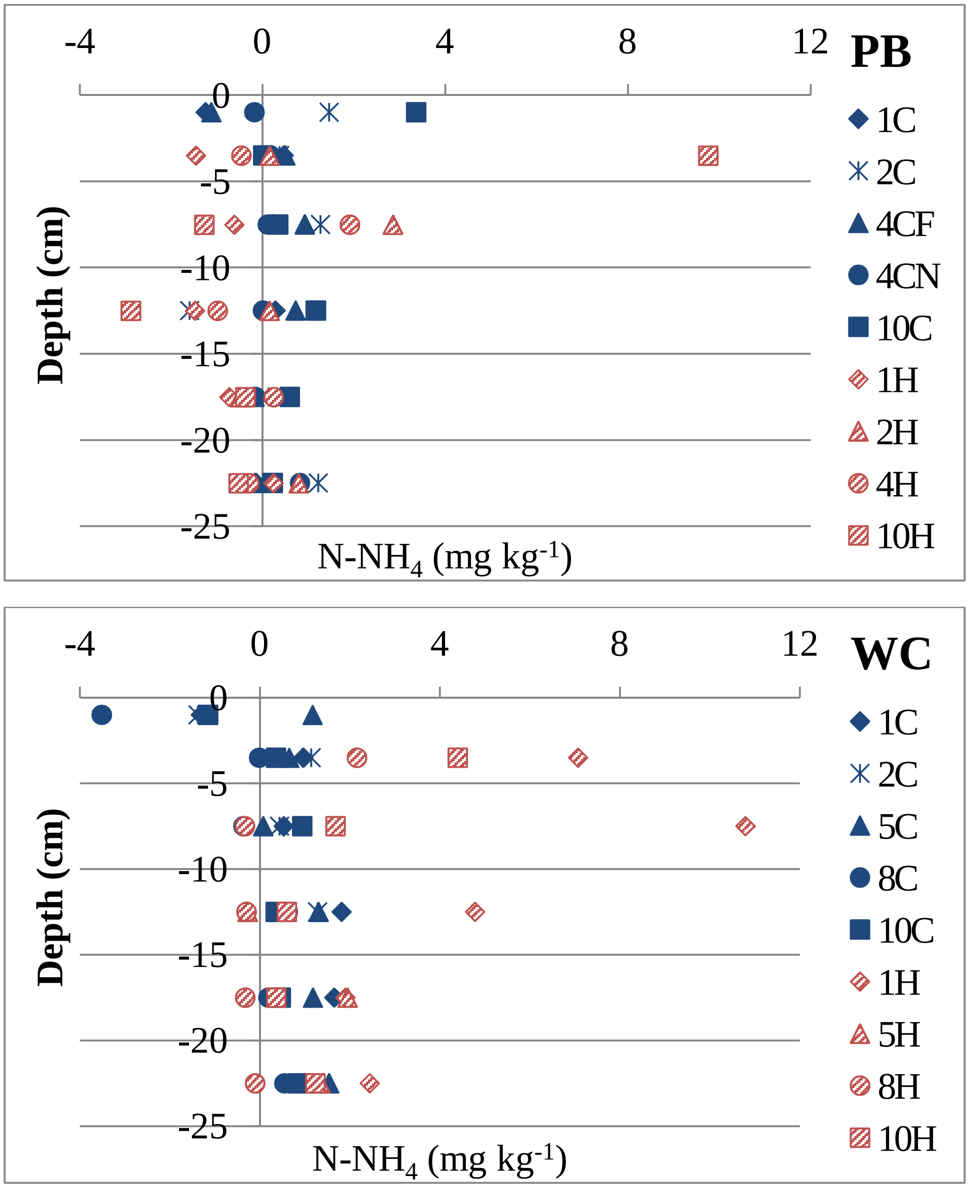
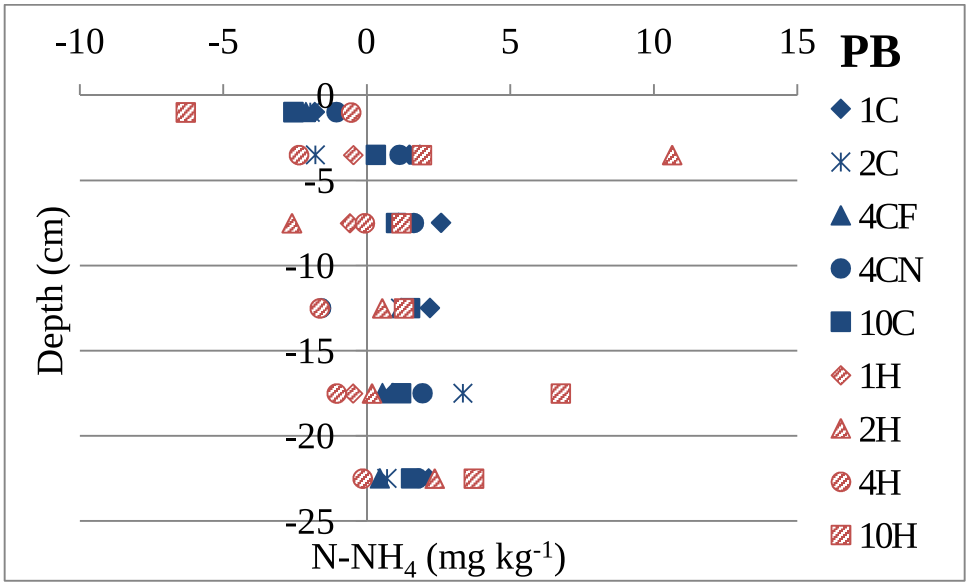


**Figure 3.7** Changes in $NH_4$ concentrations relative to the summer median for the same depth in samples taken 2/12/2010 at PB and 2/1/2010 at WC. One very large increase in $NH_4$ in the top 2cm at both PB and WC is not shown.



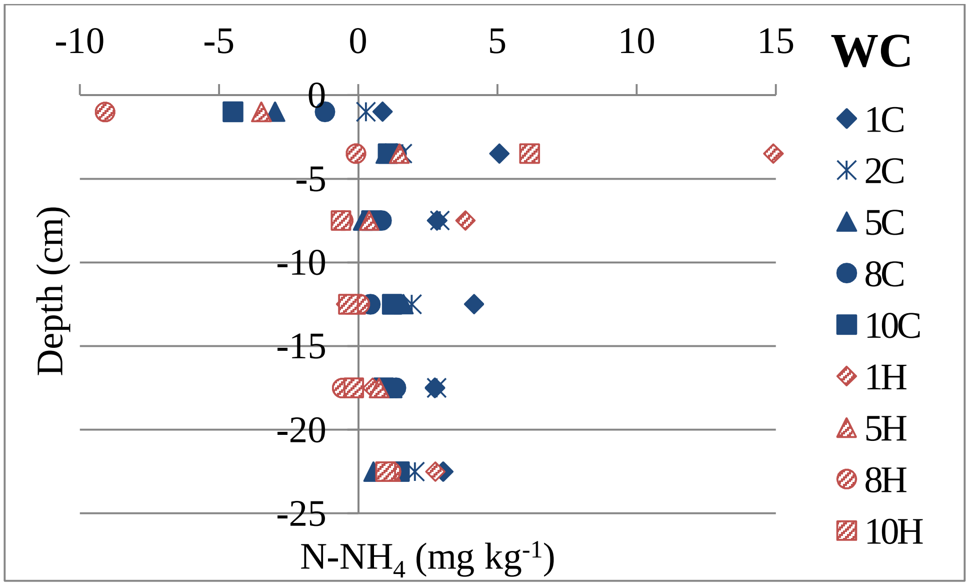
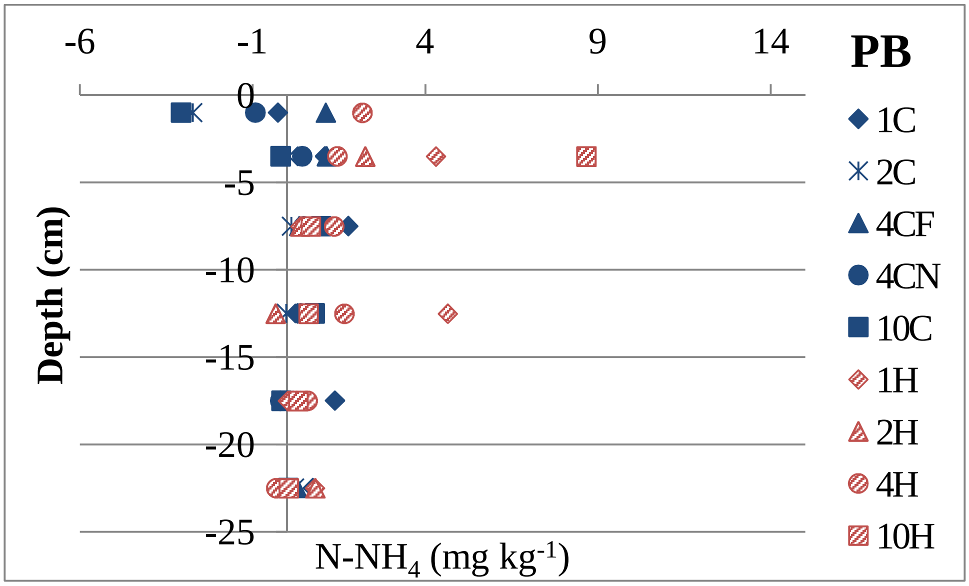


**Figure 3.8** Changes in $NH_4$ concentrations relative to the summer median for the same depth in samples taken 4/29/2010 at PB and 5/6/2010 at WC. Three very large increases in $NH_4$ in the top 2cm of PB and WC are not shown.



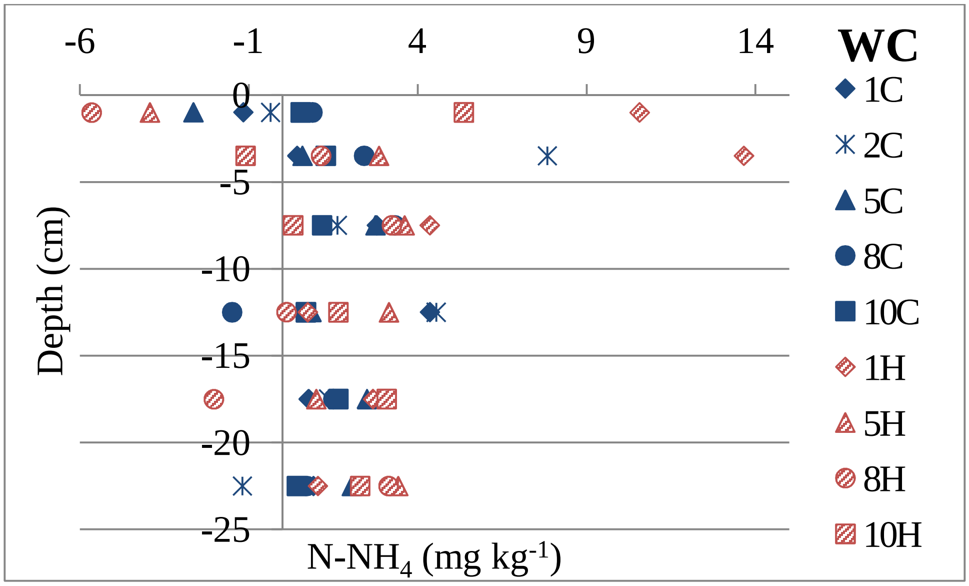
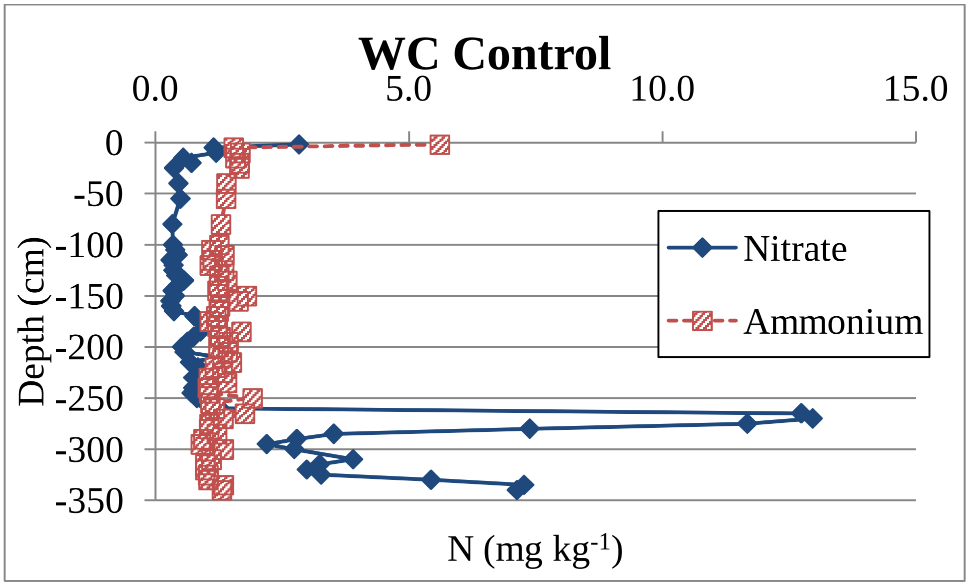
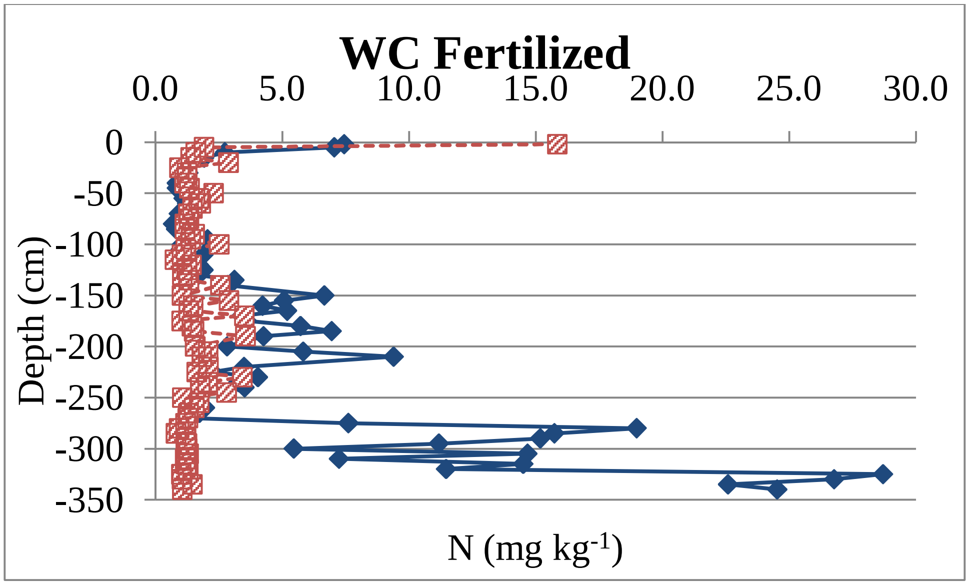
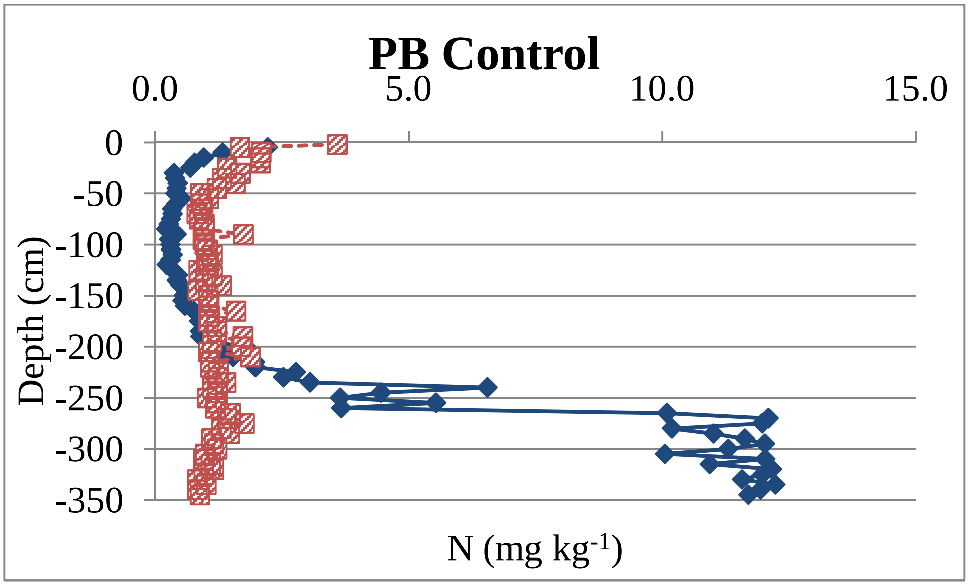
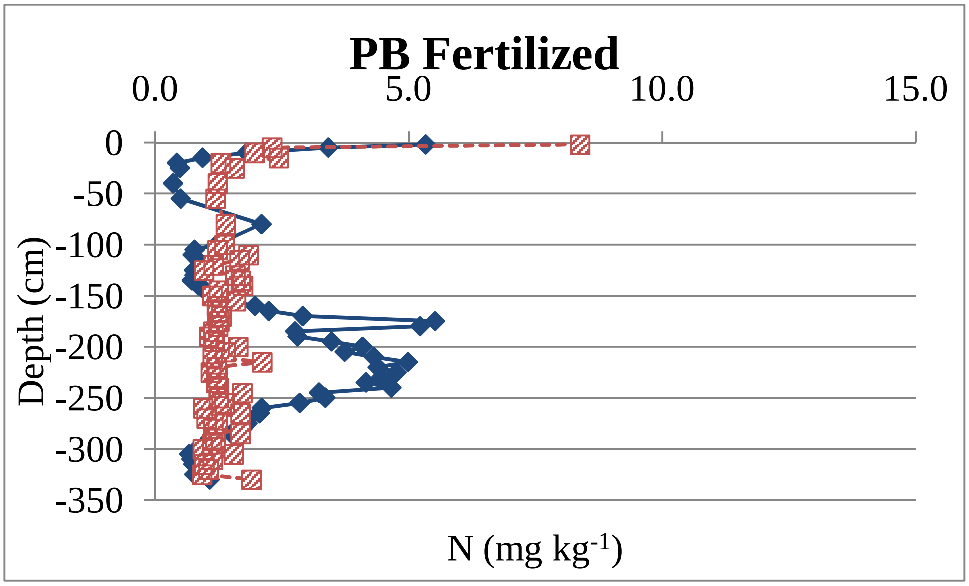


**Figure 3.9** $NO_3$ and $NH_4$ measurements in deep cores taken in a control plot and a fertilized plot at both WC and PB in Fall 2010.






PB Control
0.0
5.0
10.0
15.0
0
-50
-100
-150
-200
-250
-300
-350
Depth (cm)
N (mg kg-1)


PB Fertilized
0.0
5.0
10.0
15.0
0
-50
-100
-150
-200
-250
-300
-350
Depth (cm)
N (mg kg-1)

## General Conclusions

The research discussed in this dissertation underscores the critical role of the hydrological cycle in determining the availability of nitrogen to plants in arid ecosystems. Chapter 2 highlighted limitations in the applicability of hydrological models developed for agricultural soils to desert soils when estimating liquid water flow at moderate potentials during the growing season. The van Genuchten-Mualem (VGM) model, which is not accurate at very low water contents, most likely underestimated the amount of water required to raise the water potential from highly negative summer values at the beginning of the growing season. This was hypothesized to result in an overestimation by the HYDRUS model of the amount of water removal necessary to cause potentials measured by the sensors to decline below the measureable range. Rainwater remaining in the soil at the end of the growing season is likely lost slowly at very low potentials during the summer, as was indicated by neutron probe measurements. The resulting inability of the VGM model to simulate water flow in the moderately wet range during the winter demonstrates the impact of water loss during the summer at very low potentials on the overall water flow in deserts.

A significant proportion of winter rainwater remaining during the summer at very low potentials may also affect predictions for the desert nitrogen cycle. A smaller proportion of rainwater available for uptake by plants during the growing season would presumably result in a smaller proportion of nutrients dissolved in that water being available for uptake. Determining specifically how water is removed from the soil at low potentials during the summer may help clarify why a substantial proportion of $NO_3$ remained in the soils of Pinto Basin and Wide Canyon throughout the summer and why $NO_3$ has accumulated in the deep root zones of deserts throughout the Holocene.

Chapter 3 was focused on the analysis of how $NO_3$ measurements taken throughout the top 100cm of the soil at two desert sites varied with precipitation. The anthropogenic deposition of $NO_3$ during the summer was determined to have a negligible effect on an annual basis since the increase in $NO_3$ following the first precipitation indicated a rapid production of $NO_3$ that dwarfs deposition estimates. The greater increase of $NO_3$ in fertilized plots relative to unfertilized plots after the first rains implied that some N from fertilizer that was assimilated in previous years was being mineralized. This shows the potential for deposited N to accumulate, since greater N availability resulting from greater N uptake in previous years could be supplemented by continued deposition.

Leaching with subsequent rains appeared to limit the potential for uptake of the $NO_3$ by short-rooted annual plants. With later rain events not observed to produce the rapid increases in $NO_3$ that followed the first, leaching was assessed to most likely be a major factor in N limitation among desert annuals. This was ascertained to result in an important role for deep-rooted desert shrubs in maintaining the availability of $NO_3$ in the root zones of the annuals since the uptake of deep $NO_3$ can restore it to the surface with later mineralization. However, $NO_3$ leached below the root zones of the annual plants was not taken up entirely by the creosote bushes, which was observed in the maintenance of higher $NO_3$ measurements in the fertilized plots than the unfertilized plots throughout the summer. It was not clear if this resulted from substantial water left in the soil at low potential during the summer or if the fertilized creosote bushes are experiencing some symptoms of N saturation. Based on consistently higher concentrations of $NO_3$ measured to 230cm in deep cores taken in fertilized plots, a significant amount of N from fertilizer appears to be lost to the desert nitrogen cycle and may ultimately accumulate in the deep root zone. If the observed loss of $NO_3$ deep into the root zone occurs naturally in sandy arid soils, it would be expected to exacerbate N limitation in deserts by necessitating sufficient deposition or N-fixation to balance leached $NO_3$. The strong dependence of $NO_3$ availability to annual plants on precipitation is likely to result in the desert N cycle being highly susceptible to disruption by climate change. How the N cycle is being altered by climate change, as well as by the spread of invasive species and the deposition of anthropogenic N, requires further study.

The analysis of $NH_4$ measurements was the focus of Chapter 4, with a primary emphasis on the role $NH_4$ may play in providing N to annual plants. $NH_4$ appeared to adsorb to the desert soils at the study sites more strongly than literature estimates suggest. The reasons for the relatively strong adsorption were unclear and further tests are needed, but the adsorption was hypothesized to increase the opportunity for uptake by annual plants by slowing leaching. With the leaching of $NO_3$ from root zones of annual plants likely a major factor in N limitation, $NH_4$ is likely very important to maintaining N available for plant uptake in the upper soil. The inhibition of leaching may cause a higher proportion of deposited $NH_4$ to contribute to the long term accumulation of N in the biomass and organic matter relative to deposited $NO_3$.

With the complexity of the role of $NH_4$ in the N cycle, drawing conclusions from measured $NH_4$ concentrations is difficult. The lack of a significant difference in $NH_4$ concentration between the fertilized and unfertilized plots observed below the top 25cm indicated that the $NH_4$ from the fertilizer did not leach deep into the soil. The disappearance of $NH_4$ from the fertilizer after the rains in January 2010 likely resulted from loss through nitrification followed by leaching of $NO_3$, volatilization, or uptake by plants and microorganisms. Although fertilized soils remained elevated relative to unfertilized soils in the spring of 2010, fertilizer added in December 2009 did not cause a further increase in $NH_4$ relative to the previous summer, which suggests that the timing and amount of precipitation may be a factor in how much fertilizer remains in the soil.

Although further research is necessary to understand the intricacies of the hydrological and nitrogen cycles in desert soils, this research illustrated some important connections between them. Expanding the understanding of the hydrological cycle in desert soils is critical for improving comprehension of the nitrogen cycle, which can influence the fire cycle and shifts in species composition in desert ecosystems. With anthropogenic N deposition affecting diverse ecosystems throughout the world, increasing the available knowledge of the N cycle will be critical to understanding and mitigating the consequences.