This is to certify that the
dissertation entitled

CHANGES IN MAJOR SOLUTE CHEMISTRY AS WATER INFILTRATES SOILS: COMPARISONS BETWEEN MANAGED AGROECOSYSTEMS AND UNMANAGED VEGETATION

presented by

AMANDA LORD KURZMAN

has been accepted towards fulfillment
of the requirements for the

Ph.D. degree in ZOOLOGY

Stephen K Hamilton
Major Professor's Signature

AUGUST 23, 2006
Date

CHANGES IN MAJOR SOLUTE CHEMISTRY AS WATER INFILTRATES SOILS: COMPARISONS BETWEEN MANAGED AGROECOSYSTEMS AND UNMANAGED VEGETATION

VOLUME I

By

Amanda Lord Kurzman

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Zoology

2006

CH
SOI

soils o

tensior

Long T

plantat

agrono

S

calcium

Early a

poplar

Agricul

precipi

S

(organi

row crc

concen

inputs c

ABSTRACT

CHANGES IN MAJOR SOLUTE CHEMISTRY AS WATER INFILTRATES SOILS: COMPARISONS BETWEEN MANAGED AGROECOSYSTEMS AND UNMANAGED VEGETATION

By

Amanda Lord Kurzman

This study examined chemical changes in water residing in sandy loam soils on glacial drift. Soil solutions were collected over several years from tension samplers beneath 10 treatments at the Kellogg Biological Station's Long Term Ecological Research site, including deciduous forest, conifer plantations, successional ecosystems, and row crops under varying intensity of agronomic management.

Soil solutions were enriched in solutes relative to precipitation. Nitrate, calcium, magnesium, and alkalinity differed most markedly among treatments. Early and late successional communities as well as a rapidly growing perennial poplar plantation had ionically dilute solutions with low nitrate concentrations. Agricultural treatments were significantly enriched in major solutes relative to precipitation.

Soil solution concentrations of nitrate indicated that the zero input (organic) row-crop treatment had lower potential nitrate leaching than the other row crop treatments. The no-till treatment had the next lowest nitrate concentrations, but had high variance in concentrations, perhaps due to its high inputs of nitrogen.

L

correla

to the

cations

pollutio

soil thr

soils b

by agr

can eit

pH. Sc

row-cro

dioxide

0.63), s

dissolu

balance

collecte

Losses of calcium and magnesium were significantly and positively correlated with nitrate (r = 0.9 and 0.8, respectively) across treatments, pointing to the importance of nitrification as a source of protons that release divalent cations from the soil exchange complex. This in turn causes both the potential pollution of ground and surface waters and the concomitant degradation of the soil through the loss of important macronutrients.

Native carbonate minerals are absent from the upper 1-1.5 m of these soils but are abundant at depth. Liming is necessary to counteract acidification by agriculture. Carbonate minerals, whether native or as lime amendments, can either release or sequester carbon dioxide as they dissolve, depending on pH. Soil solution chemistry suggests that dissolution of lime in the agricultural row-crop treatments results in the net release of carbon in the form of carbon dioxide. This release was strongly and positively correlated with nitrate (r = 0.63), suggesting that biological nitrification is an important control on lime dissolution and thus carbon sequestration or release. However the overall C balance of liming could not be determined from this study because the samplers collected matric water as well as water infiltrating by gravity flow.

For my
and wh

And for
world ri

DEDICATION

For my mom, Margaret Lord Kurzman, Ph.D., whose love has marked my soul and whose curiosity has lit my way.

And for my husband, Steve, whose passion for life and for me has made my world richer, happier, and immeasurably more interesting.

Birds flying high, you know how I feel
Sun in the sky, you know how I feel
Breeze drifting on by, you know how I feel
It's a new dawn, it's a new day
It's a new life for me,
And I'm feeling good . . .

"Feeling good"
Written by: Leslie Bricusse
and Anthony Newley

ACKNOWLEDGEMENTS

I am grateful for the encouragement of many friends: Sara Young, Janet Green, and Annie Watters; Tom and Mary; Daryl and Simone; and my friend Jennifer Bigelow who stubbornly refuses to accept anything but the best from me. Thanks also to my siblings and to my cousin, Gail Johnson, whose wisdom and clarity somehow gave me strength at a time when I both needed it and couldn't find it elsewhere. I'd like to acknowledge my father, Stanley Warren Kurzman, whose commitment to education in my youth provided me with a solid foundation for future academic growth. Thanks also to my co-workers, supervisors, managers, directors, and executive directors at General Motors who supported my academic efforts: Sharon Sawyer, Jeff Jatczak, Joe Toth, Dawn Cleary, Dave Stroup, Ray Tessier, and Dave Skiven. I appreciated the support of my committee members: Dr. Kay Gross, Dr. Phil Robertson, Dr. Nathaniel Ostrom, and the hard work of David Weed, our Lab Manager. Thanks also to Suzanne Sippel, whose company, cooking, and data managerial skills I have enjoyed and benefited from! To all the KBS Graduate Students, Faculty, and Post-Docs whose acts of kindness and words of encouragement have sustained me over the years, I thank you! Last but not least, I'd like to thank my Major Professor for both challenging me and supporting my efforts: Dr. Stephen K. Hamilton.

TABLE OF CONTENTS

VOLUME I

Co

Cor

Calciu

Magn

Ammo

Sulfate

Sum

Succ

pH (SF

Condu

Calciu

Magne

Sodiur

Chloric

Ammo

Nitrate

Pot

Sul

Silic

Tota

S

C

pH..

Sodi

Nitra

Potas

Sulfa

Silica

Alkali

Total

Sum

Con

pH (T1

Calciu

Potass

Sulfate

Total D

Silica (

Magne

Chloric

Nitrate

pl

Co

Ca

Mag

Sod

Chlo

Amm

Nitrat

Potas

Sulfat

Silica

Total

Total

Sur

Per

Cond

Calciu

Magne

Sul
Pot
Chl
Nitra
Sod
Silica
Su
Su
Su
pH...
Cond
Calci
Magn
Sodiu
Amm
Nitrat
Potas
Sulfat
Silica
Alkali
Total
Sum
SF vs
SF vs
T5 vs

SF v

Se

In

Con

Decic

Succe

Treat

T2:

T3:

T4:

T5: F

T6:

T7:

Re

Re

Pe

D

Ma

Ref

App

App

VOLUME II

LIST OF TABLES

LIST OF FIGURES

Fig
T6.

Fig
and

Fig
and

Fig
T6.

Fig
org

Fig
(μS

Fig
Tre

Figu
Tre

Figu
Trea

Figu
SF,

Figu
by re

Figu

Figu

Figu

Figu

Figu

Figu

Figu

Figu

Cl

Int

the
ret
dov
thr
to r
sou
con
(NR
for
Coc
IL 6
con
pre

into
gair
as a
and
influ

Chapter 1: Major Solute Chemistry

Introduction

In humid, temperate, glaciated regions like southern Michigan, most of the precipitation that falls infiltrates soils. Most of this water is eventually returned to the atmosphere via evapotranspiration, but some remains to move downward and form groundwater. Precipitation gains solutes in the atmosphere through scavenging of aerosols and dissolution of gases, and these gains tend to reflect regional industrial and other human activity. Precipitation in southwestern Michigan is acidic with a mean pH of 4.45 and a mean specific conductance of 26 μS/cm (25°C)(National Atmospheric Deposition Program (NRSP-3)/National Trends Network means of annual volume-weighted means for 1979-96 from the KBS station (MI26), printed 2 Dec 1997. NADP/NTN Coordination Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.) Rheaume (1990) observed an inverse relation between pH and conductance at a nearby precipitation collection station, which is due to the predominance of strong acid anions (NO_3^- and SO_4^{2-}) in precipitation.

Precipitation that is not lost through evapotranspiration is transformed into groundwater, which is of markedly different ionic composition. Solutes are gained or lost from precipitation as the water migrates through the soil primarily as a function of microbial activity, plant nutrient uptake, chemical weathering, and adsorption of ions to charged soil particles. Agricultural activities can also influence the evolution of precipitation to groundwater through the addition of fert

rem

evo

me

soi

fror

Rhe

of g

to t

abu

Loc

mag

on t

che

drin

agri

obse

Tilm

che

deca

agric

fertilizers and other amendments, the disposal of manure, the planting and removal of vegetation, and physical soil preparation. Because the chemical evolution of precipitation to groundwater is, for the most part, biologically mediated, the transformation is completed primarily in the upper portion of the soil profile, above the C-horizon.

Hydrochemical information on local ground waters is available mainly from analyses of domestic wells and is presented by Allen et al. (1972), Rheaume (1990), and Kehew and Brewer (1992). The major solute chemistry of ground waters in this area differs considerably from that of precipitation due to the influence of mineral weathering and dissolution, and in particular to the abundance of readily soluble carbonate minerals in the glacial till and outwash. Local ground waters can generally be classified as waters of the calcium-magnesium-bicarbonate type with high hardness and alkalinity.

Previous studies have found that agriculture can have profound effects on the composition of groundwater. Agriculturally induced changes in major ion chemistry of groundwater, particularly nitrate, have resulted in degradation of drinking water quality (Fan and Steinberg, 1996) and the discharge of agriculturally impacted groundwater to surface water bodies has resulted in observable ecological effects (Howarth et al., 2000; Böhlke 2002). A review by Tilman et al. (2001) notes that in many areas of the world, the major-element chemical loads of water recharging unconfined aquifers in the last several decades have been dominated by constituents derived directly or indirectly from agricultural management practices and amendments.

Lor

site

ber

che

ove

wo

this

fror

Stu

Bio

is w

fron

high

site

Hap

perr

hold

LTE

the

be a

In this dissertation, I took advantage of the Kellogg Biological Station's Long-Term Ecological Research (LTER) site that includes unmanaged forested sites and managed agroecosystems. Soil solution samples were collected beneath the study sites for four years. Samples were analyzed for major solute chemistry, which could then be related to land cover and management. My overarching hypothesis was that the major solute composition of soil pore water would be determined by surface land cover and management regimes and that this difference in regimes would be reflected in the soil pore waters collected from the study sites.

Study Sites

The study sites are part of the Michigan State University, Kellogg Biological Station (KBS) holdings and are located in southwest Michigan, which is within the eastern portion of the U.S. cornbelt. Soils in this area developed from a mature glacial outwash plain and moraine complex, and are typically high in carbonates and of moderate fertility. The dominant soils of the study sites are Kalamazoo and Oshtemo series, both loamy, mixed, mesic Typic Hapludalfs that tend to be moderately permeable in the upper part and rapidly permeable in the lower part. Detailed maps and descriptions of KBS and its holdings, including soil and vegetation characteristics, are available on the KBS LTER website (http://lter.kbs.msu.edu). Note: From this point forward, when the reader is referred to the KBS LTER website for additional information, it can be assumed that this is the web address unless otherwise noted.

ag

ec

Ec

ra

se

ma

fie

Fig

ser

from

sta

con

from

field

rem

to th

San

the

abc

Of the ten treatments included in this study, six are managed agroecosystems and four are unmanaged successional and forested ecosystems. The 42-ha KBS main experimental site for the Long Term Ecological Research (LTER) program is subdivided into 1-ha plots, in a randomized complete block design of six blocks and seven treatments. The seven treatments include four managed annual cropping systems; two managed perennial cropping systems; and one unmanaged successional old-field community. The KBS LTER main experimental site layout is depicted in Figure 1. Treatment details are summarized in Table 1.

Located within 5 km of the main experimental site on the same soil series are three additional unmanaged forested treatments that range in age from 40 to >60 years old, each replicated three times. The deciduous forest stands include two old-growth and one 40-60 year post-cutting stand; the coniferous forest treatments include three conifer plantations ranging in age from 40-60 years old; the successional forest treatment consists of three old-field sites that were abandoned over 40 years ago, of which treatment SF-1 remains more sparsely wooded. The locations of these treatment plots relative to the main experimental site are identified in Figure 2.

Sampling and Analytical Methods

Lysimeters

Low-tension soil-solution samplers (lysimeters) were installed beneath the KBS LTER site in 1995, near or just within the top of the C-horizon and above the depth of indigenous soil carbonates. Within the study sites, the transition from the B- to the C-horizon is located approximately 1 – 1.2 m below ground surface. One collector was installed in each of three replicates of each treatment. Each collector draws from a tube that branches underground to three separate samplers spaced a few meters apart. The samplers were located near the edge of treatment plots for ease of access. A full description of the installation protocol is available from the KBS LTER website.

The low-tension soil solution samplers were purchased from Prenart Equipment ApS (www.prenart.dk). The samplers are constructed of stainless steel, porous Teflon (PTFE), and silica flour. Figure 3 depicts a typical soil solution sampling set up that is also representative of the equipment set up at the KBS LTER Study Sites.

From 1999 through 2003, samples were collected on a periodic basis from the soil-solution samplers from March through December as dictated by precipitation and soil frost levels. Suction (-0.5 atm) was applied to each collector and the resulting solution collected in Erlenmeyer flasks over a 24-hour period. A description of the soil-solution sample collection method is available from the KBS LTER website.

These soil-solution samplers yield samples that can be studied to indicate soil processes, but the samples are not necessarily representative of waters infiltrating downward via saturated flow towards the ground water. This is because the soil solutions are collected by suction, and thus they represent variable proportions of saturated flow and matric water (Lajtha *et al.* 1999). As soil water content diminishes, a greater fraction of the sample will be matric water. Very dry soils do not yield any water. An approximate indicator of soil water status at the time of sampling comes from the dilution factors; dilution was necessary when sample volumes fell below a certain threshold (discussed later).

Water Analyses

All samples collected during the study were put on ice following collection. Upon return to the lab, samples were refrigerated (alkalinity, conductance) or filtered through Gelman Supor 0.45-µm membrane filters and then refrigerated (anions, silica) or acidified with 8 N HNO_3 (cations) until analysis.

Conductance was measured in the lab using an Orion model 135 conductance meter (Analytical Technology, Inc.). The pH of unfiltered samples was measured in the laboratory within a few days of collection and therefore should be closer to the solution pH at atmospheric equilibrium because most of the excess dissolved CO_2 that is typical of soil solutions would have escaped. Ca^{2+}, Mg^{2+}, Na^+, and K^+ were measured by flame atomic absorption spectrometry, with addition of lanthanum before Ca^{2+} and Mg^{2+} measurement to suppress interferences. Total alkalinity, which generally represents HCO_3^- in these waters, was determined by titration with 0.3 N HCl between pH 4.0 and 3.3 and calculation of the Gran function (Cantrell et al. 1993). SO_4^{2-}, Cl^-, and NO_3^- were measured by membrane suppression ion chromatography. Si was measured colorimetrically by the ammonium molybdate method (Wetzel and Likens 2000).

Other nutrients were measured for samples collected between March 1999 and November 2000. NH_4^+ was measured colorimetrically following an adapted version of the phenylhypochlorite method (Aminot et al. 1997). Total Dissolved Phosphorus (TDP) was measured following persulfate digestion, using the acid molybdate colorimetric method (Wetzel and Likens 2000).

On occasion, small sample size prohibited analysis of conductance, pH and silicate. During times of lower soil water content, dilution with deionized water was frequently necessary to obtain enough volume (250 mL) to conduct all the analyses.

Statistical Analyses

All statistical analyses were done using SYSTAT version 8.0 (SPSS Inc. 1998) on a PC with a Windows ME operating system.

NADP/NTN Precipitation Data

Precipitation data, including water volumes and major ion concentrations, were obtained from the National Atmospheric Deposition Program/National Trends Network for the period of this study. Data can be obtained from the website http://nadp.sws.uiuc.edu, for Station MI26, Kellogg Biological Station, Kalamazoo County, Michigan. Seasons are defined under the NADP/NTN program as follows (month/day): Winter 12/1 – 3/1; Spring 3/1 – 6/1; Summer 6/1 – 9/1; and Fall 9/1 – 12/1.

Agronomic Inputs

In addition to evaluating the effect of tillage practices, variation in the nature and quantity of soil amendments was incorporated into the agronomic treatment design (Table 2). Treatments 1 and 2 are conventional “high input” treatments (e.g., fertilizers, pesticides), while Treatment 3 is managed as “reduced input” and Treatment 4 is managed as ”zero input”. Treatments 1, 2, 3, and 6 received dolomitic lime ($CaMg(CO_3)_2$) applications in 1999, and Treatments 1, 2, and 3 were fertilized each year in April or May (with the exception of 2000) with an ammonium nitrate solution. Ammonium sulfate was added to Treatment 1 in 2001, to Treatment 2 in 2000, 2001, and 2003, but not to Treatment 3 during the study period. Potash (KCl) was applied to Treatments 1, 2, and 3 in April 2002 and to Treatments 1 and 2 in April 2003. Treatment 7 did not receive any amendments, but surface vegetation was burned in May 2002 and again in April 2003 to discourage woody plant colonization. Agronomic field logs containing detailed descriptions of LTER Main Site activities can be obtained by visiting the KBS LTER Website. A summary of the major ions and elements added by treatment is provided in Table 3.

Quality Assurance

The data were examined extensively to identify and eliminate any errors or quality problems.

First, where the complete suite of major cation and anion analytical data was available, which was the case for nearly all samples, charge balances were calculated using the software AquaChem, Version 3.7 for Windows 95/98/NT, Waterloo Hydrogeologic, Inc., Waterloo, Canada. Charge balances were also calculated in Microsoft Excel for samples. Excellent agreement between the two methods was obtained, and minor differences can be accounted for by the fact that Aquachem accounts for ion base pairing while the spreadsheet does not (Figure 5, Top).

Second, theoretical conductance was compared to measured conductance. Theoretical conductance was calculated by determining the expected contribution of each ion to the conductance by multiplying the ionic conductance per meq by the concentration in meq/L of the sample (Golterman and Clymo, 1969) (Table 4 and Figure 5, Middle).

Third, time series were graphed for each analyte by replicate. Outliers were scrutinized to determine if an apparent analytical or data entry error had occurred.

Fourth, specific hypotheses were examined to determine whether or not certain factors were responsible for and/or correlated with percent ion difference. The factors ruled out in this examination included unusually dry soils as indicated by drought indices or by sample dilution, particularly low or high total ion content as indicated by conductance (Figure 5, Bottom), sample site, and sample date.

After reviewing outliers and correcting any analytical or data entry errors identified, 201 samples (17%) remain that have a charge imbalance greater than 20%. 45% come from the forested sites, which comprise less than 30% of the samples (Figure 6, Top).

Overall, the analyses of soil solution samples tend to indicate more anions than cations, indicating a possible unmeasured cation component if we assume that the other ion measurements are accurate (Figure 6, Bottom). I believe that the measurements I report here are sufficiently accurate that analytical errors cannot explain such large charge imbalances. One possible unmeasured cation that could result in a significant imbalance was identified: Positively charged aluminum hydroxy ions whose contribution to the cation exchange complex varies with pH (Figure 7). If positively charged aluminum hydroxy ions were partially responsible for the ion imbalance, one would expect that in treatments whose pH range was lower over the study period, percent ion differences would show no correlation with pH; however, for treatments where the range of pH was higher and crossed a certain pH threshold (the threshold where exchangeable aluminum hydroxy ions are converted to bound aluminum), then a negative correlation between pH and the percent ion difference would be expected. In these latter cases, as pH increases, the percent ion difference would decrease because unmeasured, exchangeable, positively charged aluminum hydroxy ions would make up less and less of the exchangeable ion pool. In fact, these expected relationships are present in the data set. Agronomic treatments exhibiting a higher mean pH have fewer samples with a > 20 percent ion difference (Figure 6, Top). When plotted, the number of samples exhibiting a > 20 percent ion difference decreases with increasing pH (Figure 8). In addition, there are significant negative correlations within treatments between pH and percent ion difference in those treatments where the range of pH is greatest (Figures 9 and 10).

Another line of evidence that supports the hypothesis that aluminum hydroxy ions are responsible for the observed charge imbalance comes from examining the ion imbalance of Replicates T2-R3 and T4-R3. These are the only replicates within the data set with pH above 8.0. If unmeasured aluminum hydroxy ions which are present at a pH below 8.0 are responsible for the imbalances, we would expect these two replicates with a pH above 8.0 to have the lowest median percent ion difference values of all replicates within the entire data set, In fact, this is this case. The median percent ion difference in Replicates T2-R3 and T4-R3 is -0.79% and -0.97%, respectively.

In the unmanaged treatments, it is possible that the decomposition of leaf litter in the absence of liming is contributing organic acids to the soil solution and thereby lowering soil pH and favoring the ionized aluminum form. However, the carboxylic acid groups on unmeasured organic acids would contribute to the charge imbalance in the opposite direction, thus potentially compensating partly for any unmeasured contribution of aluminum.

Results

Precipitation

During the study period of 1999-2003, the mean annual precipitation was 72.5 cm/year. The long-term mean (1942-96) annual precipitation for stations in the vicinity of KBS is 92 cm (Hamilton, unpublished data). The pattern of precipitation during the study period is depicted in Figure 9, Top. 2000 was the driest year (47.4 cm), primarily due to unusually low precipitation during the spring and summer seasons when only 12.1 cm fell. In contrast, the average precipitation for the other four years during the spring and summer seasons was 44.2 cm (Figure 10, Bottom).

Over the study period, the average annual pH of precipitation was 4.6. The dominant cation was ammonium with an annual volume-weighted mean concentration of 26.0 μeq/L, followed by H^+ and Ca^{2+}. The dominant anion was sulfate, with an annual volume-weighted mean concentration of 37.1 μeq/L, followed by nitrate (Figure 11).

Soil Solution Chemistry

Major solute chemistry is summarized in Table 5. Due to the high level of seasonal variability and the tendency for skewed frequency distributions, medians and interquartile ranges are reported to summarize and compare the frequency distributions of major solute concentrations. A pair-wise Pearson Correlation Matrix with associated Bonferroni-corrected probabilities for each of the variables, based on data from all treatments combined, is provided in Table 6.

In this section, I compare data distributions across treatments using notched box plots. The box plots provide a convenient and compact summary of asymmetric frequency distributions that includes medians and quartiles. The notches indicate the approximate 95% confidence intervals around the median and the boxes extend across the interquartile range (i.e., from the 25^{th} to 75^{th}

percentiles). Units of concentration were presented as mg/L in Table 5, but in the figures appearing hereafter, ion concentrations are converted to meq/L to facilitate intercomparisons of the relative importance of the various ionic species.

pH

The Coniferous Forest Treatment (CF) exhibited the lowest median air-equilibrated pH at 6.05, but was only slightly lower than the Deciduous Forest Treatment (DF) with a median air-equilibrated pH of 6.07 (Table 5 and Figure 12, Top). The Conventional Input, No-Till Treatment (T2) had the highest median air-equilibrated pH at 7.59.

Combining hydrochemical data across all treatments, pH was significantly ($p<0.001$) and positively correlated with alkalinity, calcium, magnesium, potassium, silica, and conductance, and significantly and negatively correlated with sulfate (Table 6). The strongest correlation was associated with alkalinity ($r = 0.63$) and the weakest, yet still significant correlation was with potassium ($r = 0.16$). There was no overall correlation between pH and nitrate.

Conductance

The Successional Forest Treatment (SF) had the lowest median value for specific conductance (41 µS/cm @ 25°C) (Table 5 and Figure 12, Bottom). The Perennial Alfalfa Treatment (T6) had the highest median specific conductance at 249.

Across all treatments combined, conductance was significantly ($p<0.001$) and positively correlated with pH, silica, alkalinity, calcium, magnesium, sodium, potassium, chloride, and nitrate, and significantly and negatively correlated with sulfate (Table 6). The strongest correlation was with calcium ($r = 0.96$) and the weakest, yet still significant correlation was with sulfate ($r = -0.30$).

Calcium

The Successional Forest Treatment (SF) exhibited the lowest median calcium concentration, 4.32 mg/L (0.216 meq/L) (Table 5 and Figure 13, Top). The highest median concentration, 34.33 mg/L (1.713 meq/L), was found in the Perennial Alfalfa Treatment (T6).

Across all treatments combined, calcium was significantly ($p<0.001$) and positively correlated with conductance, pH, silica, alkalinity, magnesium, sodium, potassium, chloride, and nitrate, and was significantly ($p<0.001$) and negatively correlated with sulfate (Table 6). The strongest correlation was with conductance ($r = 0.96$) and the weakest, yet still significant correlation was with potassium ($r = 0.23$).

Magnesium

Median concentrations for magnesium ranged from a low of 0.98 mg/L (0.081 meq/L) in the Successional Forest Treatment (SF) to a high of 7.00 mg/L (0.576 meq/L) in the Perennial Alfalfa Treatment (T6) (Table 5 and Figure 13, Top). Magnesium concentrations were lower than those of calcium.

Across all treatments combined, magnesium was significantly ($p<0.001$) and positively correlated with conductance, pH, silica, alkalinity, calcium, sodium, chloride, and nitrate, and significantly and negatively correlated with sulfate (Table 6). The strongest correlation was with calcium (r = 0.85) and the weakest, yet still significant correlation was with sulfate (r = -0.22).

Alkalinity

The Deciduous Forest Treatment (DF) exhibited the lowest median total alkalinity concentration, 10.15 mg HCO_3^-/L (0.167 meq/L) (Table 5 and Figure 14, Top). The highest median concentration, 56.36 mg HCO_3^-/L (0.924 meq/L), was found in the Conventional Input, No-Till Treatment (T2).

Across all treatments combined, alkalinity was significantly ($p<0.001$) and positively correlated with conductance, pH, silica, calcium, magnesium, and sodium, and significantly and negatively correlated with sulfate (Table 6). The strongest correlation was with magnesium (r = 0.72) and the weakest, yet still significant correlation was with sulfate (r = -0.21).

Sulfate

Median concentrations for sulfate ranged from a low of 4.21 mg/L (0.088 meq/L) in the Perennial Alfalfa Treatment (T6) to a high of 17.65 mg/L (0.367 meq/L) in the Perennial Poplar Treatment (T5) (Table 5 and Figure 14, Bottom). Across all treatments combined, sulfate was negatively and significantly ($p<0.001$) correlated with conductance, pH, alkalinity, calcium, magnesium, potassium, chloride, and nitrate (Table 6). The strongest correlation was with pH (r = -0.33) and the weakest, yet still significant correlation was with chloride (r = -0.21).

Potassium

Median concentrations for potassium ranged from a low of 0.23 mg/L (0.01 meq/L) in the Successional Forest Treatment (SF) to a high of 5.44 and 5.45 mg/L (0.139 and 0.139 meq/L) in the Reduced Input, Conventional Till (T3) and Conventional Input, Conventional Till (T1) Treatments, respectively (Table 5 and Figure 15, Top).

Across all treatments combined, potassium was significantly ($p<0.001$) and positively correlated with conductance, pH, calcium, chloride, and nitrate, and negatively and significantly ($p<0.001$) correlated with silica and sulfate (Table 6). The strongest correlation was with nitrate ($r = 0.42$) and the weakest, yet still significant correlation was with pH ($r = 0.16$).

Chloride

Median concentrations for chloride ranged from a low of 0.49 mg/L (0.014 meq/L) in the Successional Forest Treatment (SF) to a high of 1.89 mg/L (0.053 meq/L) in the Perennial Alfalfa Treatment (T6) (Table 5 and Figure 15, Bottom).

Across all treatments combined, chloride was significantly ($p<0.001$) and positively correlated with conductance, calcium, magnesium, sodium, potassium, and nitrate, and significantly and negatively correlated with sulfate (Table 6). The strongest correlation was with nitrate ($r = 0.60$) and the weakest, yet still significant correlation was with sulfate ($r = -0.21$).

Ammonium-N

Median concentrations of Ammonium-N ranged from a low of 0.009 mg/L (0.001 meq/L) in the Reduced Input, Conventional Till Treatment (T3) and the

Reduced Input, Organic Treatment (T4), to a high of 0.040 mg/L (0.002 meq/L) in the Deciduous Forest Treatment (DF), closely followed by the Successional Forest Treatment (SF)(Table 5 and Figure 16, Top).

Across all treatments combined, ammonium was significantly ($p<0.001$) and positively correlated with total dissolved phosphorus ($r = 0.60$) and, albeit more weakly, with sodium ($r = 0.29$) (Table 6).

Nitrate-N

Median concentrations for nitrate ranged from a low of 0.00 mg N/L (0.00 meq N/L) in the Perennial Poplar Treatment (T5) to a high of 16.00 mg N/L (1.142 meq N/L) in the Perennial Alfalfa Treatment (T6)(Table 5 and Figure 16, Bottom). Agricultural treatments (T1-T4 and T6) had markedly higher concentrations than the forested and successional field treatments. The analytical detection limit of the ion chromatography system was ~0.015 mg/L.

Across all treatments combined, nitrate was significantly ($p<0.001$) and positively correlated with conductance, calcium, magnesium, sodium, potassium, and chloride, and significantly and negatively correlated with sulfate (Table 6). The strongest correlation was with conductance ($r = 0.75$) and the weakest, yet still significant correlation was with sulfate ($r = -0.30$).

Dissolved Organic Carbon (DOC)

The Perennial Poplar Treatment (T5) exhibited the lowest median concentration for DOC, 2.29 mg C/L, and the Coniferous Forest Treatment (CF) exhibited the highest median concentration, 4.46 mg C/L (Table 5 and Figure 17, Top). The CF treatment also had the largest interquartile range by far, although occasional samples with elevated DOC concentrations were found in most treatments.

Across all treatments combined, dissolved organic carbon was not significantly correlated with any other variable (Table 6).

Total Dissolved Phosphorus (TDP)

Median concentrations for TDP ranged from a low of 0.007 mg/L in the Deciduous Forest Treatment (DF) to a high of 0.048 in the Conventional Input, No-Till Treatment (T2), which also showed a particularly large interquartile range (Table 5 and Figure 17, Bottom). The forested treatments CF, DF, SF, and T5 tended to be lower in TDP concentrations.

Across all treatments combined, total dissolved phosphorus was significantly ($p<0.001$) and positively correlated with sodium ($r = 0.26$) and ammonium ($r = 0.60$) (Table 6).

Sodium

Median concentrations for sodium ranged from a low of 1.31 mg/L (0.057 meq/L) in the Successional Forest Treatment (SF) to highs of 2.13 and 2.14 mg/L (0.093 and 0.093 meq/L) in the Perennial Alfalfa Treatment (T6) and the Coniferous Forest Treatment (CF), respectively (Table 5, and Figure 18, Top).

Across all treatments combined, sodium was positively and significantly ($p<0.001$) correlated with conductance, total dissolved phosphorus, silica, calcium, potassium, ammonium, chloride, and nitrate (Table 6). The strongest correlation was with conductance ($r = 0.48$) and the weakest, yet still significant correlation was with potassium ($r = 0.25$).

Silica

Median concentrations for silica ranged from a low of 4.57 mg Si/L in the Successional Field Treatment (T7) to a high of 9.58 mg Si/L in the Coniferous Forest Treatment (CF) (Table 5 and Figure 18, Bottom).

Across all treatments combined, silica was significantly ($p<0.001$) and positively correlated with alkalinity, calcium, magnesium, sodium, conductance, and pH, and negatively and significantly correlated with potassium (Table 6). The strongest correlation was with alkalinity ($r = 0.62$) and the weakest, yet still significant correlation was with potassium ($r = -0.17$).

Comparisons of Frequency Distributions among Treatments

Comparisons between treatment pairs presented here are those for which I expected to see contrasts based on vegetation cover and agronomic practices. The notched box plots are explained at the beginning of the previous section. Note: A Summary of Observed Patterns is provided at the end of each treatment comparison section.

Coniferous Forest versus Deciduous Forest Treatments

The Coniferous and Deciduous Forest Treatments are unmanaged treatments that are located in close proximity to each other on similar soils that are presumed to vary only in vegetative cover.

Most major solutes were elevated in the forest treatments compared to concentrations in precipitation; only ammonium and H^+ (as indicated by pH) showed the converse trend. No significant differences between the Coniferous

Forest and Deciduous Forest Treatments were identified for pH, conductance, nitrate, chloride, potassium, sodium, alkalinity, dissolved organic carbon, total dissolved phosphorus, or silica. Concentrations of sulfate, ammonium, magnesium, and calcium differed significantly between treatments (Figures 19-25). The variables with significant overall differences are discussed below, and in those cases I also consider the variability among replicates within treatments.

Calcium (CF vs. DF)

The median soil solution concentration of calcium in the CF Treatment was significantly higher than in the DF Treatment (Figure 20, Top). The median concentration of calcium in the CF Treatment was 11.70 mg/L (0.59 meq/L) and the median concentration in the DF Treatment was 7.37 mg/L (0.37 meq/L) (Table 5).

With respect to individual replicates, the median concentrations for the three CF replicates were significantly different from each other and the three DF replicates were significantly different from each other (Figure 26, Top). DF-R1 and CF-R2 were not significantly different from each other; DF-R3 and CF-R1 were not significantly different from each other; DF-R2 was significantly different from all other replicates (CF and DF); and CF-R3 was significantly different from all other replicates (CF and DF). Variability among replicates within treatments was thus higher than variability between treatments.

Magnesium (CF vs. DF)

The median soil solution concentration of magnesium in the DF Treatment was significantly higher than the CF Treatment (Figure 20, Bottom). The median soil solution concentration of magnesium in the CF Treatment was 1.78 mg/L (0.15 meq/L) and the median concentration in the DF Treatment was 3.42 mg/L (0.28 meq/L) (Table 5).

With respect to individual replicates, none of the CF replicates were significantly different from each other. DF-R2 was significantly different from DF-R1 and DF-R3, but not significantly different from any of the CF replicates (Figure 26, Bottom).

Ammonium-N (CF vs. DF)

The median soil solution concentration of ammonium in the DF Treatment was significantly higher than the CF Treatment (Figure 22, Top). The median soil solution concentration of ammonium in the CF Treatment was 0.021 mg-N/L (0.001 meq/L) and the median concentration in the DF Treatment was 0.040 mg-N/L (0.002 meq/L) (Table 5).

With respect to individual replicates, none of the DF replicates was significantly different from the others. CF-R1 was significantly different from CF-R2 and CF-R3, but not significantly different from any of the DF replicates (Figure 27, Top).

Sulfate (CF vs. DF)

The median soil solution concentration of sulfate was significantly different and lower in the Deciduous Forest (DF) than in the Coniferous Forest (CF) treatment (Figure 23, Bottom). The median soil solution concentration was 17.35 mg/L (0.36 meq/L) in the CF Treatment and 13.69 mg/L (0.29 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, all replicates within the Deciduous Forest Treatment (DF) were significantly different from each other, although DF-R3 was not significantly different from CF-R1, CF-R2, and CF-R3. DF-R2 evidently explains much of the difference in overall medians for DF vs. CF. CF-R1, CF-R2, and CF-R3 were not significantly different from each other (Figure 27, Bottom).

Summary of Observed Patterns (CF versus DF)

Median concentrations of calcium, sulfate, and total dissolved phosphorus were significantly higher in the CF Treatment, while median concentrations of magnesium and ammonium-N were significantly lower (Figures 19 – 25). In the case of calcium, however, variability among replicates within treatments was higher than variability between treatments, and in the case of sulfate, one replicate (DF-R2) appears to be responsible for the observed differences in median concentrations between the two treatments (Figures 26 and 28). Most notable, perhaps, are the ways in which these treatments do not differ, including pH, nitrate-N, and alkalinity.

Successional versus Deciduous Forest Treatments

The Successional and Deciduous Forest Treatments are unmanaged treatments that are located in close proximity to each other on similar soils, and presumably vary only in vegetative cover and age of the stand.

No significant differences between the Successional Forest and Deciduous Forest Treatments were identified for soil solution concentrations of dissolved organic carbon or alkalinity (Figures 19-25).

Soil solution concentrations of pH, conductance, total dissolved phosphorus, silica, calcium, magnesium, sodium, potassium, ammonium, chloride, sulfate, and nitrate differed significantly between treatments (Figures 19-25).

pH (SF vs. DF)

The median soil solution pH in the Successional Forest Treatment (SF) was 6.72 versus the median value for pH in the Deciduous Forest Treatment of 6.07 (Table 5).

Examining individual replicates within each treatment, all replicates within the Deciduous Forest Treatment (DF) were significantly different from each other, although DF-R2 was not significantly different from SF-R1, SF-R2, or SF-R3. SF-R3 was significantly different from the other two SF replicates (Figure 29, Top).

Conductance

The median soil solution conductance was 41 μS/cm @ 25°C in the SF Treatment versus the median conductance of 84 in the DF Treatment (Table 5).

Examining individual replicates within each treatment, all replicates within the DF Treatment were significantly different from each other, although DF-R2 was not significantly different from SF-R1. All replicates within the SF Treatment were highly significantly ($p<0.001$) different from each other (Figure 29, Bottom).

Calcium

The median soil solution concentration of calcium was 7.37 mg/L (0.37 meq/L) in the DF Treatment and 4.32 mg/L (0.22 meq/L) in the SF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly different from the other two DF replicates, but not significantly different from SF-R1 and SF-R3, and SF-R2 was significantly different from and lower than all other replicates (SF and DF) (Figure 30, Top).

Magnesium

The median soil solution concentration of magnesium was 3.42 mg/L (0.28 meq/L) in the DF Treatment and 0.98 mg/L (0.08 meq/L) in the SF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly different from and lower than DF-R1 and DF-R3, and SF-R1 was significantly higher than SF-R2 and SF-R3 (Figure 30, Bottom).

Sodium

The median soil solution concentration of sodium was 2.04 mg/L (0.09 meq/L) in the DF Treatment and 1.31 mg/L (0.06 meq/L) in the SF Treatment (Table 5).

Examining individual replicates within each treatment, none of the SF replicates were significantly different from each other, or from DF-R2. DF-R2 was significantly different from and lower than DF-R1 and DF-R3, which were not significantly different from each other (Figure 31, Top).

Chloride

The median soil solution chloride concentration was 1.48 mg/L (0.04 meq/L) in the DF Treatment and 0.49 mg/L (0.01 meq/L) in the SF Treatment (Table 5).

Examining individual replicates within each treatment, none of the DF replicates were significantly different from each other, and none of the SF replicates were significantly different from each other (Figure 31, Bottom). Thus the DF replicates were consistently higher in chloride than the SF replicates.

Ammonium-N

The median soil solution concentration of ammonium was 0.019 mg N/L (0.001 meq/L) in the SF Treatment versus 0.40 mg N/L (0.002 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, none of the replicates within the DF was significantly different from the others. Within the SF Treatment, SF-R3 was not significantly different from any of the DF replicates, although it was significantly different from SF-R1 and SF-R2 (which were not significantly different from each other) (Figure 32, Top).

Nitrate

The median nitrate concentration in the DF Treatment soil solution was 3.46 mg N/L (0.25 meq/L) and 0.08 mg N/L (0.006 meq/L) in the SF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly different from and far lower than the other two DF replicates, but not significantly different from any of the SF replicates. None of the SF replicates were significantly different from each other (Figure 32, Bottom).

Potassium

The median soil solution concentration of potassium was 0.40 mg/L (0.01 meq/L) in the DF Treatment and 0.23 mg/L (0.006 meq/L) in the SF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly higher than all other replicates (SF and DF). DF-R1 and DF-R3 were not significantly different from each other, and SF-R1 and SF-R2 were not significantly different from each other. SF-R3 was significantly higher than the other two SF replicates, but not significantly different than DF-R1 or DF-R3 (Figure 33, Top).

Sulfate

The median soil solution sulfate concentration was 13.69 mg/L (0.29 meq/L) in the DF Treatment and 8.44 mg/L (0.18 meq/L) in the SF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly different from and lower than the other two DF replicates, but not significantly different from SF-R3. SF-R1 was significantly different from and higher than the other two SF replicates, but not significantly different from DF-R2 (Figure 33, Bottom).

Silica

The median soil solution concentration of silica was 9.08 mg Si/L in the DF Treatment and 6.13 mg Si/L in the SF Treatment (Table 5).

Examining individual replicates within each treatment, all of the replicates within the DF Treatment were significantly different from each other. Within the SF Treatment, SF-R2 and SF-R3 were not significantly different from each other, but SF-R1 was significantly different from both (Figure 34, Top).

Total Dissolved Phosphorus

The median soil solution concentration of total dissolved phosphorus was 0.007 mg/L in the DF Treatment and 0.014 mg/L in the SF Treatment (SF) (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly different from DF-R1 and DF-R3, but not significantly different from SF-R1. DF-R2 also exhibited a much larger interquartile range than any other replicate. DF-R1 and DF-R3 were not significantly different from each other, and SF-R2 and SF-R3 were not significantly different from each other. SF-R1 was significantly different from all other replicates, with the exception of SF-R3 and DF-R2 (Figure 34, Bottom).

Summary of Observed Patterns (DF vs SF)

While both pH and the median concentration of total dissolved phosphorus were significantly lower in the DF Treatment, median concentrations of ammonium-N, calcium, chloride, magnesium, nitrate-N, potassium, silica, sodium, sulfate are all significantly higher in the DF Treatment, and as would then be expected, conductance is also significantly higher in the DF Treatment (Figures 19-25). Most notable among the differences between treatments, the median concentration of nitrate-N in the DF Treatment was 40 times greater than the median concentration of nitrate-N in the SF Treatment, which was only 0.006 meq/L (Table 5, Figure 22, Bottom).

Conventional Till (T1) versus No-Till (T2)

Both the Conventional Till (T1) and the No-Till (T2) received the same amendments at the same time and rate during the study period, with the exception of lime and ammonium sulfate. In 1999, based on recommendations from soil tests, more lime was applied to the No-Till Treatment (T2) than the Conventional Till Treatment (T1), 0.8 tons/acre and 0.5 tons/acre, respectively (Table 2). Ammonium sulfate was applied in the No-Till Treatment (T2) at a rate of 8 lbs/ha in 2000, while no ammonium sulfate was applied to the Conventional Till Treatment (T1) that year.

No significant differences between T1 and T2 were identified for soil solution conductance and concentrations of calcium, dissolved organic carbon, ammonium, or chloride (Figures 35-41).

pH and soil solution concentrations of total dissolved phosphorus, silica, alkalinity, sodium, potassium, sulfate, and nitrate differed significantly between the T1 and T2 treatments (Figures 35-41).

pH

The median air-equilibrated pH was significantly higher in the No-Till Treatment (T2) compared to T1 (Figure 35, Top). The median air-equilibrated pH in the Conventional Till (T1) Treatment was 6.54 and the median air-equilibrated pH in the No-Till Treatment was 7.59 (Table 5). The interquartile range was greater in T1 than in T2.

With respect to variability between individual replicates within each treatment, one replicate within each treatment was significantly different from the other two (Figure 42, Top).

Sodium

The median soil solution concentration of sodium was significantly but not greatly higher in T2 than T1 (Figure 37, Top). The median soil solution concentration of sodium in T1 was 1.58 mg/L (0.07 meq/L), and the median concentration in T2 was 2.00 mg/L (0.09 meq/L) (Table 5). The interquartile range was also greater in T2.

With respect to variability between individual replicates within each treatment, replicate T2-R3 was significantly different from and higher than all other replicates, none of which differed significantly from each other.

Nitrate

The median soil solution concentration of nitrate was significantly higher in T1 than T2 (Figure 38, Bottom). The median soil solution concentration of nitrate in T1 was 11.29 mg N/L (0.81 meq/L), and the median concentration in T2 was 7.25 mg N/L (0.52 meq/L) (Table 5). The interquartile range was greater in T1.

With respect to variability between individual replicates within each treatment, none of the replicates in Treatment T2 differ significantly from each other. In Treatment T1, replicate T1-R3 differs significantly from T1-R2 (Figure 43, Top).

Potassium

The median soil solution concentration of potassium was significantly higher in T1 than T2 (Figure 39, Top). The median soil solution concentration of potassium in T1 was 5.45 mg/L (0.14 meq/L), and the median concentration in T2 was 1.59 mg/L (0.04 meq/L) (Table 5). The interquartile range was also much greater in T1.

With respect to variability between individual replicates within each treatment, one replicate within Treatment T1 was significantly different from the other two, and in Treatment T2, all replicates were significantly different from each other (Figure 43, Bottom).

Sulfate

The median soil solution concentration of sulfate was significantly higher in T1 than T2 (Figure 39, Bottom). The median soil solution concentration of sulfate in T1 was 10.52 mg/L (0.22 meq/L), and the median concentration in T2 was 6.33 mg/L (0.13 meq/L) (Table 5). The interquartile ranges for both treatments were similar.

With respect to variability between individual replicates within each treatment, all replicates in Treatment T2 differed significantly from each other, and in Treatment T1, one replicate was significantly different from the other two (Figure 44, Top).

Silica

The median soil solution concentration of silica was significantly higher in T2 than T1 (Figure 40, Top). The median soil solution concentration of silica in T1 was 4.81 mg Si/L, and the median concentration in T2 was 9.38 mg Si/L (Table 5). The interquartile range was also greater in T2.

With respect to variability between individual replicates within each treatment, one replicate within Treatment T1 was significantly different from the other two. In Treatment T2, all replicates were significantly different from each other (Figure 44, Bottom).

Alkalinity

The median soil solution concentration of total alkalinity was significantly higher in T2 than T1 (Figure 40, Bottom). The median soil solution concentration of alkalinity in T1 was 19.75 mg HCO_3^-/L (0.32 meq /L), and the median concentration in T2 was 56.36 HCO_3^- mg/L (0.92 meq/L) (Table 5). The interquartile range was also much greater in T2.

With respect to variability between individual replicates within each treatment, one replicate within each treatment was significantly different from the other two (Figure 45, Top).

Total Dissolved Phosphorus

The median soil solution concentration of total dissolved phosphorus was significantly higher in T2 than T1 (Figure 41, Top). The median soil solution concentration of total dissolved phosphorus in T1 was 0.024 mg/L, and the median concentration in T2 was 0.048 mg/L. The interquartile range was also greater in T2 than T1 (Table 5).

With respect to variability between individual replicates within each treatment, one replicate within each treatment was significantly different from the other two (Figure 45, Bottom).

Summary of Observed Patterns (T1 vs T2)

pH and median concentrations of total dissolved phosphorus, total alkalinity, silica, and sodium were significantly higher in the No-Till (T2) treatment (Figures 35-41). Median concentrations of nitrate-N, potassium, and sulfate are significantly higher in the Conventional (T1) treatment. Replicate T2-R3 was significantly higher than all other replicates in both treatments for pH, total dissolved phosphorus, silica, alkalinity, sodium and sulfate, and appears to be responsible for the significant differences seen between T1 and T2 for total dissolved phosphorus and sodium (Figures 42-45). In replicate T2-R3, median concentrations of potassium are significantly lower than the other two replicates, and nitrate-N, while not significantly lower than the other two replicates had an overall tendency to be lower as demonstrated by the lower interquartile range (Figure 43, Top). Significantly higher median concentrations of total dissolved phosphorus (Figure 45, Bottom), silica (Figure 44, Bottom), total alkalinity (Figure 45, Top) and pH (Figure 42, Top) were also observed in replicate T1-R4 as compared to T1-R2 and T1-R3.

Conventional Input (T1) versus Reduced Input (T3) versus Zero Input (T4)

Treatments T1, T3, and T4 vary in the level of agronomic inputs each receives, but are otherwise managed in the same manner (Table 2).

Significant differences between treatments were identified for all soil solution variables with the exception of conductance, alkalinity, ammonium-N, and dissolved organic carbon (Figures 35-41).

pH (T1 vs. T3 vs. T4)

The median pH was significantly higher in the Reduced Input (T3) Treatment than it was in the Conventional Input (T1) or the Reduced Input Organic (T4) Treatments (Figure 35, Top). T1 and T4 did not differ significantly from each other. The median pH in the Conventional Till (T1) Treatment was 6.54; the median pH in the Reduced Input (T3) Treatment was 7.14; and the pH in the Reduced Input Organic (T4) Treatment was 6.7 (Table 5). The interquartile range was greatest in T4, and similar in T1 and T3.

With respect to variability between individual replicates within each treatment, all replicates within Treatment T3 were significantly different from each other. Within Treatments T1 and T4, replicates T1-R4 and T4-R3 were significantly higher than the other two replicates within each treatment (Figure 46, Top).

Calcium (T1 vs. T3 vs. T4)

The median soil solution concentration of calcium was significantly lower in T4 than T1 or T3, which did not differ significantly from each other (Figure 36, Top). The median soil solution concentration of calcium in T1 was 20.01 mg/L (1.00 meq/L); the median concentration in T3 was 21.35 mg/L (1.07 meq/L); and the median concentration in T4 was 13.54 mg/L (0.68 meq/L) (Table 5). The interquartile range was similar for all treatments, although slightly greater in T4.

With respect to variability between individual replicates within each treatment, replicates T3-R3 and T4-R3 significantly higher than the other two replicates within each treatment (Figure 46, Bottom). In Treatment T1, all replicates were significantly different from each other, and T1-R4 had the highest median concentration.

Potassium (T1 vs. T3 vs. T4)

The median soil solution concentration of potassium was significantly lower in T4 than T1 or T3 (Figure 39, Top). Median concentrations in T1 and T3 did not differ significantly from each other. The median soil solution concentration of potassium in T1 was 5.45 mg/L (0.14 meq/L); the median concentration in T3 was 5.44 mg/L (0.14 meq/L); and the median concentration in T4 was 1.79 mg/L (0.05 meq/L) (Table 5). The interquartile range was less in T4 than the other two treatments.

With respect to variability between individual replicates within each treatment, none of the replicates within Treatment T4 were significantly different from each other (Figure 47, Top). In Treatments T1 and T3, T1-R2 and T3-R4 were significantly lower than the other two replicates within each treatment.

Sulfate (T1 vs. T3 vs. T4)

The median soil solution concentration of sulfate was significantly higher in T1 than T3 or T4, which did not differ significantly from each other (Figure 39, Bottom). The median soil solution concentration of sulfate in T1 was 10.52 mg/L (0.22 meq/L); the median concentration in T3 was 6.70 mg/L (0.14 meq/L); and the median concentration in T4 was 6.78 mg/L (0.14 meq/L) (Table 5). The interquartile range was least in T4, and similar for Treatments T1 and T3.

With respect to variability between individual replicates within each treatment, none of the replicates in Treatment T3 were significantly different from each other (Figure 47, Bottom). In Treatment T1, replicate T1-R3 was significantly lower than the other two replicates. While replicate T4-R3 had the lowest median concentration and was significantly lower than T4-R4, it was not significantly lower than T4-R2.

Total Dissolved Phosphorus (T1 vs. T3 vs. T4)

The median soil solution concentration of total dissolved phosphorus was significantly lower in T4 than T1 or T3 (Figure 41, Top). The median soil solution concentration of total dissolved phosphorus in T1 was 0.024 mg/L; the median concentration in T3 was 0.022 mg/L; and the median concentration in T4 was 0.009 mg/L (Table 5). The interquartile range was least in T4, and similar for T1 and T3.

With respect to variability between individual replicates within each treatment, replicate T1-R4 was significantly higher than T1-R3, and replicate

T4-R2 was significantly lower than T4-R3 (Figure 48, Top). In Treatment T3, T3-R3 was significantly higher than the other two.

Silica (T1 vs. T3 vs. T4)

The median soil solution concentration of silica differed significantly between T1 and T3; however, T1 and T3 did not differ significantly from T4 (Figure 40, Top). The median soil solution concentration of silica in T1 was 4.81 mg Si/L; the median concentration in T3 was 5.80 mg Si/L; and the median concentration in T4 was 5.31 mg Si/L (Table 5). The interquartile range was similar for T1 and T4, and least in T3.

With respect to variability between individual replicates within each treatment, replicate T3-R2 was significantly lower than the other two replicates, and replicate T1-R4 was significantly higher than the other two replicates within each treatment (Figure 48, Bottom). All replicates in Treatment T4 were significantly different from each other, and replicate T4-R3 was significantly higher than the other two.

Magnesium (T1 vs. T3 vs. T4)

The median soil solution concentration of magnesium differed significantly between T1 and T3; however, T1 and T3 did not differ significantly from T4 (Figure 36, Bottom). The median soil solution concentration of magnesium in T1 was 2.56 mg/L (0.21 meq/L); the median concentration in T3 was 3.39 mg/L (0.28 meq/L); and the median concentration in T4 was 3.05

mg/L (0.25 meq/L) (Table 5). The interquartile range was greatest in T4 (primarily due to replicate T4-R3) and similar for T1 and T3.

With respect to variability between individual replicates within each treatment, none of the replicates in Treatment T1 differ significantly from each other (Figure 49, Top). In Treatment T3, replicate T3-R2 is significantly lower than the other two. In Treatment T4, Replicate T4-R3 is significantly higher than the other two replicates.

Chloride (T1 vs. T3 vs. T4)

The median soil solution concentration of chloride differed significantly between T4 and T3; however, T4 and T3 did not differ significantly from T1 (Figure 37, Bottom). The median soil solution concentration of chloride in T1 was 0.90 mg/L (0.03 meq/L); the median concentration in T3 was 1.19 mg/L (0.03 meq/L); and the median concentration in T4 was 0.64 mg/L (0.02 meq/L) (Table 5). The interquartile range was least in T4.

With respect to variability between individual replicates within each treatment, none of the replicates differed significantly from each other (Figure 49, Bottom).

Nitrate (T1 vs. T3 vs. T4)

The median soil solution concentration of nitrate differed significantly between T4 and T3; however, T4 and T3 did not differ significantly from T1 (Figure 38, Bottom). The median soil solution concentration of nitrate in T1 was 11.29 mg N/L (0.81 meq/L); the median concentration in T3 was 12.53 mg N/L

(0.90 meq/L); and the median concentration in T4 was 8.33 mg N/L (0.60 meq/L) (Table 5). The interquartile range was least in T4.

With respect to variability between individual replicates within each treatment, replicate T1-R3 was significantly lower than T1-R2 (Figure 50, Top). In Treatments T3 and T4, none of the replicates differed significantly from each other.

Sodium (T1 vs. T3 vs. T4)

The median soil solution concentration of sodium differed significantly between T1 and T4; however, T1 and T4 did not differ significantly from T3 (Figure 37, Top). The median soil solution concentration of sodium in T1 was 1.58 mg/L (0.07 meq/L); the median concentration in T3 was 1.78 mg/L (0.08 meq/L); and the median concentration in T4 was 1.88 mg/L (0.08 meq/L) (Table 5). The interquartile range was least in T4.

With respect to variability between individual replicates within each treatment, none of the replicates in T1 were significantly different from each other (Figure 50, Bottom). In Treatment T3, replicate T3-R4 was significantly higher than T3-R3, but did not differ significantly from T3-R2. In Treatment T4, replicate T4-R3 was significantly higher than T4-R2, but did not differ significantly from T4-R4.

Summary of Observed Patterns (T1 vs. T3 vs. T4)

T1 vs. T3

Conductance and median concentrations of dissolved organic carbon, total alkalinity, ammonium-N, calcium, potassium, total dissolved phosphorus chloride, nitrate-N, and sodium did not differ significantly between the Conventional (T1) and Reduced-Input (T3) treatments (Figures 35-41). pH and median concentrations of silica and magnesium were significantly higher in T3, while the median concentration of sulfate was significantly lower.

T1 vs. T4

pH, conductance, and median concentrations of dissolved organic carbon, total alkalinity, ammonium-N, silica, magnesium, chloride and nitrate-N did not differ significantly between the Conventional (T1) and Zero-Input (T4) treatments (Figures 35-41). Concentrations of calcium, potassium, sulfate, and total dissolved phosphorus were significantly higher in T1 than T4, while median concentrations of sodium were significantly lower.

T3 vs. T4

Conductance and median concentrations of sulfate, dissolved organic carbon, total alkalinity, ammonium-N, silica, magnesium, and sodium did not differ significantly between the Reduced-Input (T3) and Zero-Input (T4) treatments (Figures 35-41). pH and median concentrations of calcium, potassium, total dissolved phosphorus, chloride, and nitrate-N were significantly higher in T3.

T1 vs. T3 vs. T4

There were no significant differences observed in conductance, dissolved organic carbon, total alkalinity, or ammonium-N between treatments (Figures 35-41).

pH was significantly higher in T3 than in T1 or T4, which did not differ significantly from each other.

Median concentrations of calcium, potassium, and total dissolved phosphorus were significantly lower in T4 than T1 or T3, which did not differ significantly from each other.

Median concentrations of silica and magnesium were significantly lower in T1 than T3, although T1 did not differ significantly from T4, and T4 and T3 did not differ significantly from each other.

Median concentrations of chloride and nitrate-N were significantly lower in T4 than T3, although T4 did not differ significantly from T1, and T3 and T1 did not differ significantly from each other.

Median concentrations of sulfate were significantly higher in T1 than either T3 or T4, which did not differ significantly from each other.

Although significantly higher median concentrations of calcium, silica, and magnesium and pH was observed in replicate T4-R3, this did not appear to affect the pattern of overall differences observed between treatments.

Conventional Input / Conventional Till (T1) vs. Deciduous Forest (DF)

In this section, soil solutions in a typical agronomic ecosystem are compared against soil solutions in a native forest ecosystem. Concentrations of all soil solution variables differed significantly between the Conventional Input / Conventional Till Treatment (T1) and the Deciduous Forest Treatment (DF), except for concentrations of dissolved organic carbon. (Figures 35-41) Those variables with significant overall differences are discussed below, and in those cases I also consider the variability among replicates within treatments.

pH (T1 vs. DF)

The median pH was significantly higher in T1 than in DF Treatment (Figure 35, Top). The median pH was 6.5 in the T1 and 6.1 in the DF Treatment (Table 5).

Examining individual replicates within each treatment, all replicates within the DF Treatment were significantly different from each other, and from the replicates in Treatment T1 (Figure 51, Top). Replicates T1-R2 and T1-R3 did not differ significantly from each other, but Replicate T1-R4 was significantly higher than both.

Conductance (T1 vs. DF)

The median conductance was significantly higher in Treatment T1 than in DF Treatment (Figure 35, Bottom). The median conductance was 169 in Treatment T1 and 84 in the DF Treatment (Table 5).

Examining individual replicates within each treatment, all replicates within the DF treatment were significantly different from each other, although replicate DF-R3 was not significantly different from replicates T1-R2 and T1-R3

(Figure 51, Bottom). Replicate T1-R4 was significantly different from and higher than all other replicates from both treatments.

Calcium (T1 vs. DF)

The median soil solution concentration of calcium was significantly higher in Treatment T1 than in the DF Treatment (Figure 36, Top). The median soil solution concentration was 20.01 mg/L (1.00 meq/L) in Treatment T1 and 7.37 mg/L (0.37 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, replicate DF-R2 was significantly lower than replicates DF-R1 and DF-R3, which did not differ significantly from each other. All replicates within the DF Treatment were significantly different from and lower than the replicates in Treatment T1 (Figure 52, Top). All replicates within Treatment T1 were significantly different from each other, and replicate T1-R4 exhibited the highest median soil solution concentration of calcium.

Magnesium (T1 vs. DF)

In contrast to calcium, the median soil solution concentration of magnesium was significantly higher in the DF Treatment than in Treatment T1 (Figure 36, Bottom). The median soil solution concentration was 2.56 mg/L (0.21 meq/L) in Treatment T1 and 3.42 mg/L (0.28 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly lower than replicates DF-R1 and DF-R3, which did not differ significantly from each other (Figure 52, Bottom). None of the replicates within Treatment T1 differed significantly from each other, and replicate DF-R1 did not differ significantly from any replicates in Treatment T1.

Sodium (T1 vs. DF)

The median soil solution concentration of sodium was significantly higher in the DF Treatment than in Treatment T1 (Figure 37, Top). The median soil solution concentration was 1.58 mg/L (0.07 meq/L) in Treatment T1 and 2.04 mg/L (0.09 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly lower than replicates DF-R1 and DF-R3, which did not differ significantly from each other (Figure 53, Top). None of the replicates within Treatment T1 differed significantly from each other, and replicate DF-R2 did not differ significantly from any replicates in Treatment T1.

Chloride (T1 vs. DF)

The median soil solution concentration of chloride was significantly higher in the DF Treatment than in Treatment T1 (Figure 37, Bottom). The median soil solution concentration was 0.09 mg/L (0.03 meq/L) in Treatment T1 and 1.48 mg/L (0.04 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, none of the replicates within Treatment DF differed significantly from each other and none of the replicates within Treatment T1 differed significantly from each other (Figure 53, Bottom). Between treatments, replicate DF-R2 did not differ significantly from any of the replicates within Treatment T1, while replicates DF-R1 and DF-R3 were significantly higher than all the replicates within Treatment T1.

Ammonium-N (T1 vs. DF)

The median soil solution concentration of ammonium-N was significantly higher in the DF Treatment than in Treatment T1 (Figure 38, Top). The median soil solution concentration was 0.020 mg/L (0.001 meq/L) in Treatment T1 and 0.040 mg/L (0.002 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, none of the replicates within the DF Treatment differed significantly from each other (Figure 54, Top). Replicate T1-R4 was significantly higher than replicates T1-R2 and T1-R3, which did not differ significantly from each other. Replicate T1-R4 did not differ significantly from any of the replicates within the DF Treatment.

Nitrate-N (T1 vs DF)

The median soil solution concentration of nitrate-N was significantly higher in Treatment T1 than in the DF Treatment (Figure 38, Top). The median soil solution concentration was 11.29 mg/L (0.81 meq/L) in Treatment T1 and 3.46 mg/L (0.25 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, all replicates within the DF Treatment differed significantly from each other (Figure 54, Bottom). Within Treatment T1, replicate T1-R3 was significantly lower than replicates T1-R2 and T1-R4, which did not differ significantly from each other.

Between treatments, replicate DF-R1 did not differ significantly from replicate T1-R3, and replicate DF-R3 did not differ significantly from any of the replicates within Treatment T1.

Potassium (T1 vs. DF)

The median soil solution concentration of potassium was significantly higher in Treatment T1 than in the DF Treatment (Figure 39, Top). The median soil solution concentration was 5.45 mg/L (0.14 meq/L) in Treatment T1 and 0.40 mg/L (0.01 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly higher than replicates DF-R1 and DF-R3, which did not differ significantly from each other (Figure 55, Top). All of the replicates in the DF Treatment were significantly lower than the replicates in Treatment T1. Replicate T1-R2 was significantly lower than replicates T1-R3 and T1-R4, which did not differ significantly from each other.

Sulfate (T1 vs. DF)

The median soil solution concentration of sulfate was significantly higher in the DF Treatment than in Treatment T1 (Figure 39, Bottom). The median soil solution concentration was 10.52 mg/L (0.22 meq/L) in Treatment T1 and 13.69 mg/L (0.29 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, DF-R2 was significantly lower than replicates DF-R1 and DF-R3, which did not differ significantly from each other (Figure 55, Bottom). Replicate T1-R4 was significantly lower than T1-R2 and T1-R3, which did not differ significantly from each other. Between treatments, replicate DF-R1 did not differ significantly from T1-R2 and Replicate DF-R2 did not differ significantly from replicate T1-R4.

Silica (T1 vs. DF)

The median soil solution concentration of silica was significantly higher in the DF Treatment than in Treatment T1 (Figure 40, Top). The median soil solution concentration was 4.81 mg/L in Treatment T1 and 9.08 mg/L in the DF Treatment (Table 5).

Examining individual replicates within each treatment, all replicates within the DF Treatment are significantly different from each other and significantly different from the replicates in Treatment T1 (Figure 56, Top). Replicate T1-R4 is significantly higher than replicates T1-R2 and T1-R3, which do not differ significantly from each other.

Total Alkalinity (T1 vs. DF)

The median total alkalinity of the soil solution was significantly higher in Treatment T1 than in the DF Treatment (Figure 40, Bottom). The median total alkalinity was 19.75 mg/L (0.32 meq/L) in Treatment T1 and 10.15 mg/L (0.17 meq/L) in the DF Treatment (Table 5).

Examining individual replicates within each treatment, replicate DF-R2 is significantly higher than replicates DF-R1 and DF-R3, which do not differ significantly from each other (Figure 56, Bottom). All of the replicates within the

DF Treatment differ significantly from the replicates in Treatment T1. Replicate T1-R4 is significantly higher than replicates T1-R2 and T1-R3, which did not differ significantly from each other.

Total Dissolved Phosphorus (T1 vs. DF)

The median soil solution concentration of total dissolved phosphorus (TDP) was significantly higher in the Treatment T1 than in the DF Treatment (Figure 41, Top). The median soil solution concentration was 0.024 mg/L in Treatment T1 and 0.007 mg/L in the DF Treatment (Table 5).

Examining individual replicates within each treatment, replicate DF-R2 is significantly higher than replicates DF-R1 and DF-R2, which do not differ significantly from each other (Figure 57). Replicate T1-R4 is significantly higher than replicates T1-R2 and T1-R3, which do not differ significantly from each other. Replicate T1-R4 does not differ significantly from replicate DF-R2.

Summary of Observed Patterns (T1 vs. DF)

Significantly higher pH, conductance, and median soil solutions concentrations of TDP, silica, total alkalinity, calcium, potassium, and nitrate-N were observed in Treatment T1 (Figures 35-41). Significantly higher median soil solution concentrations of magnesium, silica, sodium, chloride, and sulfate were observed in the DF Treatment. No significant differences between treatments in the median concentration of dissolved organic carbon were observed (Figure 41, Bottom).

Perennial Poplar (T5) versus Perennial Alfalfa (T6)

While both these treatments are perennials, T6 received one-time agronomic inputs that included lime and ammonium sulfate during the study period, while T5 did not. Alfalfa is also a nitrogen-fixing legume, while the clonal poplar tree is not.

Significant differences between Treatments T5 and T6 were identified for all soil solution variables with the exception of pH, dissolved organic carbon, alkalinity, ammonium, and total dissolved phosphorus (Figures 12-18).

Conductance (T5 vs. T6)

The median conductance was significantly higher in the Perennial Alfalfa (T6) Treatment (Figures 12-18). The median conductance in the Perennial Poplar (T5) Treatment was 65 µS/cm @25°C and the median conductance in T6 was 249 µS/cm @25°C (Table 5). The interquartile range was much greater in T6 than in T5 for this variable.

With respect to variability between individual replicates within each treatment, one replicate in T6 was significantly higher than the other two replicates (Figure 58, Top). In Treatment T5, all three replicates were significantly different from each other.

Calcium (T5 vs. T6)

The median soil solution concentration of calcium was significantly higher in T6 (Figure 13, Top). The median soil solution concentration of calcium in T5 was 7.31 mg/L (0.37 meq/L), and the median concentration in T6 was 34.33 mg/L (1.71 meq/L) (Table 5). The interquartile range was also much greater in T6.

With respect to variability between individual replicates within each treatment, one replicate in Treatment T6 was significantly higher than the other two replicates (Figure 58, Bottom). In Treatment T5, all three replicates were significantly different from each other.

Magnesium (T5 vs. T6)

The median soil solution concentration of magnesium was significantly higher in T6 (Figure 13, Bottom). The median soil solution concentration of magnesium in T5 was 1.84 mg/L (0.15 meq/L), and the median concentration in T6 was 7.00 mg/L (0.58 meq/L) (Table 5). The interquartile range was also much greater in T6.

With respect to variability between individual replicates within each treatment, one replicate in Treatment T5 was significantly higher than the other two replicates (Figure 59, Top). In Treatment T6, replicate T6-R4 was significantly different from T6-R3, but not significantly different from T6-R2.

Sulfate (T5 vs. T6)

The median soil solution concentration of sulfate was significantly higher in T5 (Figure 14, Bottom). The median soil solution concentration of sulfate in T5 was 17.65 mg/L (0.367 meq/L), and the median concentration in T6 was 4.21 mg/L (0.088 meq/L) (Table 5). The interquartile range was greater in T5.

With respect to variability between individual replicates within each treatment, all three replicates within Treatment T5 differed significantly from one another (Figure 59, Bottom). In Treatment T6, replicate T6-R4 was significantly different from replicate T6-R2.

Potassium (T5 vs. T6)

The median soil solution concentration of potassium was significantly higher in T5 (Figure 15, Top). The median soil solution concentration of potassium in T5 was 1.82 mg/L (0.05 meq/L), and the median concentration in T6 was 1.04 mg/L (0.03 meq/L) (Table 5). The interquartile range was slightly greater in T5.

With respect to variability between individual replicates within each treatment, one replicate in Treatment T6 was significantly higher than the other two replicates (Figure 60, Top). In Treatment T5, one replicate was significantly different and lower than the other two replicates.

Chloride (T5 vs. T6)

The median soil solution concentration of chloride was significantly higher in T6 (Figure 15, Bottom). The median soil solution concentration of chloride in T5 was 1.84 mg/L (0.02 meq/L), and the median concentration in T6 was 7.00 mg/L (0.05 meq/L) (Table 5). The interquartile range was also much greater in T6.

With respect to variability between individual replicates within each treatment, none of the replicates differed significantly from another (Figure 60, Bottom).

Nitrate (T5 vs. T6)

The median soil solution concentration of nitrate was significantly higher in T6 (Figure 16, Bottom). The median soil solution concentration of nitrate in T5 was 0.00 mg N/L (0.00 meq/L), and the median concentration in T6 was 16.00 mg N/L (1.142 meq/L) (Table5). The interquartile range was also much greater in T6.

With respect to variability between individual replicates within each treatment, none of the replicates differed significantly from each other (Figure 61, Top).

Sodium (T5 vs. T6)

The median soil solution concentration of sodium was significantly higher in T6 (Figure 18, Top). The median soil solution concentration of sodium in T5 was 1.53 mg/L (0.07 meq/L), and the median concentration in T6 was 2.13 mg/L (0.09 meq/L). The interquartile range was also much greater in T6.

With respect to variability between individual replicates within each treatment, replicate T5-R2 was significantly different from T5-R3. None of the replicates in Treatment T6 were significantly different from each other (Figure 61, Bottom).

Silica (T5 vs. T6)

The median soil solution concentration of silica was significantly higher in T6 (Figure 18, Bottom). The median soil solution concentration of silica in T5 was 5.77 mg Si/L, and the median concentration in T6 was 8.88 mg Si/L (Table 5). The interquartile range was also much greater in T6.

With respect to variability between individual replicates within each treatment, each treatment had one replicate that was significantly different from and higher than the other two (Figure 62).

Summary of Observed Patterns (T5 vs. T6)

No significant differences were observed in the median concentrations of dissolved organic carbon, total alkalinity, ammonium-N, total dissolved phosphorus, or pH (Figures 12-18).

Conductance and the median concentrations of silica, calcium, magnesium, chloride, sodium, and nitrate-N were significantly higher in the Alfalfa (T6) treatment. Median concentrations of potassium and sulfate were significantly higher in the Poplars (T5).

Although replicates T5-R3 and T6-R3 had higher median values for calcium and magnesium, this was not responsible for the overall differences observed between treatments (Figures 58, Bottom and 59, Top).

Successional Forest (SF) versus Perennial Poplar (T5) versus Early Successional Community (T7)

The Early Successional Community (T7) is herbaceous, while the Successional Forest Treatment (SF) is a mixture of herbaceous and woody plants. The Perennial Poplar Treatment (T5) consists of a fast-growing clonal tree.

Significant differences between treatments were identified for all soil solution variables with the exception of dissolved organic carbon and chloride.

pH

The median air-equilibrated pH was significantly higher in T7 than in SF; however, SF and T7 did not differ significantly from T5 (Figure 63, Top). The median air-equilibrated pH in the SF Treatment was 6.72; the median air-equilibrated pH in T5 was 6.88; and the pH in T7 was 7.05 (Table 5). The interquartile range was greatest in T5, and similar in SF and T7.

With respect to variability between individual replicates within each treatment, each treatment had one replicate that was significantly different from the other two (Figure 70, Top).

Conductance

The median conductance was significantly lower in Treatment SF than either T5 or T7, which did not differ significantly from each other (Figure 63, Bottom). The median conductance in the SF Treatment was 41 μS/cm@25°C; the conductance in T5 was 65 μS/cm@25°C; and the conductance in T7 was

54 µS/cm@25°C (Table 5). The interquartile range was least in SF, and similar in T5 and T7.

With respect to variability between individual replicates within each treatment, Treatments SF and T7 each had one replicate that was significantly different from the other two (Figure 70, Bottom). In Treatment T5, all replicates were significantly different from each other.

Calcium

The median soil solution concentration of calcium was significantly lower in Treatment SF than either T5 or T7, which did not differ significantly from each other (Figure 64, Top). The median calcium concentration in the SF Treatment was 4.32 mg/L (0.22 meq/L); the median calcium concentration in T5 was 7.31 mg/L (0.15 meq/L); and the median calcium concentration in T7 was 8.10 mg/L (0.40 meq/L) (Table 5). The interquartile range was smallest in SF.

With respect to variability between individual replicates within each treatment, all replicates within Treatments T5 and T7 differed significantly from each other (Figure 71, Top). In Treatment SF, one replicate was significantly lower than the other two.

Magnesium

The median soil solution concentration of magnesium was significantly higher in Treatment T5 than in either SF or T7, which did not differ significantly from each other (Figure 64, Top). The median magnesium concentration in the SF Treatment was 0.98 mg/L (0.08 meq/L); the median magnesium concentration in T5 was 1.84 mg/L (0.15 meq/L); and the median magnesium concentration in T7 was 1.16 mg/L (0.10 meq/L) (Table 5). The interquartile range was least in SF.

With respect to variability between individual replicates within each treatment, one replicate within Treatment SF was significantly different from the other two (Figure 71, Bottom). In Treatment T7, replicate T7-R3 was significantly different from replicate T7-R4, and in Treatment T5, all replicates were significantly different from each other.

Sodium

The median soil solution concentration of sodium was significantly lower in Treatment SF than either T5 or T7, which did not differ significantly from each other (Figure 65, Top). The median sodium concentration in the SF Treatment was 1.31 mg/L (0.06 meq/L); the median sodium concentration in T5 was 1.53 mg/L (0.07 meq/L); and the median sodium concentration in T7 was 1.47 mg/L (0.064 meq/L) (Table 5). The interquartile range was least in T5.

With respect to variability between individual replicates within each treatment, none of the replicates within Treatment SF are significantly different from each other (Figure 72, Top). In Treatment T5, replicate T5-R2 is significantly different from replicate T5-R4, and in Treatment T7, replicate T7-R3 differed significantly from replicate T7-R4.

Ammonium

The median soil solution concentration of ammonium-N was significantly higher in Treatment SF than T5; however, SF and T5 were not significantly different from T7 (Figure 66, Top). The median ammonium-N concentration in the SF Treatment was 0.019 mg N/L (0.001 meq/L); the ammonium-N concentration in T5 was 0.010 mg N/L (0.001 meq/L); and the ammonium-N concentration in T7 was 0.01 mg N/L (0.001 meq/L) (Table 5). The interquartile range was least in T5 and greatest in SF.

With respect to variability between individual replicates within each treatment, none of the replicates within Treatment T5 or T7 were significantly different from each other (Figure 72, Bottom). In Treatment SF, one replicate differed significantly from the other two.

Nitrate

The median soil solution concentration of nitrate-N was significantly lower in Treatment T5 than either SF or T7, which did not differ significantly from each other (Figure 66, Bottom). The median nitrate-N concentration in the SF Treatment was 0.08 mg N/L (0.006 meq/L); the median nitrate-N concentration in T5 was 0.00 mg N/L (0.000 meq/L); and the median nitrate-N concentration in T7 was 0.23 mg N/L (0.017 meq/L) (Table 5). The interquartile range was greatest in T7 and least in SF.

With respect to variability between individual replicates within each treatment, none of the replicates within Treatment T5 differed significantly

(Figure 73, Top). Within Treatments SF and T7, each had one replicate that was significantly higher than the other two.

Potassium

The median soil solution concentrations of each treatment are significantly different from each other, with SF having the lowest median concentration and T7 having the highest median concentration (Figure 67, Top). The median potassium concentration in the SF Treatment was 0.23 mg/L (0.006 meq/L); the median potassium concentration in T5 was 1.82 mg/L (0.05 meq/L); and the median potassium concentration in T7 was 2.44 mg/L (0.06 meq/L) (Table 5). The interquartile range was least in T5.

With respect to variability between individual replicates within each treatment, all three treatments had one replicate that differed significantly from the other two (Figure 73, Bottom)).

Sulfate

The median soil solution concentration of sulfate was significantly higher in Treatment T5 than in either SF or T7, which did not differ significantly from each other (Figure 74, Top). The median sulfate concentration in the SF Treatment was 8.44 mg/L (0.18 meq/L); the median sulfate concentration in T5 was 17.65 mg/L (0.37 meq/L); and the median sulfate concentration in T7 was 21.26 mg/L (0.20 meq/L) (Table 5). The interquartile range was greatest in T5, and similar in SF and T7.

With respect to variability between individual replicates within each treatment, Treatments SF and T7 each had one replicate that differed significantly from the other two (Figure 74, Top). In Treatment T5, all three replicates differed significantly from each other.

Silica

The median soil solution concentration of silica was significantly lower in Treatment T7 than either SF or T5, which did not differ significantly from each other (Figure 68, Top). The median silica concentration in the SF Treatment was 6.13 mg Si/L; the median silica concentration in T5 was 5.77 mg Si/L; and the median silica concentration in T7 was 4.57 mg Si/L (Table 5). The interquartile range was least in T7 and greatest in SF.

With respect to variability between individual replicates within each treatment, each treatment had one replicate that was significantly different from the other two (Figure 74, Bottom).

Alkalinity

The median soil solution concentration of alkalinity was significantly lower in Treatment SF than in either T5 or T7, which did not differ significantly from each other (Figure 68, Bottom). The median alkalinity concentration in the SF Treatment was 15.89 mg HCO_3^-/L (0.26 meq/L); the median alkalinity concentration in T5 was 24.14 mg HCO_3^-/L (0.40 meq/L); and the median alkalinity concentration in T7 was 24.22 mg HCO_3^-/L (0.40 meq/L) (Table 5). The interquartile range was similar for all treatments.

With respect to variability between individual replicates within each treatment, none of the replicates in Treatment T7 were significantly different from each other (Figure 75, Top). In Treatment T5, one of the replicates differed significantly from the other two, and in Treatment SF, all replicates differed significantly from each other.

Total Dissolved Phosphorus

The median soil solution concentration of total dissolved phosphorus (TDP) was significantly higher in Treatment T7 than either SF or T5, which did not differ significantly from each other (Figure 69, Top). The median TDP concentration in the SF Treatment was 0.014 μg/L; the TDP concentration in T5 was 0.011 μg/L; and the TDP concentration in T7 was 0.021 μg/L (Table 5). The interquartile range was least in T5 and greatest in T7.

With respect to variability between individual replicates within each treatment, none of the replicates within Treatments T5 or T7 differed significantly from each other (Figure 75, Bottom). In Treatment SF, replicate SF-R2 was significantly different from SF-R1.

Summary of Observed Patterns (SF vs. T5 vs. T7)

SF vs. T5

No significant differences were observed between treatments with respect to pH or median concentrations of dissolved organic carbon, total dissolved phosphorus, silica, or chloride (Figures 63-69).

Significantly higher median concentrations of total alkalinity, calcium, magnesium, sodium, sulfate, and potassium, and conductance were observed in T5.

Treatment SF exhibited significantly higher median concentrations of nitrate and ammonium than Treatment T5.

SF vs. T7

No significant differences between median concentrations of dissolved organic carbon, chloride, nitrate, magnesium, sulfate, or ammonium-N were observed between treatments (Figures 63-69).

pH and conductance were significantly higher in T7, as were median concentrations of total alkalinity, calcium, sodium, potassium, and total dissolved phosphorus.

Median concentrations of silica were significantly higher in SF.

T5 vs. T7

No significant differences between pH and conductance, and median concentrations of dissolved organic carbon, chloride, total alkalinity, calcium, sodium, or ammonium-N were observed (Figures 63-69).

Median concentrations of silica, magnesium, and sulfate were significantly higher in T5.

Median concentrations of potassium, nitrate-N and total dissolved phosphorus were significantly higher in T7.

SF vs. T5 vs. T7

Not significant differences between median concentrations of dissolved organic carbon and chloride were observed between treatments (Figures 63-69).

Conductance and median concentrations of alkalinity, calcium, and sodium were significantly lower in Treatment SF than T5 or T7, which did not differ significantly from each other.

pH was significantly higher in T7 than SF, but T7 did not differ significantly from T5, and T5 and SF did not differ significantly from each other.

Median concentrations of silica were significantly lower in T7 than either T5 or SF, which did not differ significantly from each other.

Median concentrations of magnesium and sulfate were significantly higher in T5 than either T7 or SF, which did not differ significantly from each other.

Median concentrations of nitrate-N were significantly lower and potassium significantly higher in T5 than either T7 or SF, which did not differ significantly. It is important to note that while there were significant differences between treatments, the median nitrate-N concentrations were very low in all treatments, ranging from a low of 0.00 mg N/L (T5) to a high of 0.23 mg N/L (T7), while in comparison, agronomic treatments ranged from a low of 7.25 mg N/L (T2) to a high of 16.00 mg N/L (T6).

Median concentrations of ammonium-N were significantly higher in SF than T5, although SF did not differ significantly from T7, and T5 and T7 did not differ significantly from each other.

The median concentration of total dissolved phosphorus was significantly higher in T7 than SF or T5, which did not differ significantly from each other.

Seasonal Patterns in Soil Solution Chemistry, Including Effects of Agronomic Inputs

Interpreting seasonal patterns is complicated by evapotranspiration effects which cannot be corrected for; rain, snow, and snowmelt events which are random in nature; dry periods which preclude sample collection; and the variable proportions of matric water and saturated flow as a result of the sample collection method. In addition, if the upward water movement by capillary flow intersects the depth of the soil water sampler at any time during the course of the study, the resulting mixture of soil solutions can obfuscate our interpretation of the characteristics of the water that is the subject of this study: the water moving down through the soil profile from the surface.

Coniferous Forest

Conductance, pH, and magnesium concentrations showed no consistent seasonal pattern or overall trends over the study period. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here (Figures 76-80). Individual ions exhibiting an Interesting temporal pattern or other characteristic of interest in the CF treatment are discussed below.

Silica (CF)

Silica appeared to vary seasonally, being lowest in April and increasing throughout the summer season (Figure 76, Bottom). Concentrations are similar between replicates, which vary together over time.

Calcium (CF)

CF-R1 shows a generally decreasing trend over the study period, while replicate CF-R2 and CF-R3 exhibit a generally increasing trend. Like nitrate, chloride, and potassium, a sharp increase in calcium concentrations occurred at the end of the study period, particularly in CF-R1 (Figure 77, Top).

Alkalinity (CF)

No consistent seasonal pattern was identified for alkalinity. However, a generally increasing trend was evident in all three replicates over the study period (Figure 77, Bottom).

Sodium (CF)

Although the pattern is somewhat erratic, like silica, sodium appears to be lowest in April and increasing over the summer period (Figure 78, Top)

Potassium (CF)

No consistent seasonal pattern was identified for potassium. Like nitrate and chloride, potassium concentrations increase in all three replicates at the end of the study period, but dramatically so in CF-R1 which consistently exhibits higher concentrations than the other two replicates throughout the study period

(Figure 78, Middle). While precipitation monitoring data show that wet deposition of potassium during the same period was also increasing, it was not unusually high relative to preceding spring seasons.

Chloride (CF)

No consistent seasonal pattern was identified for chloride. Like nitrate, chloride concentrations increased at the end of the study period (Figure 78, Bottom). Wet deposition of chloride during this time was also increasing.

Nitrate (CF)

In replicates CF-R1 and CF-R2, nitrate varied seasonally, peaking in late spring and being lowest in the fall. CF-R3 shows an opposite pattern. Both CF-R2 and CF-R3 show a sharp rise in nitrate concentrations at the end of the study period (Figure 79, Top). While wet deposition of nitrate during the same period was also increasing, it was not unusually high relative to preceding spring seasons.

Sulfate (CF)

No consistent seasonal pattern was identified for sulfate. However, there was an overall decreasing trend for each replicate (Figure 79, Middle). Wet deposition data for sulfate over the same period showed no increase.

Deciduous Forest

Conductance, pH, and silica, sodium, nitrate and sulfate concentrations showed no consistent seasonal pattern or overall trends over the study period. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here (Figures 81-85).

Individual ions exhibiting a pattern or other characteristic of interest in the DF treatment are discussed below.

Calcium (DF)

No consistent seasonal pattern was observed. DF-R1 and DF-R2 showed a generally decreasing trend over the study period, while replicate DF-R3 did not, mainly as a result of the sharp increase in calcium concentrations at the end of the study period (Figure 82, Top)).

Magnesium (DF)

No consistent seasonal pattern was observed. Two of the three replicates showed a generally decreasing trend over the study period (Figure 82, Middle).

Alkalinity (DF)

No consistent seasonal pattern was identified for alkalinity. However, a generally increasing trend was evident in all three replicates over the study period (Figure 82, Bottom).

Potassium (DF)

No consistent seasonal pattern was identified for potassium. Like chloride, potassium concentrations increased in all three replicates at the end of the study period (Figure 83, Middle). While wet deposition of potassium during the same period was also increasing, it was not unusually high relative to preceding spring seasons.

Chloride (DF)

No consistent seasonal pattern was identified for chloride. Chloride concentrations increased at the end of the study period (Figure 83, Bottom). Wet deposition of chloride during this time was also increasing.

Successional Forest

No consistent seasonal pattern was observed for any of the major ions in the SF treatment over the study period (Figures 86-90). Higher concentrations of calcium, magnesium, alkalinity, and conductance were observed in replicate SF-R1 in 1999 and 2000 (Figure 86 and 87). Concentrations then fell to at or below those of the other replicates. Generally decreasing trends were observed for silica and sulfate, with the exception of SF-R2 which showed no trend for silica and a generally increasing trend for sulfate (Figures 86 and 89). In the summer and fall of 2001, very high nitrate concentrations were observed in Replicate SF-R3 (Figure 89, Top). At the end of the study period, chloride was observed to increase sharply in all replicates, and was the only major ion to do so (Figure 88, Bottom). Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here.

Treatment 1: Conventional Input / Conventional Till

Agricultural amendments applied during the study period are summarized in Table 2. Amendments to this treatment include lime, ammonium sulfate, ammonium nitrate, liquid N solution and potash. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here. Individual ions exhibiting an interesting temporal pattern or other characteristic of interest in T1 are discussed below (Figures 91-95).

pH (T1)

Higher pH values were consistently observed in Replicate T1-R4 over the study period (Figure 91, Top).

Conductance (T1)

No consistent seasonal pattern in conductance was observed. A sharp increase in conductance was observed at end of study period in T1-R4, and this increase was not immediately preceded by any agronomic input (Figure 91, Middle).

Calcium (T1)

No consistent seasonal pattern in soil solution calcium concentrations was observed (Figure 92, Top). Higher concentrations were consistently observed in Replicate T1-R4 over the study period. Calcium concentrations decreased slightly over the study period, with the exception of T1-R4 where a sharp increase in calcium concentrations was observed at the end of the study period.

Magnesium (T1)

No consistent seasonal pattern in soil solution concentrations of magnesium was observed (Figure 92, Middle). Concentrations were similar in all three replicates until the end of the study period, when T1-R4 increased sharply. T1-R2 and T1-R3 also increased, but not above concentrations seen in previous seasons. NPK was added to all three replicates at the end of the study period.

Alkalinity (T1)

Higher concentrations of total alkalinity were consistently observed in the soil solution of Replicate T1-R4 over the study period (Figure 92, Bottom). Generally increasing trends were observed in Replicates T1-R2 and T1-R3 (T1-R4 was flat). A sharp decrease was observed in alkalinity in all treatments following the addition of ammonium sulfate in August 2001.

Silica (T1)

Soil solution concentrations of silica were lowest in the spring, increased throughout summer and fall, and dropped back down in winter (Figure 91, Bottom).

Nitrate (T1)

No consistent seasonal pattern was observed for soil solution concentrations of nitrate-N (Figure 94, Top). A sharp increase in nitrate-N was observed in Replicate T1-R4 at the end of the study period, and Replicate T1-R2 also increased sharply, but less dramatically. R3 also increased, but not above levels seen previously.

Sodium (T1)

No consistent seasonal pattern or overall trend was observed in the soil solution concentration of sodium in any of the replicates (Figure 93, Top). Increases in concentration were observed at the end of the study period, but these increases did not exceed previously observed concentrations.

Potassium (T1)

Consistently lower concentrations of potassium in the soil solution were observed in replicate T1-R2 over the study period (Figure 92, Middle). T1-R4 appeared to be lowest at the beginning of summer and highest at the end of the summer. T1-R2 and T1-R3 exhibited a similar pattern in some of the study years. Potassium (in the form of potash) was added to these replicates in April 2002 and again in April 2003. Increases in potassium concentrations are observed following each addition, with particularly sharp increases seen in 2003 in Replicates T1-R3 and T1-R4.

Chloride (T1)

No consistent seasonal pattern was observed in the soil solution concentrations of chloride (Figure 93, Bottom). A sharp increase at end of study period was observed in Replicate T1-R4. R3 also increased sharply, but less dramatically. R2 also increased, but not above levels seen previously. The increase began in 2002, following the addition of Potash in April. Potash was again added in April of 2003, and the chloride concentrations shot upward.

Sulfate (T1)

No consistent seasonal pattern of soil solution sulfate concentrations was observed, although there was a generally decreasing trend for all three replicates over study period (Figure 94, Middle).

T2: Conventional Input / No Till

Agricultural amendments applied during the study period are summarized in Table 2. No samples were collected from Replicate T2-R3 after

7/2/2002. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here. Individual ions exhibiting an interesting pattern or other characteristic of interest in T2 are discussed below (Figure 96-100). .

pH (T2)

No consistent seasonal pattern of pH was observed (Figure 96, top). The pH in Replicate T2-R3 was consistently higher than the other two replicates after the winter 2000 and spring 2001.

Conductance (T2)

Conductance was consistently higher in Replicate T2-R3 over the study period (Figure 96, Middle). In general, conductance increased throughout each summer season.

Silica (T2)

Silica was consistently higher in Replicate T2-R3 over the study period (Figure 96, Bottom). In general, silica increased throughout each summer season.

Calcium (T2)

Higher soil solution concentrations of calcium were observed in Replicate T2-R3 throughout the study period (Figure 97, Top). At the end of the study period, concentrations increased sharply in T2-R2 and T2-R4. (No data available for T2-R3).

Magnesium (T2)

Higher concentrations were observed in the soil solution of Replicate T2-R3 throughout the study period (Figure 97, Middle). At the end of the study period, concentrations increased sharply in T2-R2 and T2-R4. (No data available for T2-R3).

Alkalinity (T2)

Higher soil solution concentrations of alkalinity were observed in Replicate T2-R3 throughout the study period (Figure 97, Bottom). Alkalinity levels decreased sharply at the end of the study period.

Sodium (T2)

Sodium soil solution concentrations increased each year from April through August (Figure 98, Top).

Potassium (T2)

Potassium concentrations increased from April through August each year (Figure 98, Middle). A sharp increase in potassium concentrations occurred at the end of the study period, beginning in April 2002 following a potash addition.

Chloride (T2)

No consistent season pattern of soil solution concentrations of chloride was observed over the study period (Figure 98, Bottom). A sharp increase in concentrations was observed beginning in 7/2002 through the end of the study period.

Nitrate (T2)

No consistent seasonal pattern was observed in the soil solution concentrations of nitrate-N over the study period (Figure 99, Top). Replicates

T2-R2 and T2-R4 increased sharply at the end of the study period. (No data is available for T2-R3).

Sulfate (T2)

No consistent seasonal pattern was observed in the soil solution concentrations of sulfate over the study period (Figure 99, Middle). A generally decreasing trend was observed in all three replicates over the study period.

T3: Reduced Input / Conventional Till

Agricultural amendments applied during the study period are summarized in Table 2. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here. Individual ions exhibiting a pattern or other characteristic of interest are discussed below (Figures 101-105).

pH (T3)

No consistent seasonal pattern in soil solution pH was observed during the study period (Figure 101, Top).

Conductance (T3)

No consistent seasonal pattern was observed during the study period (Figure 101, Middle). A generally increasing trend in conductance was observed following the addition of potash in April 2002.

Calcium (T3)

No consistent seasonal pattern was observed during the study period (Figure 102, Top). Replicate T3-R3 tended to exhibit higher concentrations of calcium during the study period. The lowest concentrations for all replicates were observed in 2002.

Magnesium (T3)

No consistent seasonal pattern was observed during the study period (Figure 102, Middle). Concentrations of magnesium were similar across replicates, and replicates tended to vary together. The lowest concentrations were observed in 2002.

Alkalinity (T3)

No consistent seasonal pattern was observed during the study period (Figure 102, Bottom). Replicate T3-R3 tended to exhibit higher levels of alkalinity than the other two replicates. There was a general, albeit slight, increasing trend over the study period in all three replicates.

Sodium (T3)

No consistent seasonal pattern was observed during the study period (Figure 103, Top). Concentrations were lowest for all three replicates in 2002.

Potassium (T3)

No consistent seasonal pattern was observed during the study period (Figure 103, Middle). Potassium concentrations were lowest in 2002. Following the addition of potash in April 2002, potassium concentrations increased in all three replicates.

Chloride (T3)

No consistent seasonal pattern was observed during the study period (Figure 103, Bottom). Similar concentrations were observed in all replicates, and the replicates tended to vary together. Following the addition of potash in April 2002, chloride concentrations increased in all three replicates.

Nitrate (T3)

No consistent seasonal pattern was observed during the study period (Figure 104, Top). Similar concentrations were observed in all replicates, and the replicates tended to vary together. The lowest nitrate concentrations were observed in 2002.

Sulfate (T3)

No consistent seasonal pattern was observed during the study period (Figure 104, Middle). Similar concentrations were observed in all replicates, although the replicates did not vary together. The lowest sulfate concentrations were observed in 2002.

T4: Organic / Conventional Till

No agricultural amendments were used during this study. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here. Individual ions exhibiting a pattern or other characteristic of interest are discussed below (Figures 106-110).

pH (T4)

No consistent seasonal pattern was observed during the study period (Figure 106, Top). A generally decreasing trend was observed for Replicates T4-R2 and T4-R4. Replicate T4-R3 showed no such trend, and consistently exhibited a higher pH than the other two replicates for the duration of the study period.

Conductance (T4)

No consistent seasonal pattern was observed during the study period (Figure 106, Middle). Replicate T4-R3 consistently exhibited higher conductance than the other two replicates over the course of the study period.

Silica (T4)

A general seasonal trend was observed for silica (Figure 106, Bottom). Silica began increasing in early spring each year, peaking in September. Replicate T4-R3 consistently exhibited higher concentrations of silica than the other two replicates over the study period.

Calcium (T4)

No consistent seasonal pattern was observed during the study period (Figure 107, Top). Concentrations were consistently higher in Replicate T4-R3 than the other two replicates over the course of the study period.

Magnesium (T4)

No consistent seasonal pattern was observed during the study period (Figure 107, Middle). Concentrations were consistently higher in Replicate T4-R3 than the other two replicates over the course of the study period.

Alkalinity (T4)

No consistent seasonal pattern was observed during the study period (Figure 107, Bottom). Concentrations were consistently higher in Replicate T4-R3 than the other two replicates over the course of the study period.

Sodium (T4)

No consistent seasonal pattern was observed during the study period (Figure 108, Top). No consistent overall trend was observed across replicates.

Potassium (T4)

No consistent seasonal pattern was observed during the study period (Figure 108, Middle). The lowest potassium concentrations were observed at the end of the 2001 through May of 2002. The highest concentrations were observed at the end of the study period in 2003.

Chloride (T4)

No consistent seasonal pattern was observed during the study period (Figure 108, Bottom). The highest concentrations were observed at the end of the study period in 2003.

Nitrate (T4)

No consistent seasonal pattern was observed during the study period (Figure 109, Top). Concentrations were generally similar between replicates. The lowest nitrate concentrations were observed at the end of the 2001 through May of 2002. Overall, the highest concentrations were observed in 2000 and 2003.

Sulfate (T4)

No consistent seasonal pattern was observed during the study period (Figure 109, Middle). The lowest sulfate concentrations were observed at the end of the 2001 through May of 2002. A slight decreasing trend over the course of the study period was observed in all three replicates.

T5: Perennial / Poplar Trees

No agricultural amendments were used during this study. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here. Individual ions exhibiting a pattern or other characteristic of interest are discussed below (Figures 111-115).

pH (T5)

No consistent seasonal pattern or overall trend (Figure 111, Top).

Conductance (T5)

No consistent seasonal pattern or overall trend was observed (Figure 111, Middle). Replicate T5-R3 exhibited consistently higher conductance than the other two replicates over the study period.

Silica (T5)

Generally, Silica concentrations were lowest in the spring (April) increasing throughout the growing season and peaking in early fall (September) (Figure 111, Bottom). All three replicates tended to vary together.

Calcium (T5)

No consistent seasonal pattern was observed (Figure 112, Top). Calcium concentrations tended to be higher over the study period in T5-R3 and lowest in T5-R4.

Magnesium (T5)

No consistent seasonal pattern was observed (Figure 112, Middle). Magnesium concentrations tended to be higher over the study period in T5-R3 and lowest in T5-R4.

Alkalinity (T5)

No consistent seasonal pattern was observed (Figure 112, Bottom). Calcium concentrations tended to be higher over the study period in T5-R3 and lowest in T5-R4.

Sodium (T5)

No consistent seasonal pattern was observed (Figure 113, Top). Concentrations were similar in all three replicates, and all three replicates tended to vary together.

Potassium (T5)

In Replicates T5-R3 and T5-R4, soil solution concentrations of potassium generally increased from April through the end of July (Figure 113, Middle). Consistently lower concentrations of potassium were observed in T5-R2.

Chloride (T5)

Chloride showed no consistent seasonal patterns (Figure 113, Bottom). Concentrations of chloride in the soil solutions of all three replicates increased at the end of the study period.

Nitrate (T5)

Nitrate levels were very low in all three replicates and showed no consistent seasonal pattern or overall trend (Figure 114, Top).

Sulfate (T5)

Sulfate showed no consistent seasonal patterns; however, all three replicates showed a decreasing trend throughout the study period (Figure 114, Middle).

T6: Perennial / Alfalfa

Soil moisture was insufficient in all three replicates to yield samples between 6/5/2002 and 4/2/2003. Dolomitic lime was added in April 1999 and ammonium sulfate was added in August 2001. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here. Individual ions exhibiting an interesting pattern or other characteristic of interest in T6 are discussed below (Figures 116-120).

<u>pH (T6)</u>

No consistent seasonal pattern was observed over the study period (Figure 116, Top).

<u>Conductance (T6)</u>

No consistent seasonal pattern was observed over the study period (Figure 116, Middle). Conductance diverged among replicates after 2000.

<u>Silica (T6)</u>

Generally, concentrations in all three replicates tended to be lowest in April, increasing throughout the growing season and peaking in September or October (Figure 116, Bottom). All three replicates tended to vary together.

<u>Calcium (T6)</u>

No consistent seasonal pattern was observed during the study period (Figure 117, Top). An overall decreasing trend was observed in all three replicates. The highest concentrations of calcium were observed in 2000. Replicate T6-R3 consistently exhibited higher concentrations of calcium than the other two replicates over the course of the study period.

Magnesium (T6)

No consistent seasonal pattern was observed during the study period (Figure 117, Middle). An overall decreasing trend was observed in all three replicates. The highest concentrations of magnesium were observed in 2000.

Alkalinity (T6)

No consistent seasonal pattern was observed during the study period (Figure 117, Bottom). An overall increasing trend was observed in all three replicates, although the trend in T6-R2 was slight. The highest alkalinity concentrations were observed in 2002. Replicate T6-R3 consistently exhibited higher alkalinity concentrations than the other two replicates over the course of the study period.

Sodium (T6)

No consistent seasonal pattern was observed during the study period (Figure 118, Top). A decreasing trend was observed in all three replicates over the course of the study. The highest concentrations of sodium were observed in 2000, and the lowest were observed in 2002.

Potassium (T6)

No consistent seasonal pattern was observed during the study period (Figure 118, Middle). The highest potassium concentrations were observed in 2000.

Chloride (T6)

No consistent seasonal pattern was observed during the study period. Chloride concentrations were highest from February to April 2000, steadily declining through the end of November where they remained through the end of the study (Figure 118, Bottom).

Nitrate (T6)

No consistent seasonal pattern was observed during the study period (Figure 119, Top). In fact, distinct and opposite trends were observed in 2000 and 2001. In 2000, nitrate concentrations were highest in April, decreasing steadily through August. In 2001, nitrate concentrations were lowest in April, steadily increasing through July. Following the addition of ammonium sulfate on August 29, 2001, nitrate concentrations continued to fall and concentrations remained low for the remainder of the study period.

Sulfate (T6)

No consistent seasonal pattern was observed during the study period (Figure 119, Middle). Within 2 months of the ammonium sulfate addition, the highest concentrations of sulfate over the course of the study period were observed in T6-R2 and T6-R4. Insufficient soil pore water prevented sample collection at this time from T6-R3. While concentrations in soil solution samples collected T6-R4 returned to pre-addition levels by November, concentrations in

T6-R2 remained elevated through June 2002, when sample collection was disrupted due to low soil moisture.

T7: Early Successional / Herbaceous

Soil moisture was insufficient in all three replicates to yield samples between 7/17/2002 and 4/2/2003. All replicates were burned on May 15, 2002 and again on April 11, 2003. Total dissolved phosphorus, dissolved organic carbon, and ammonium-N were only measured for one season and will not be discussed here. Individual ions exhibiting an interesting pattern or other characteristic of interest in T7 are discussed below (Figures 121-125).

pH (T7)

No consistent seasonal pattern or overall trend was observed during the study period (Figure 121, Top).

Conductance (T7)

No consistent seasonal pattern or overall trend was observed during the study period (Figure 121, Middle).

Silica (T7)

Silica concentrations were highest in 2000 (Figure 121, Bottom). Each year, silica showed a seasonal pattern as concentrations increased from a low in the spring to a high in the fall.

Calcium (T7)

No consistent seasonal pattern or overall trend was observed during the study period (Figure 122, Top).

Magnesium (T7)

No consistent seasonal pattern or overall trend was observed during the study period (Figure 122, Middle). Magnesium concentrations were highest in the spring of 2000.

Alkalinity (T7)

No consistent seasonal pattern was observed during the study period (Figure 122, Bottom). In all three replicates, an increasing trend was observed during the study.

Sodium (T7)

No consistent seasonal pattern or overall trend was observed during the study period (Figure 123, Top). A sharp increase in sodium concentrations was observed in Replicate T7-R2 at the end of the study period in 2003.

Potassium (T7)

No consistent seasonal pattern or overall trend was observed during the study period (Figure 123, Middle). A sharp increase in concentrations was observed in all three replicates at the end of the study period in 2003 following the burn that occurred on 4/11/2003. No such increase was observed following the burn on 5/15/2002.

Chloride (T7)

In 2000 and 2001, chloride concentrations appear to be highest in spring decreasing through summer (Figure 123, Bottom). Concentrations are lowest in 2002 and highest in 2003. A sharp increase in all three replicates is observed at the end of the study period in 2003.

Nitrate (T7)

In general, nitrate concentrations appear to be peak in the spring and decrease through the summer (Figure 124, Top).

Sulfate (T7)

No consistent seasonal pattern was observed during the study period (Figure 124, Middle). Overall, a decreasing trend was observed in all three replicates over the course of the study.

Discussion

Vegetation affects the soil and soil solution in a number of ways, and these effects can often be species specific (Nihlgard, 1971, Dahlgren et al., 1991; Jobbagy and Jackson, 2003; Richter et al., 1994; Johnson-Maynard et al., 1997; Hagen-Thorn et al., 2004). Nutrient uptake and production of organic detritus are two obvious effects, but others are more subtle. Plant growth can acidify the soil through the uptake and storage of nutrients, through respiration which generates carbonic acid, and through the production of organic acids, and harvest of biomass can exacerbate soil acidification (Helyar and Porter 1989). Plants alter the water cycle through transpiration and soil temperature effects, thereby altering the moisture content of the soil (Baron et al., 1998). These effects can in turn affect soil microbial activity, the rate of mineral weathering, the cation exchange capacity of the soil, and nutrient concentrations in the soil and soil solution.

The evapotranspiration of soil moisture by plants would be expected to result in evaporative concentration of the solutes compared to precipitation. Mean annual recharge to the groundwater is about 28 cm on outwash plains such as the LTER site (Rheaume 1990), which is ~32% of the mean annual precipitation; the remaining 68% is lost by evapotranspiration. The actual evaporative concentration at any particular time over the growing season is difficult to predict. Nevertheless, while evapoconcentration must contribute to increased solute concentrations in soil solution compared to precipitation, the observed increases reported here are not congruent (i.e., solute proportions change relative to the source water), indicating that there must be sources and sinks of solutes in the soil environment.

Even the surface and surface structure of the plants above the ground can have an effect on the chemistry of precipitation via leaching and uptake processes during canopy throughfall and stem flow (these terms refer to precipitation passing through canopies or running down trunks, branches, and stems). Precipitation that contacts the vegetation canopy carries with it dry deposition that has accumulated on the surface of the plants and can even leach out nutrients from the leaves themselves (Johnson-Maynard et al., 2005). Throughfall in coniferous forests have been shown to lower the pH (Ugolini 1997), while contributing fewer base cations (Johnson-Maynard et al., 2005), although such effects of canopy leaching via throughfall appear to be most marked in older stands (Miller 1984).

Vegetation can affect the microbial community through competition for nutrients and symbiotic associations with microbes (Fenchel et al. 1998), which in turn affects the type and amounts of nutrients in the soil solution. Changes in vegetation also affect nitrogen mineralization rates, mainly as a result of changes in available organic nitrogen in the soil (Willson 1998, Grunzweig, et al., 2003), and this has implications for nitrate leaching.

All of the above processes contribute to the chemical evolution of precipitation into the soil solution. In humid climates, soil solutions ultimately recharge groundwater, which in turn discharges into surface water bodies. We rely on groundwater as a source of drinking and irrigation water, and groundwater-fed surface water bodies also serve as water supplies, as well as for recreation and fisheries. The most marked and important biological transformations of the soil solution take place in the rooting zone, and further transformations occur as the infiltrating water comes into equilibrium with the minerals in the soil parent material. Thus the various biogeochemical processes that influence the chemical evolution of soil waters close to the surface also impact the quality of groundwater and groundwater-fed surface waters. To the extent that land use and cover affect these processes, they impact subsurface and surface water quality at the landscape scale.

This study has revealed strong and often differential impacts of land use and cover on the chemical evolution of soil solutions. In the subsequent sections, I will compare the different vegetation types and management regimes to consider their most important impacts on soil solution chemistry.

Chemical Evolution in the Absence of Agriculture

Evolution of Soil Solutions from Precipitation in Forests

Relative to precipitation, soil solutions in the native Deciduous Forest were significantly enriched with calcium, magnesium, sodium, potassium, chloride, sulfate, and nitrate (Table 5). Conductivity and pH were also significantly higher in the soil solutions than in precipitation. In contrast, ammonium was significantly higher in precipitation than in the soil solution. Ammonium in precipitation was likely rapidly taken up by vegetation and microbes upon contact with roots and soil biota, or nitrified if present in excess of biotic demand (Qualls et al., 1991).

Relative to the Deciduous Forest Treatment, median soil solution concentrations of ammonium and magnesium were significantly lower in the Coniferous Forest Treatment. On the other hand, the soil solutions beneath the Coniferous Forest Treatment were significantly enriched in calcium, sulfate, and total dissolved phosphorus. However, in the case of calcium, variability among replicates within treatments was higher than variability between treatments, and in the case of sulfate, one replicate (DF-R2) appears to be responsible for the observed differences in median concentrations between the two treatments. In addition, the treatments do not differ in pH or median soil solution concentrations of nitrate or alkalinity (Figures 19-26). The lack of significant differences between the DF and CF treatments may be a result of the age of the conifer stands. Studies of canopy throughfall pH have found that conifer stands that are less than 60 years old do not differ significantly from broad-leaf stands, while the throughfall pH in older conifer stands is significantly lower (Miller, 1984). In one study of land use effects on soil N, P, C and pH, it was found that the vegetation and management effects persisted over 40–80 years of forest growth on agricultural soils (Falkengren-Grerup, et al., 2005). Even nitrification rates have been found to be strongly influenced by prior land use (Compton and Boone, 2000). The forest plantations that form the Coniferous Treatment range in age from 40 – 60 years, and these studies suggest that the lack of strong differences observed between the Coniferous and Deciduous Forests in the KBS LTER could be because canopy throughfall, nitrification rates, and soil composition may still be significantly influenced by prior land use.

Relative to the Deciduous Forest Treatment, the Successional Forest Treatment had significantly higher pH and median concentrations of total dissolved phosphorus (Figures 19-26). Median concentrations of ammonium, calcium, chloride, magnesium, nitrate-N, potassium, silica, sodium, and sulfate were all significantly lower in the Successional Forest Treatment. Most notable among the differences between treatments was that the median concentration of nitrate in the DF Treatment was 40 times greater than in the SF Treatment, where nitrate was only 0.08 mg/L (0.006 meq/L) (Table 5). This result is consistent with the theory put forth by Vitousek and Reiners (1975) that nitrate losses are expected to increase as stands age because ecosystem retention of limiting nutrients should decrease from strong retention in stands that are rapidly accumulating biomass to essentially no net retention in steady-state old growth systems. In fact, median soil solution concentrations of nitrate were also very low in both the early successional treatment (T7) and in the fast-growing clonal poplar treatment (T5), which had median soil solution concentrations of 0.23 mg N/L (0.02 meq/L) and 0.00 mg N/L (0.00 meq/L), respectively.

Chemical Evolution in the Presence of Agriculture

Effects of Agriculture: Conventional Agriculture compared to Deciduous Forest

Compared to the native Deciduous Forest Treatment (DF), soil solutions in the Conventional Agriculture Treatment (T1) were significantly higher in pH and conductivity as well as median concentrations of total dissolved phosphorus, total alkalinity, calcium, potassium, and nitrate (Figures 35-41). In contrast, the DF treatment had significantly higher median soil solution concentrations of magnesium, silica, sodium, chloride, and sulfate. No significant differences between treatments in the median concentration of dissolved organic carbon were observed.

Increased soil solution concentrations of calcium, potassium, total dissolved phosphorus, nitrate and alkalinity in the conventional agriculture system (T1) are not surprising given the fertilizers and other agricultural amendments this system receives (Tables 2 and 5). The impacts of some of these amendments on subsurface water quality are well known (Böhlke 2002). Concerns regarding agrichemical contaminants in water leaving agricultural land through runoff and groundwater seepage continue to intensify among ecologists (Matson et al., 1997; Fen et al, 1998; Jackson et al., 2001) and human health officials (Fan and Steinberg, 1996; Shroder et al., 2004).

Explanations of the relatively elevated concentrations in the deciduous forest treatment of magnesium, silica, sodium, chloride, and sulfate are perhaps less obvious. In research on groundwater and surface water bodies, chloride has been identified as a conservative ion and sulfate as a semi-conservative ion that can be used to estimate evaporative concentration (Claassen and Halm, 1996; Leydecker and Melack 2000). The higher concentrations of sulfate and chloride in the soil solution may indicate that evaporative concentration of soil solutes in the deciduous system is greater than in the agricultural system. Greater evapotranspiration by the forest vegetation might be expected because it has a longer growing season, deeper roots, and a greater canopy leaf surface area than the annual row crops.

Lower median soil solution concentrations of magnesium were also found in the coniferous forest treatment (CF) relative to the deciduous forest treatment, while chloride concentrations were not significantly different. Therefore, between these two systems, differing concentrations of magnesium may be the result of differences in nutrient cycling and not the result of evapoconcentration. However, it is not possible to distinguish the effects of evapoconcentration and nutrient cycling in the deciduous system (DF) relative to conventional agriculture (T1), and the differences in median soil solution concentrations of magnesium may be the result of differences in both evapotranspiration and nutrient cycling.

Effects of Tillage Practices: Conventional Till (T1) vs. No Till (T2)

Both row-crop treatments T1 and T2 received the same amendments at the same time and rate, with the exception of lime and ammonium sulfate. In 1999, more lime was applied to the no-till system (T2) than the conventional till system (T1), 0.8 tons/acre and 0.5 tons/acre, respectively. Ammonium sulfate was applied in the no-till system (T2) at a rate of 8 lbs/ha in 2000, while no ammonium sulfate was applied to the conventional system (T1) that year. Median soil solution concentrations of nitrate, potassium, and sulfate were all significantly higher in the conventional till system (Figures 35-41). pH and median concentrations of total dissolved phosphorus, total alkalinity, silica, and sodium were significantly higher in the no-till treatment; however, one replicate in the no-till treatment (Replicate T2-R3) is responsible for the significant differences between the two treatments for sodium and total dissolved phosphorus (Figures 42 and 45, Bottom).

The remaining significant differences include nitrate, potassium, sulfate (higher in conventional till), and pH, silica, and alkalinity (lower in conventional till).

Lower pH (higher acidity) is associated with higher weathering rates of silicate minerals and the consumption of alkalinity. One reason why the pH is lower in the conventional till system (T1) may be the incomplete dissolution of lime, which was added as a soil amendment to both systems. The conventional till system (T1) consistently showed the presence of carbonate in the upper meter of soil while the no-till system did not (Figure 125). Analysis of soil cores taken nearby the treatment plots and adjacent to monoliths at the KBS "Interactions" plots south of the LTER plots established that the depth of the carbonate-leached zone is approximately 1.3 m to 1.8 m; therefore, one can assume that the carbonate detected in the upper meter of soil in the conventional till system (T1) is due to the application of lime to the surface

(Hamilton et al., in review). Ascertaining the impediments to lime dissolution in the conventional till system is beyond the scope of this study.

Despite additional nitrogen being added to the no-till system (T2) in 2000 in the form of ammonium sulfate, the conventional till system (T1) had significantly higher median soil solution concentrations of nitrate. The finding of higher nitrate beneath conventional till systems is consistent with a previous study performed in Georgia, U.S.A. (House et al., 1984). The reasons for increased soil solution concentrations of nitrate beneath conventional till may be the result of increased uptake of nitrogen by weeds in the no-till system and higher rates of N mineralization in conventional till systems (Stinner et al., 1984), which is thought to be stimulated by tillage. The study performed by Stinner et al., (1984) did not find any significant difference in soil solution concentration of potassium beneath no-till and conventional till systems.

The higher median soil solution concentration of sulfate in the no-till system can be explained by the additional application of ammonium sulfate in 2000 to only the no-till system (T2).

Effects of Varying Levels of Inputs: Conventional Input vs. Reduced Input vs. Zero Input Row-Cropping Systems

Conventional Input (T1) vs. Reduced Input (T3)

The reduced input treatment (T3) did not receive any ammonium sulfate, but otherwise received the same amendments as the conventional input treatment (T1), but at a reduced level and/or frequency (Table 2). Both treatments were tilled and otherwise managed in the same manner.

Conductivity and median concentrations of dissolved organic carbon, total alkalinity, ammonium, nitrate, calcium, potassium, total dissolved phosphorus, chloride, and sodium did not differ significantly between Treatments T1 and T3. pH and median concentrations of silica and magnesium were significantly higher in T3, while the median concentration of sulfate was significantly lower.

The lower median soil solution concentration of sulfate can be explained by the fact that the ammonium sulfate was applied to the conventional input treatment (T1), but not applied to the reduced input treatment (T3).

Lower pH (greater acidity) is associated with higher concentrations of silica (Table 2); therefore, it is not surprising that the conventional input treatment (T1) had a higher median soil solution concentration of silica than the reduced input treatment (T3).

The conventional input treatment (T1) and the reduced input treatment (T3) both received 0.5 tons/acre of lime in 1999. However, not all of the lime in the conventional till treatment (T1) dissolved, as indicated by soil carbonate screening of the upper meter of soil several years later (Figure 35-41). In addition, the conventional input treatment (T1) also received higher rates of nitrogen inputs. Additional nitrogen inputs may have depressed the pH in the conventional input treatment (T1) due to nitric acid generation from plant uptake and nitrification.

Interestingly, despite the higher inputs of nitrogen in the conventional till system (T1), the median soil solution concentrations of nitrate were not significantly different between the two treatments and had nearly the same median concentration and interquartile ranges (Table 5, Figure 38, Bottom). The conventional treatment (T1) received approximately twice as much N fertilizer, but a winter legume cover crop was planted in the reduced input treatment (T3) following wheat and corn rotations, and the N mineralization potential was higher in the zero input treatment (T4) than in the conventional input treatment (T1) (Robertson et al., 2000). It is possible that the legume cover crop and higher N mineralization potential in the zero input treatment (T4) coincidentally resulted in similar nitrate concentrations between these two treatments.

The significantly lower median concentration of magnesium in the soil solution of the conventional input treatment (T1) relative to the reduced input treatment (T3) is interesting. Dolomitic limestone is the only amendment added to either system that contains magnesium. The lower dissolution rates of the lime in the conventional input treatment (T1), as indicated by the presence of carbonate in the upper meter of soil (Figure 125), would lead one to predict that magnesium concentrations would also be lower in this treatment, and this was the case. The magnesium values in the conventional treatment (T1) are not significantly different from the unlimed treatment (T4).

Conventional Input (T1) vs. Zero Input (T4)

pH, conductivity, and median concentrations of dissolved organic carbon, total alkalinity, ammonium, nitrate, silica, sodium, magnesium, and chloride and did not differ significantly between Treatments T1 and T4. Concentrations of calcium, potassium, sulfate, and total dissolved phosphorus were significantly higher in T1 than T4, while median concentrations of sodium were significantly lower (Figures 35-41).

Higher median soil solution concentrations of calcium, potassium sulfate, and total dissolved phosphorus in the conventional input treatment (T1) can be explained by the application of fertilizer and lime to the conventional input treatment (T1).

Due to the ecological and human health concerns of nitrate pollution, it is of interest that median soil solution concentrations of nitrate in the zero input treatment (T4) were not significantly different from those in the conventional input treatment (T1) (Figure 38, Bottom). As is the case in the reduced input treatment (T3), a winter legume cover crop is planted in the zero input treatment (T4) following wheat and corn in the crop rotation. In addition, the zero input treatment (T4) had a higher N mineralization potential than the conventional input treatment (T1) (Robertson et al., 2000). As was suggested for T1 vs. T3 above, is possible that the legume cover crop and higher N mineralization potential in the zero input treatment (T4) resulted in similar nitrate concentrations between the T1 and T4 treatments.

The conventional input treatment (T1) received potash (mainly KCl) while the zero input treatment (T4) did not. The potassium from potash may be taken up by plants but the chloride should behave conservatively in these soils. However, there was no significant difference in median soil solution concentrations of chloride between the T1 and T4 treatments. The median soil solution concentration in the conventional input treatment (T1) was 0.90 mg/L (0.03 meq/L) with an interquartile range of 0.42 to 2.22 mg/L (0.01 – 0.06 meq/L). The median soil solution concentration of the zero input treatment (T4) was 0.64 mg/L (0.02 meq/L) with an interquartile range of 0.27 mg/L to 0.95 mg/L (0.01 – 0.03 meq/L) (Table 5). Despite the lack of a significant difference between the two treatments, the chloride additions in the conventional input treatment (T1) appear to cause the soil solution concentrations in this treatment to be more variable and rise to higher concentrations than in the zero input treatment (T4). It is likely that the chloride added in potash was rapidly flushed from the soils, resulting in little effect on the median concentrations.

Chapter 2: The Fate of Carbon in Lime

Introduction

The future course of global climate change depends critically on near-term CO_2 mitigation measures, including the sequestration of CO_2-C in organic or inorganic forms (Caldeira *et al.* 2004). On a global scale, one of the most important chemical weathering reactions is the dissolution of carbonate minerals by reaction with carbonic acid, which consumes CO_2 to yield dissolved inorganic carbon in the form of carbonate alkalinity (Stumm & Morgan 1996). In humid and subhumid climates, carbonate alkalinity is subsequently transported through groundwater flow paths and eventually into streams and rivers, with little back-precipitation (Reardon *et al.* 1979, Gaillardet *et al.* 1999, Drees *et al.* 2001, Szramek & Walter 2004), and ultimately reaches the oceans. On geological time scales this alkalinity input to the oceans may be approximately balanced by precipitation of carbonate minerals (Milliman 1993, Berner 1999). However, in relation to the immediate problem of anthropogenic CO_2 as a driver of global climate change, the time scale for transport from the sites of mineral weathering in soils through groundwater and ultimately to the oceans is long (centuries), and this balance may be disrupted by changes in atmospheric CO_2 (Andersson & Mackenzie 2004). Thus changing rates of carbonate mineral weathering and subsequent re-precipitation play an important role in today's atmospheric CO_2 balance, a major driver of climate change.

The weathering of indigenous carbonate minerals has been augmented by the widespread use of agricultural "lime," most often applied as calcite or dolomite [$CaCO_3$ or $CaMg(CO_3)_2$, respectively]. Periodic liming is necessary to counteract soil acidification in cultivated soils, which usually results mainly from nitrogen and sulfur fertilizers, cultivation of N-fixing crops, and crop harvest (Helyar & Porter 1989, Fisher *et al.* 2003). Liming has long been a foundation of agriculture in humid regions throughout the world, and has increased with agricultural intensification. In the U.S. alone, ~30 Tg y-1 of lime are applied to agricultural fields (West & McBride 2005), which is equivalent to about 3.7 Tg y-1 of carbon. While not large compared to other terms in the global or U.S. CO_2 budget, this lime carbon flux represents 31 % of the annual change in the U.S. CO_2 loading rate (12 Tg C y-1 for 2002-2003), and thus is potentially significant from the standpoint of atmospheric CO_2 stabilization. Moreover this flux is also significant when compared to the potential *maximum* carbon sequestration associated with mitigation measures such as no-till agriculture that increase soil organic matter; such measures are estimated to be capable of sequestering at most 100-150 Tg C y-1 in the U.S. during several decades (CAST 2004). Projections of the worldwide expansion of intensive agriculture suggest that global lime use may increase nearly 3-fold in the next 50 years (Tilman *et al.* 2001). Thus it becomes even more important to consider the implications of liming for terrestrial carbon sequestration when contemplating the impact of agriculture on global climate change (West & McBride 2005).

Liming of agricultural soils takes on greater importance when other greenhouse gas fluxes in addition to carbon are considered. In an analysis of the global warming potential (GWP) of different agricultural systems, Robertson *et al.* (2000) found agricultural liming to be the second most important source of GWP in their annual crop systems (after N_2O release), and the most important source in their alfalfa system. Robertson *et al.*'s calculations assumed that the inorganic carbon in these minerals eventually becomes CO_2 as the lime is consumed, following IPCC emissions guidelines (Houghton *et al.* 1997). Lime is typically applied every few years to agricultural soils to keep soil pH within a range favorable for crop growth; if all of this lime dissolves to CO_2 prior to the next lime application, then on average 23-34 g CO_2-C/m2 per year was released in their conventionally farmed annual crops and 80 g C/m^2 per year was released in their alfalfa system. This contrasts with N_2O emissions of around 58 g C-equivalents/m^2 per year in all cropping systems, and in the no-till system it negated a significant portion of the mitigation potential associated with soil organic carbon storage, ca. 110 g C/m^2 per year (Table 14), a typical value for Midwest U.S. no-till cropping systems (Lal *et al.* 1999). CO_2 contributions from liming are thus large relative to other sources of GWP in these systems and also relative to estimates of CO_2 originating from carbonate precipitation caused by dryland irrigation with alkaline groundwater (ca. 12 g C m-2 y-1: Schlesinger 1999, 2000).

Notwithstanding the IPCC assumption that all lime C ultimately becomes CO_2, biogeochemical theory suggests that the dissolution of carbonate minerals can act as either a net source or sink for CO_2. In moderately acid (pH 5-6.5), neutral and alkaline soils, most of the dissolution of carbonate minerals can be ascribed to carbonic acid weathering, which is the major natural process of limestone weathering and the primary source of alkalinity to most surface and ground waters (Stumm & Morgan 1996). Dissolved CO_2 from root and microbial respiration exists in equilibrium with the weak acid H_2CO_3, and hereafter we refer to the sum of these forms as "soil CO_2". Soil CO_2 reacts with solid carbonates as shown in this reaction using dolomite as an example:

$$CaMg(CO_3)_2 + 2H_2CO_3 \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad \text{Eq. 1}$$

Note that carbonic acid weathering is a *sink* for soil CO_2 because every mole of lime-derived C that dissolves yields 2 moles of HCO_3^- (the dominant form of carbonate alkalinity at the pH of most soil waters). Dissolution is enhanced in soils with high biological activity because respiratory CO_2 typically accumulates to partial pressures one to two orders of magnitude above atmospheric levels, with consequent increases in carbonic acid.

Alternatively, in the presence of a strong acid such as HNO_3 produced by the nitrification of NH_4^+ to NO_3^-, the dissolution of carbonate minerals acts as a CO2 *source* rather than a CO_2 sink:

$$CaMg(CO_3)_2 + 4HNO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4NO_3^- + 2CO_2 + 2H_2O \qquad \text{Eq. 2}$$

This reaction becomes important at pH < 5 and greatly enhances the rate of dissolution of carbonate minerals (Plummer *et al.* 1979). In this reaction no HCO_3^- alkalinity is produced.

Similarly, if the HCO_3^- produced by carbonic acid weathering subsequently comes into contact with H^+, which may occur after downward transport by infiltration, it will be consumed and CO_2 will be produced. The net result of these reactions is for the carbon in lime to become a source of CO_2 in the soil and, ultimately, to contribute to emission of CO_2 to the atmosphere. The lime derived cations (Ca^{2+} and Mg^{2+}) remain in solution, balanced in charge by the strong acid anions (e.g., NO_3^- in Eq. 2).

In this study, I seek to better understand the fate of carbon in lime by comparing the chemistry of soil solutions beneath unmanaged vegetation and limed row crops. This represents one facet of a broader study on this topic that also evaluates soil water data from other KBS sites and from streams and tile drainage (Hamilton et al. in review).

Methods

Study sites

Soils at the KBS site are well drained sandy loams of moderate fertility developed on glacial till and outwash. Mean annual temperature is 9.7 °C. Annual precipitation is 930 mm, with monthly precipitation exceeding evapotranspiration from Oct-Apr; annual recharge is 280 mm. The dominant soil series are alfisols, which are typical of soils developing on uplands under forest vegetation, and include the Kalamazoo (fine-loamy, mixed, mesic Typic Hapludalfs) and Oshtemo (coarse-loamy, mixed, mesic Typic Hapludalfs) series. Clay content ranges from 13-30% and dominant silicate minerals include plagioclase, K-feldspar, quartz and amphibole. Carbonate minerals (dolomite and calcite) occur in the glacial drift but are leached out of the upper soil profile, as is typical of glacial soils in this region (Drees *et al.* 2001). Calcite and dolomite occur in roughly equal abundance by mass at depths of ~1.5-3 m (L. Jin, unpublished data). Cation exchange capacity in the upper meter of these soils ranges from 4-15 cmol(+) kg-1 and organic matter content of the surface plow layer in the farmed soils is about 2-3%. Permeability is moderate to high, generally increasing with depth.

Sampling soil solution chemistry

Soil solutions in the unsaturated zone were sampled across the experimental treatments of the KBS Long-Term Ecological Research (LTER; http://lter.kbs.msu.edu). These treatments include intensive row-crop systems (corn/soybean/wheat rotations or continuous alfalfa) that receive conventional inputs of fertilizer, lime, and potash, as well as nearby unmanaged deciduous forests of early and late successional ages that provide a reference against which the effects of agriculture can be compared.

Soil solutions from 1-1.2 m depth in the LTER experimental plots were collected under low tension using samplers constructed of stainless steel, porous Teflon, and silica flour (Prenart®), which can sample matric water held in the soil below field capacity (Lajtha *et al.* 1999). These solutions were collected from above the depth of indigenous carbonate minerals (See Results).

The samplers were installed in 1995 in 10 of the LTER treatments by coring at an angle beneath an undisturbed soil profile. Each collector draws from three separate samplers spaced a few meters apart. Tension (0.5 atm) was applied to the samplers and the resulting solution was collected after 24 h. Samples were filtered with glass fiber filters (pore size 0.45 μm) and immediately refrigerated.

Soil solutions were collected biweekly over 4 years (1999-2003) during the frost-free part of the year (Mar-Dec) when there was enough water to yield a sample. Crushed dolomitic lime (molar ratio of Mg:Ca = 0.92) was added to each cropping system treatment when prescribed by soil tests and at quantities recommended by standard lime-requirement protocols. Over the period 1997-2003, dolomitic lime was added in 1997 and 1999 at 1.1-2.2 Mg/ha to the alfalfa and corn/soybean/wheat rotations.

Water Analyses

As noted in Chapter 2, air-equilibrated pH was measured in the lab on samples from lysimeters; the pH electrodes were calibrated using buffers of pH 4 and 7. Water samples for analysis of solutes were filtered on the day of collection through 0.45-μm membrane filters and refrigerated. Subsamples for dissolved Ca^{2+} and Mg^{2+} were preserved with 0.5% nitric acid.

Subsamples for analysis of total alkalinity were either filtered (soil waters) or unfiltered (stream waters) and refrigerated until analysis. Tests confirmed the stability of these samples in storage, and that filtration made no difference for the alkalinity measurements in the stream samples.

Total alkalinity was measured by Gran titration on unfiltered samples (Cantrell *et al* 1990). Given the ion concentrations and pH of these solutions, total alkalinity is almost entirely carbonate alkalinity in the form of HCO_3^-, therefore total alkalinity is considered a measure of HCO_3^-. While gently stirring the sample, titrant (0.3 N HCl) was added to bring the pH below 4.0, then 6-8 acid additions were made to produce a titration curve in the range of pH 3.3-4.0. Total alkalinity was calculated by extrapolation of the Gran plot to the endpoint using linear regression. The normality of the titrant stock solution of HCl was verified using Na_2CO_3.

Dissolved Ca^{2+} and Mg^{2+} were analyzed by flame atomic absorption spectrophotometry (AAS) after addition of an acidic solution of lanthanum chloride to suppress interferences. Standards bracketing sample concentrations were prepared from certified stock solutions. Other analyses that were conducted on most samples but are peripheral to this paper included Na+ and K+ (flame AAS), Cl^-, NO_3^-, and SO_4^{2-} (ion chromatography), and silica (molybdenum blue colorimetry).

Soil Cores

Soil cores were collected to ~1-m depth from across the study sites in 1999 for the LTER decadal carbon survey. Cores were taken with a pneumatic coring device (Geoprobe®), after which the coring holes were backfilled with sand and capped with bentonite to avoid creating preferential flow paths for infiltrating waters. Soil horizons were delineated by Dr. Delbert Mokma of the Department of Crop and Soil Sciences at MSU. The cores were sectioned by horizon and analyzed for organic and inorganic carbon. Note: The cores were collected in April, following the addition of dolomitic lime to Treatments 1, 2, 3 and 6.

Soil Analysis

Finely milled samples (< 0.5 mm diameter) from each horizon of the soil-core samples collected in 1999 were screened for the presence of carbonates by measuring the pressure response of acidified samples. In general, each core yielded three samples labeled by treatment and replicate as shallow, middle, or deep. The 440 samples screened were randomly selected from the more than 800 samples available. At least five samples from each treatment were screened for the presence of carbonates, and all treatments had at least one sample screened from each depth.

Approximately 1 g of dry soil was acidified using 5 M HCl and the pressure response, as measured by an MKS Baratron Type 122A Absolute Pressure Gauge, was recorded after five minutes and again after two hours. The method was developed based upon the work of Evangelou et al. (1994) and Loeppert and Suarez (1996). By measuring the pressure produced by CO_2 evolution between five minutes and two hours, we could partition it into calcite ($CaCO_3$) and dolomite ($(CaMgCO_3)_2$) sources, the former reacting immediately and the latter being more resistant to acid dissolution.

Conceptual model of carbonate mineral dissolution

Figure 128 presents a conceptual model for partitioning carbonate mineral dissolution into C source or sink terms. The model applies to weathering of indigenous carbonate minerals as well as for carbonate minerals used in liming. The dashed line depicts the 1:1 ratio of Ca^{2+} + Mg^{2+} to HCO_3^- that is expected if dissolution occurs by reaction with carbonic acid. Ratios exceeding unity are produced as the HCO_3^- is consumed by acidity. The solid line represents the elemental stoichiometry in the carbonate minerals (calcite or dolomite). Solutions plotting in "CO_2 sink" area to the right of that line represent dissolution of carbonate minerals plus sequestration of soil CO_2, while solutions plotting to the left in the "CO_2 source" area represent dissolution of carbonate minerals and conversion of at least some of the carbonate-C to CO_2.

Most lakes and rivers in watersheds containing carbonate minerals show concentrations of Ca^{2+}, Mg^{2+} and HCO_3^- that plot close to the 1:1 line in Figure 128, unless they are also strongly affected by dissolution of evaporite minerals (Wright 1984; Stallard & Edmond 1987).

In the absence of carbonate minerals, silicate mineral weathering may be the dominant source of Ca^{2+}, Mg^{2+} and HCO_3^-. However, in soils of southern Michigan, silicate weathering generally yields concentrations of Ca^{2+} and Mg^{2+} of no more than 0.2 and 0.14 meq L-1, respectively (Jin *et al.* 2006), which is a small contribution compared to the weathering of carbonate minerals where they exist. Therefore the model as used in this study does not attempt to correct for solute contributions from silicate weathering, and it is only used in cases where carbonate mineral weathering is the predominant source of these solutes, as indicated by a sum of Ca^{2+} and Mg^{2+} above 2 meq L-1 (see Results).

The CO_2-C sink strength associated with the dissolution of carbonate minerals can thus be estimated from the departure of samples from the source-sink division line, and is expressed as a percentage of the C contained in the carbonate mineral material:

$$CO_2\text{-C sink strength (\%)} = [HCO_3^- - 0.5(Ca^{2+} + Mg^{2+})]/[0.5(Ca^{2+} + Mg^{2+})]$$

Eq. 3

where concentrations are in meq L-1. This calculation yields positive values when the carbonate minerals are a net CO_2 sink (sequestering CO_2) and negative values when they are a net CO_2 source, as shown in the hypothetical examples in Figure 128.

Statistics

CO_2-C sink strength across treatments was compared using notched box plots. The box plots provide a convenient and compact summary of asymmetric frequency distributions that includes medians and quartiles. The notches indicate the approximate 95% confidence intervals around the median and the boxes extend across the interquartile range (i.e., from the 25th to 75th percentiles). The length of the notches is calculated using a formula based on the formal concept of a hypothesis test and is useful even when the assumptions of the test are not strictly met (Chambers, et al., 1983). For a detailed discussion of this statistical method and how it compares to Analysis of Variance (ANOVA), see Chapter 2.

Results

Soil Carbonate Content

Soil core samples screened for the presence of carbonate minerals by measuring the pressure response of acidified samples were separated into three categories by creating confidence intervals based on the response of blanks and spiked samples. The recovery for dolomite standards was similar to that for calcite standards (Figure 126). Results for the KBS LTER Main Site are summarized in Figure 127. No spatial pattern in the presence or absence of carbonate was observed. Carbonates were observed in all replicates of the Conventional Input / Conventional Till Treatment (T1), and in none of the replicates of the Alfalfa Treatment (T6), although both treatments received dolomitic limestone as a soil amendment in 1997 and 1999. Lime was also added to the No-Till and Reduced Input Treatments (T2 and T3). Within the No-Till Treatment (T2), carbonates were observed in six of the fifteen samples screened in Replicate T2-R1, six of the fifteen samples screened in Replicate T2-R2, four of the fifteen samples screened in Replicate T2-R5, and in one of the fifteen samples screened in Replicate T2-R6. No carbonates were detected in Replicates T2-R3 or T2-R4. In all replicates of the Reduced Input Treatment (T3), carbonates were detected in only 1 sample. In the unlimed Treatments, Zero Input, Poplar, and Successional Field, (T4, T5, and T7, respectively), carbonates were detected in only seven of the 107 samples screened for carbonates.

Of the 58 samples screened for carbonates in the Deciduous, Coniferous, and Successional Forest Treatments, carbonates were detected in only 6 samples. (Results not shown.)

Soil Solutions

The data from tension soil-solution samplers in the LTER treatments indicate the chemistry of soil solutions in the unsaturated zone beneath row crops receiving lime applications (Figure 129, Bottom). Nearby deciduous forests and successional fields (fallow for 15 years) serve as a reference for concentrations expected in these soils in the absence of agriculture and liming (Figure 129, Bottom). These samples were collected from above the depth of indigenous soil carbonates, and because of the collection method they represent variable proportions of saturated flow and matric water (Lajtha *et al.* 1999; see also Chapter 2).

The forests and successional fields usually showed Ca^{2+} + Mg^{2+} of ~2 meq/L or less. In contrast, both Ca^{2+} and Mg^{2+} often were often elevated in the limed treatments compared with the forest sites.

Referring to the conceptual model in Figure 128 and considering only samples in Figure 129 with clear evidence of carbonate mineral influence (i.e., Ca^{2+} + Mg^{2+} > 2 meq/L), these soil solutions span the entire range from close to the carbonate weathering line (i.e., indicating that dissolution has acted as a CO_2 sink equivalent to the C content of the lime, as would be expected for carbonic acid weathering) to points lying close to the y-axis (indicating nearly complete conversion of lime C to soil CO_2). The CO_2-C sink strength for these agricultural soil solutions, calculated using Eq. 3, is highly variable but suggests that, on average, liming is neither a consistent source nor a sink for CO_2 (Figure 133). The no-till treatment tended to show positive CO_2-C sink strength in contrast to the other two, but included samples spanning the entire range.

The major solute chemistry of these samples was variable but on average Ca^{2+} and Mg^{2+} were the dominant cations in all cases, and HCO_3^- was the dominant anion, followed by NO_3^- in the agricultural treatments. The molar ratio of Mg^{2+}: Ca^{2+} averaged 0.27 in the agricultural treatments and 0.46 in the unmanaged forest and old-field treatments. Concentrations of NO_3^- (mean, 1.24 meq L-1 across the 3 treatments) tended to exceed those of SO_4^{2-} (mean, 0.16 meq L-1). The air-equilibrated pH averaged 7.12 in the agricultural treatments and 6.63 in the unmanaged forest and old-field treatments.

Discussion

Sources of Ca^{2+}, Mg^{2+}, and HCO_3^- in soil solutions

Agricultural liming was the most likely source of elevated Ca^{2+}, Mg^{2+}, and HCO_3^- ions in soil solutions from the upper meter of soils around the KBS LTER site (Figure 129, Bottom). In the absence of liming (or indirect inputs of lime via compost), soil solutions in the upper meter of soils around the KBS LTER usually have concentrations of Ca^{2+} + Mg^{2+} below 1 meq/L, and carbonate mineral dissolution is evidently not the predominant source of these ions (Figure 129, Top).

Carbonate minerals are abundant in the underlying glacial drift, however, and at KBS they abruptly increase in abundance between soil depths of 1.5-2 m. Upon reaching the depth of indigenous carbonates, infiltrating soil solutions are rapidly and strongly influenced by carbonate mineral dissolution (e.g., Figure 137). In the relatively permeable, sandy loam soils that are common in southwestern Michigan, most water infiltrates the soils rather than running off over the surface, and most infiltration would reach the depth of carbonate minerals well above the water table. Thus the chemistry of groundwater-fed surface waters in this area reflects the fact that groundwater exists in equilibrium with abundant solid-phase dolomite and calcite in the glacial drift, and that it acquires its Ca^{2+}, Mg^{2+}, and HCO_3^- largely by carbonic acid dissolution (Hamilton et al. in review).

Spatial Patterns and Replicate Behavior

While treatments T2 and T4 showed some evidence of potential carbon sequestration when the carbon sink strength was calculated using the equation provided in the results section (Figure 133, Top), replicates T4-R3 and T2-R3 were significantly different from the other two replicates within their respective treatments for alkalinity and calcium and magnesium, and were also significantly different from all other replicates with respect to pH (Figures 134 and 135). These two replicates also tended to plot along the one-to-one line, indicating net carbon sequestration as the lime dissolved (Figures 130, Bottom and 131, Bottom), and when the CO_2-C sink strength is calculated by replicate, these two replicates are responsible for the overall sink effect of their respective treatments and it is only T2-R3 and T4-R3 that have confidence intervals that do not overlap zero (Figure 133, Bottom).

The treatment replicates that show the greatest carbonate mineral influence include T1-R4, T2-R3, T3-R3, T4-R3, and T6-R3 (Figures 130-132). The unlimed treatment Zero Input / Conventional Till (T4) is included here because the concentrations of Ca^{2+} + Mg^{2+} indicate evidence of carbonate mineral influence. When plotted spatially, these replicates form a spatial pattern that is consistent with the spatial pattern evident for alkalinity (Figure 138).

It is important to note that when soil samples collected from the upper meter of soil were screened for carbonates, no such pattern among the replicates emerged (Figure 127). Therefore, the pattern of carbonate mineral influence noted here cannot be the result of native carbonates or lime additions in the upper meter of soil.

The most likely explanation for these patterns is that in Replicates T2-R3 and T4-R3, the samplers are either set within a layer of native carbonates that is deeper than the 1-m cores, or that the samplers are set within a layer that is subject to upward flow of water by capillary action, and water that has been in equilibrium with native carbonates is thus collected by the sampler. Water in a loamy soil can rise by capillary action up to 45 cm (Brady 1995). If water in equilibrium with native carbonates was influencing the soil solutions, it would be expected that the soil solutions collected from Replicate T2-R3 and T4-R3 would have similar pH and similar concentrations of calcium, magnesium, and alkalinity. While Replicate T2-R3 did exhibit a higher concentration of calcium, magnesium, and total alkalinity (Figure 135, Top and Bottom), this difference can be explained by the fact that Treatment T2 receives lime and Treatment T4 does not (Table 2). In addition, the conductivity and ratio of calcium plus magnesium to alkalinity from both replicates are consistent with groundwater samples obtained from wells located near the study areas (Figure 137), which are in equilibrium with underlying native carbonates (dolomite).

The net carbon flux model cannot be applied to replicates T2-R3 and T4-R3 to determine the fate of carbon in the lime because of the possibility of influence of native carbonates. Since these are the only two replicates that exhibited positive CO_2-C sink strengths with confidence intervals that did not overlap zero, it must be concluded that the use of lime results in a net source of carbon to the atmosphere in each of the treatments within this study.

Conclusion

Although this study did not find net carbon sequestration within these treatments over the study period, the statistically significant relationship between nitrate-N concentrations and the CO_2-C sink strength (Figure 136) is consistent with the conceptual model, and the results of this study do not rule out carbonic acid dissolution of lime as a viable sequestration pathway in other systems. Hamilton et al. (in review) present a more thorough analysis of the problem, drawing on data from a variety of waters including but extending beyond the LTER soil solutions.

The difference between the results of this study and the broader study may lie in the sampling method utilized. The broader study included water collected beneath limed row crops via gravity drainage. Water remaining in the soil matrix after saturated flow ceases, such as that sampled by tension lysimeters, may be more susceptible to eventual reaction with strong acids, whereas infiltrating waters may tend to bypass sites of reaction, and/or they may tend to pass through soils during cooler times of the year when there is lower microbial activity that generates strong acidity.

Chapter 3: Effects of Vegetation and Agronomic Management Practices on Nitrogen Losses through Leaching: Implications for Management

Introduction

In unmanaged ecosystems such as deciduous forests and old fields in the midwestern U.S., most of the proximate nutrient requirement of land plants is supplied by the decomposition of organic matter in the soil, and not from new inputs from the atmosphere (including nitrogen fixation) or rock weathering (Schlesinger, 1997). The source of this organic matter is litter supplied by the terrestrial vegetation. The decomposition of this litter, whereby organic forms of nutrients are converted into inorganic forms, is known as mineralization and is mostly the result of the activity of soil microbes (Sinsabaugh et al., 1993). As inorganic nutrients are released from plant litter, soil microbes rapidly take up these nutrients. The same nutrients that are most often limiting to plant growth, nitrogen and phosphorus, are also limiting to microbial growth, pitting microbes and plants in direct competition with each other (Qualls, 1991).

The intrasystem cycle of nutrients in terrestrial systems is considered "leaky" when there are large losses of nutrients via leaching into infiltrating waters. Coniferous forests, which contribute less litter to the soil than deciduous forests, have been found to have lower rates of leaching losses than deciduous forests (Reich et al., 1995), and greater nutrient use efficiency (Cole and Rapp, 1981). However, it is important to distinguish between mature deciduous and conifer stands, versus successional stands. Vitousek and Reiners (1975) postulated that nutrient losses are expected to increase as stands age because ecosystem retention of limiting nutrients should decrease from strong retention in stands that are rapidly accumulating biomass to essentially no net retention in steady-state old growth systems.

Managed ecosystems, such as agroecosystems, differ markedly from unmanaged ecosystems in one particularly profound way: biomass is removed as harvest, reducing the ability of intrasystem nutrient cycling to satisfy plant nutrient needs. As noted earlier, most of plant nutrient needs are met through the decomposition of organic matter. When biomass is removed in conventional agroecosystems, organic matter is not returned to the soil for decomposition, resulting in the net loss of soil organic carbon and nitrogen over time (Knops and Tilman, 2000). Under these conditions, fertilizer is used to sustain optimal growth of crops. Microbial activity and plant growth generally coincide in space and time, resulting in continuous release and uptake of nutrients throughout the growing season. In contrast, additions of fertilizer are pulsed and if not carefully applied, they readily can exceed the ability of plants and microbes to take up the nutrients (Matson et al., 1997). This can result in agroecosystems being excessively "leaky," causing problems with excessive nutrient loading to groundwater and downstream flow paths leading to surface waters.

For example, previous studies have found that agriculture can greatly affect the composition of groundwater. Agriculturally induced changes in major ion chemistry of groundwater, particularly nitrate, have resulted in degradation of drinking water quality (Fan and Steinberg, 1996) and the discharge of agriculturally impacted groundwater to surface water bodies has resulted in observable ecological effects (Howarth et al., 2000; Böhlke 2002; Shroder et al., 2004). A review by Tilman et al. (2001) notes that in many areas of the world, the major ion loads of water recharging unconfined aquifers in the last several decades have been dominated by constituents derived directly or indirectly from agricultural management practices and amendments.

Changes in management practices may mitigate the magnitude of nitrate leaching associated with agroecosystems, often by making better use of natural processes for increased nutrient use efficiency. In this study, the effect of vegetation composition and different agricultural management practices on relative nitrate leaching is examined, taking advantage of the diverse treatments in place at the KBS Long Term Ecological Research (LTER) site.

Study Sites

The study sites are part of the Michigan State University's Kellogg Biological Station (KBS) holdings and are located in southwest Michigan, which is within the eastern portion of the U.S. Corn Belt. Soils in this area developed from a mature glacial outwash plain and moraine complex, and are typically high in carbonates except near the surface, and of moderate fertility. The dominant soils of the study sites are Kalamazoo and Oshtemo series, both loamy, mixed, mesic Typic Hapludalfs that tend to be moderately permeable in the upper part and rapidly permeable in the lower part. Soils are described in Soil Survey of Barry County, Michigan (Thoen, 1990).

The typical sequence of horizons in soils of the Kalamazoo Series is Ap, E, Bt, 2Bt2 and 2E/Bt. Textures of the Ap and E horizons are loam or sandy loam. The Bt1 is usually clay loam or sandy clay loam, whereas the 2Bt2 has a sandy loam texture. The E/Bt consists of lamellae of loamy sand (Bt) and sand (E). The upper 50 cm of the Bt1 plus 2Bt2 averages 18% or greater clay content. Soils developing in shallow closed depressions within mapping units seldom exhibit poor drainage in subsoil horizons but commonly have thicker and sometimes darker surface horizons with evidence of deposition of runoff sediments.

Oshtemo pedons occur in close association with the Kalamazoo pedons, generally occupying similar landscape positions. This soil can occur with or without a fine-loamy Bt horizon. If the Bt is present, the typical sequence of horizons is similar to that of the Kalamazoo soil with similar horizon textures. However, the Bt is thinner, and the upper 50 cm of the Bt1 plus 2Bt2 has an average clay content of less than 18%, thus distinguishing it from the Kalamazoo. If the fine loamy Bt is absent, the typical horizon sequence is Ap, E (sandy loam or loam), Bt (sandy loam), and E/Bt (sand and loamy sand).

Detailed maps and descriptions of KBS and its holdings, including soil and vegetation characteristics, are available on the KBS LTER website (http://lter.kbs.msu.edu). Note: From this point forward, when the reader is referred to the KBS LTER website for additional information, it can be assumed that this is the web address unless otherwise noted.

Of the ten treatments included in this study, six are managed agroecosystems and four are unmanaged successional and forested ecosystems. The 42-ha KBS main experimental site for the LTER program is subdivided into 1-ha plots, in a randomized complete block design of six blocks and seven treatments. The seven treatments include four managed annual cropping systems; two managed perennial cropping systems; and one unmanaged successional old-field community. The KBS LTER main experimental site layout is depicted in Figure 1. Treatment details are summarized in Table 1.

Located within 5 km of the main experimental site on the same soil series are three additional unmanaged forested treatments that range in age from 40 to >60 years old, each replicated three times. The deciduous forest stands include two old-growth and one 40-60 year post-cutting stand; the coniferous forest treatments include three conifer plantations ranging in age from 40-60 years old; the successional forest treatment consists of three old-field sites that were abandoned over 40 years ago, of which treatment SF-1 remains the most sparsely wooded. The locations of these treatment plots relative to the main experimental site are identified in Figure 2.

Agronomic Inputs

In addition to evaluating the effect of tillage practices, variation in the nature and quantity of soil amendments was incorporated into the agronomic treatment design (Table 2). Treatments 1 and 2 are conventional “high input” treatments (e.g., fertilizers, pesticides), while Treatment 3 is managed as “reduced input” and Treatment 4 is managed as ”zero input”. Treatments 1, 2, 3, and 6 received dolomitic lime ($CaMg(CO_3)_2$) applications in 1999, and Treatments 1, 2, and 3 were fertilized each year in April or May (with the exception of 2000) with an ammonium nitrate solution. Ammonium sulfate was added to Treatment 1 in 2001, to Treatment 2 in 2000, 2001, and 2003, but not to Treatment 3 during the study period. Potash (as KCl) was applied to Treatments 1, 2, and 3 in April 2002 and to Treatments 1 and 2 in April 2003. Treatment 7 did not receive any amendments, but surface vegetation was burned in May 2002 and again in April 2003 to discourage woody plant colonization. Agronomic field logs containing detailed descriptions of LTER Main Site activities can be obtained by visiting the KBS LTER Website. A summary of the major ions and elements added by treatment is provided in Table 3.

Lysimeters

Low-tension soil-solution samplers (lysimeters) were installed beneath the KBS LTER site in 1995, near or just within the top of the C-horizon and above the depth of indigenous soil carbonates. Within the study sites, the transition from the B- to the C-horizon is located approximately 1 – 1.2 m below ground surface. One collector was installed in each of three replicates of each treatment. Each collector draws from a tube that branches underground to three separate samplers spaced a few meters apart. The samplers were located near the edge of treatment plots for ease of access. A full description of the installation protocol is available from the KBS LTER website.

The low-tension soil solution samplers were purchased from Prenart Equipment ApS (www.prenart.dk). The samplers are constructed of stainless steel, porous Teflon (PTFE), and silica flour. Figure 3, depicts a typical soil solution sampling set up that resembles the equipment at the KBS LTER study sites.

From 1999 through 2003, samples were collected on a periodic basis from the soil-solution samplers from March through December as dictated by soil moisture and soil frost levels. Suction (-0.5 atm) was applied to each collector and the resulting solution collected in Erlenmeyer flasks over a 24-hour period. A description of the soil-solution sample collection method is available from the KBS LTER website. Sampling generally was not conducted at subfreezing temperatures, and when soils were excessively dry samples could not be obtained.

These soil-solution samplers yield samples that can be studied to indicate soil processes, but the samples are not necessarily representative of waters infiltrating downward via saturated flow towards the ground water. This is because the soil solutions are collected by suction, and thus they represent variable proportions of saturated flow and matric water (Lajtha *et al.* 1999). As soil water content diminishes, a greater fraction of the sample will be matric water. Very dry soils do not yield any water. An approximate indicator of soil water status at the time of sampling comes from the dilution factors; dilution was necessary when sample volumes fell below a certain threshold (discussed later). However, as shown later in the Results where evaporative concentration of soil solutions is considered, the treatments being compared appear to be quite similar in terms of soil water availability at any particular sampling date, thus making intercomparisons of concentrations of solutes valid even if some fraction of the sampling dates were more influenced by matric water than saturated flow water.

Water Analyses

All samples collected during the study were put on ice following collection. Upon return to the lab, samples were refrigerated (alkalinity, conductance) or filtered through Gelman Supor 0.45-µm membrane filters and then refrigerated (anions, silica) or acidified with 8 N HNO_3 (cations) until analysis.

Conductance was measured in the lab using an Orion model 135 conductance meter (Analytical Technology, Inc.). The pH of unfiltered samples was measured in the laboratory within a few days of collection and therefore should be closer to the solution pH at atmospheric equilibrium because most of the excess dissolved CO_2 that is typical of soil solutions would have escaped. Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} were measured by flame atomic absorption spectrometry, with addition of lanthanum before Ca^{2+} and Mg^{2+} measurement to suppress interferences. Total alkalinity, which generally represents HCO_3^- in these waters, was determined by titration with 0.3 N HCl between pH 4.0 and 3.3 and calculation of the Gran function (Cantrell et al. 1993). SO_4^{2-}, Cl^-, and

NO_3^- were measured by membrane suppression ion chromatography. Si was measured colorimetrically by the ammonium molybdate method (Wetzel and Likens 2000).

Other nutrients were measured for samples collected between March 1999 and November 2000. NH_4^+ was measured colorimetrically following an adapted version of the phenylhypochlorite method (Aminot et al. 1997). Total Dissolved Phosphorus (TDP) was measured following persulfate digestion, using the acid molybdate colorimetric method (Wetzel and Likens 2000).

On occasion, small sample size prohibited analysis of conductance, pH and silicate. During times of lower soil water content, dilution with deionized water was frequently necessary to obtain enough volume (250 mL) to conduct all the analyses.

NADP/NTN Precipitation Data

Precipitation data, including water volumes and major ion concentrations, were obtained from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) for the period of this study. Data can be obtained from the website http://nadp.sws.uiuc.edu, for Station MI26, Kellogg Biological Station, Kalamazoo County, Michigan. Seasons are defined under the NADP/NTN program as follows (month/day): Winter 12/1 – 3/1; Spring 3/1 – 6/1; Summer 6/1 – 9/1; and Fall 9/1 – 12/1.

Statistics

Data distributions across treatments were compared using notched box plots. The box plots provide a convenient and compact summary of asymmetric frequency distributions that includes medians and quartiles. The notches indicate the approximate 95% confidence intervals around the median and the boxes extend across the interquartile range (i.e., from the 25^{th} to 75^{th} percentiles). The length of the notches is calculated using a formula based on the formal concept of a hypothesis test and is useful even when the assumptions of the test are not strictly met (Chambers, et al., 1983). However, notch lengths are not adjusted (corrected) for multiple comparisons. The risk of committing a Type 1 error can be mitigated by applying knowledge of the underlying biological, physical, and chemical mechanisms that are likely to result in differences between treatments. Where such an explanation for differences is not evident, interpretations of significant differences should be made with caution. The use of the notched boxplot is discussed in detail in McGill, et al. (1978) and Chambers, et al. (1983).

Results were also analyzed using analysis of variance (ANOVA; Systat 9.0), testing for the effects of treatments, blocks, and interactions between treatments and blocks. An ANOVA is performed when one is attempting to determine whether differences in treatment means are likely to be reflective of true differences or due to chance. This data set exhibits rather marked violations of the assumptions of ANOVA, including departures from normality, equal variances, and independence. However, the number of samples obtained from each treatment is large ($n \geq 98$), and as a result of the central limit theorem, the ANOVA global hypothesis *F* test should be robust against violations of normality (Ito, 1980). The assumption of equal variances is also fairly robust against violations, although the stated significance levels for the *F* test may be larger or smaller than the significance level actually realized. For example, Box (1954) found that when an *F* test was conducted at the 0.05 level of significance when there was a ratio of 1:3 for smallest: largest group variance, the actual significance levels ranged from 0.056 to 0.074. With respect to the assumption of independence, Box (1954) stated:

> "Fisher (1926) recognized these potential difficulties with field plot experiments and justified random assignment of treatments to experimental units as the means to obtain valid estimates of experimental error variance. In a more detailed discussion, Fisher (1935) showed that randomization provided appropriate reference populations for statistical inferences free of any assumptions about the distribution of the observations. He showed that significance tests could be based upon the distribution created by randomization and the normal theory tests provided approximations to these test results. **Thus, the random allocation of treatments to the experimental units *simulates* the effect of independence and permits us to proceed as if the observations are independent and normally distributed** (Kuehl, 2000)." [Emphasis added].

The main experimental site represents a randomized complete block design. The forested sites are not true replicates; however, blocking by replicate was shown to be statistically effective in reducing experimental error.

Following the analysis of variance, post-hoc significance testing for individual mean comparisons was conducted using Fisher's (protected) Least Significant Difference (LSD) procedure, which if the overall ANOVA is significant, is powerful and gives proper Type-I error protection (Schabenberger, 1999).

The box plot comparisons, which addressed paired comparisons between medians, and the post-hoc ANOVA tests, which addressed paired comparisons between means, were in agreement (means and medians were significantly different) for all pairs with one exception which will be discussed further in the Results section.

Results

Precipitation

Precipitation in southwestern Michigan is acidic with a mean pH of 4.45 and a mean specific conductance of 26 μS/cm (25°C)(National Atmospheric Deposition Program (NRSP-3)/National Trends Network means of annual volume-weighted means for 1979-96 from the KBS station (MI26), printed 2 Dec 1997. NADP/NTN Coordination Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.) Rheaume (1990) observed an inverse relation between pH and conductance at a nearby precipitation collection station, which is due to the predominance of strong acid anions (NO_3^- and SO_4^{2-}) in precipitation.

During the study period of 1999-2003, the mean annual precipitation was 72.5 cm/year. The long-term mean (1942-96) annual precipitation for stations in the vicinity of KBS is 92 cm (Hamilton, unpublished data). The pattern of precipitation during the study period is depicted in Figure 9, Top. 2000 was the driest year (47.4 cm), primarily due to unusually low precipitation during the spring and summer seasons when only 12.1 cm fell. In contrast, the average precipitation for the other four years during the spring and summer seasons was 44.2 cm (Figure 10, Bottom).

Over the study period, the average annual pH of precipitation was 4.6. The dominant cation was ammonium with an annual volume-weighted mean concentration of 26.0 μeq/L, followed by H^+ and Ca^{2+}. The dominant anion was sulfate, with an annual volume-weighted mean concentration of 37.1 μeq/L, followed by nitrate (Figure 11).

General

A summary of the basic descriptive statistics of the entire data set is found in Table 5. Descriptive statistics related to nitrate are provided at the end of this volume in Table 8. Comparisons of mean and median nitrate concentrations among treatments based on vegetation and management type are discussed below.

Evaporative Concentration Effects

The evapotranspiration of soil moisture by plants would be expected to result in evaporative concentration of the solutes in soil water relative to in precipitation. Mean annual recharge to the groundwater is about 28 cm on the highly permeable soils of local outwash plains such as the LTER site (Rheaume 1990), which is 32% of the mean annual precipitation; the remaining 68% is lost by evapotranspiration. The actual evaporative concentration of water remaining in the soils over a particular growing season is difficult to predict. Nevertheless, while evapoconcentration must contribute to increased solute concentrations in soil solution compared to precipitation, the observed increases in solute concentrations are not congruent (i.e., solute proportions change relative to the source water), indicating that there must be sources and sinks of solutes in the soil environment.

In research on groundwater and surface water bodies, chloride has been identified as a conservative ion and sulfate as a semi-conservative ion that can be used to estimate evaporative concentration (Claassen and Halm, 1996; Leydecker and Melack 2000). Unfortunately, both chloride and sulfate are contained in amendments added to all of the agricultural treatments, with the exception of the zero input (organic) treatment, in the form of potash (KCl) and ammonium sulfate (Table 2). Therefore, the ability to use either of these ions as an indicator of overall evaporative concentration effects is compromised. Table 9 provides a summary of the descriptive statistics associated with chloride for each treatment.

Within the forested sites, a comparison of treatment means using Fisher's (protected) LSD procedure indicates that there is no significant difference in chloride concentrations between the means (Table 10). Therefore, when comparing nitrate concentrations (or other solutes) within the forested sites, adjustment (normalization) for a conservative solute such as chloride in an attempt to correct for evaporative concentration provides no advantage.

Within the agronomic sites, the mean concentration of chloride in the zero input (organic) treatment is not significantly different from that in the forested sites, which is interesting because it might be expected that there would be greater evapoconcentration by forest vegetation because of longer growing seasons, deeper roots, and a greater canopy leaf surface area compared with the annual row crops.

The conventional input, reduced input, and no-till systems sometimes exhibited elevated concentrations of chloride that make their overall means significantly different than chloride concentrations in the forested sites and the zero input (organic) treatment. However, the elevated concentrations cannot be ascribed to evaporative concentration effects because chloride is added to these treatments as potash. In addition, the reduced input treatment received one less potash application than the conventional input and no-till treatments (Table 2). Therefore, it is not possible to normalize the nitrogen concentrations for evaporative concentration effects even when making comparisons among these three treatments.

Evaporative concentration effects will have little bearing on the comparisons of relative leaching losses because of the relationship between chloride and nitrate concentrations in these three treatments. For example, the no-till system has the lowest mean nitrate concentration, but the highest mean chloride concentration. The conventional input system has a higher mean chloride concentration than the reduced input system, but the reduced input system has a higher mean nitrate concentration. The relationship between nitrate and chloride within these three treatments indicates that evaporative concentration is not responsible for the relative leaching losses expected among these treatments.

In addition, chloride evidently was rapidly flushed from the treatments receiving potash. The median chloride concentrations of all treatments ranges from a low of 0.014 meq/L in the successional forest treatment to a high of 0.054 meq/L in the deciduous forest treatment (Table 11), and the agronomic treatments receiving potash had median concentrations that ranged from 0.025 meq/L to 0.034 meq/L. The fact that the zero input (organic) treatment concentrations are not significantly different from the forested treatments combined with the fact that median chloride concentrations of the agronomic treatments receiving potash lie within the range of median concentrations of the forested treatments indicate that evaporative concentration is not a factor regulating the concentration of solutes in soil solution.

Influence of Forests

Relative to precipitation, the soil solution in the deciduous and coniferous forests was enriched in nitrate, while the solution in the successional forest was depleted (Figure 139, Top) The median soil solution concentrations were 3.46 mg-N/L (0.247 meq/L), 2.17 mg-N/L (0.155 meq/L), 0.08 mg-N/L (0.006 meq/L), and 1.68 mg-N/L (0.120 meq/L) in the deciduous treatment, coniferous treatment, successional treatment, and in precipitation, respectively. Median conductivities were also very low in the forested treatments relative to other treatments in the study (Figure 139, Bottom).

Fisher's (protected) LSD test and the box plot comparisons both indicate significant ($P<0.05$) differences in the mean and median nitrate soil solution concentrations between the successional and deciduous forest and between the successional and coniferous forest (Table 12, Figure 140, Top). The median and mean soil solution concentrations of nitrate in the coniferous and deciduous forest are not significantly different from one another.

Influence of Managed Agroecosystems

To determine the relative influence of conventional agriculture on nitrate leaching potential, one can compare the native deciduous forest system to a conventional agroecosystem. Relative to the deciduous forest, the median soil solution concentration of nitrate in the conventional agriculture system was enriched. The median soil solution concentration was 3.46 mg-N/L (0.155 meq/L) in the deciduous forest, and 11.29 mg-N/L (0.806 meq/L) in the conventional input / conventional till system (Table 1 and Table 5). In addition, soil solutions in agroecosystems were ionically rich relative to precipitation or forested treatments (Figure 139, Bottom).

Fisher's (protected) LSD test and the box plot comparisons both indicate that the differences in mean and median nitrate soil solution concentrations between the deciduous forest and the conventional input / conventional till system are significant at the 0.05 level (Table 12, Figure 140, Top).

Effect of Agricultural Management Practices

Tillage

The effect of conservation tillage ("no-till") practices and varying levels of agronomic chemical inputs can be evaluated by comparing the effect of different management practices on mean and median nitrate soil solution concentrations relative to a conventional input / conventional till system.

Relative to the conventional system, the median nitrate soil solution concentration in the no-till system was lower. The median soil solution concentration was 11.29 mg-N/L (0.806 meq/L) in the conventional input / conventional till system and 7.25 mg-N/L (0.518 meq/L) in the no-till system (Table 1 and Table 5).

Fisher's (protected) LSD test and the box plot comparisons both indicate that the differences in mean and median nitrate soil solution concentrations between the conventional input / conventional till system and the no-till system are significant at the 0.05 level (Table 12, Figure 140, Bottom).

Varying Levels of Input

Relative to the conventional system, the box plot comparison indicates that median soil solution concentrations of nitrate were higher in the reduced input system and lower in the zero input (organic) system. The median soil solution concentrations of nitrate were 11.29 mg-N/L (0.806 meq/L), 12.52 mg-N/L (0.895 meq/L), and 8.33 mg-N/L (0.595 meq/L) in the conventional input, reduced input, and zero input (organic) systems, respectively (Table 1 and Table 5).

Fisher's (protected) LSD test indicates that the differences in mean soil solution concentrations of nitrate are significant at the 0.05 level between the zero input and the conventional input, and also between the zero input and the reduced input (Table 12). The mean soil solution concentrations of nitrate are not significantly different between reduced input and conventional input.

Box plot comparisons of the median soil solution concentrations of nitrate indicate that the only significant difference at a 0.05 level is between the reduced input and zero input (organic) treatments (Figure 141, Top). The reason that the medians of the conventional input and zero input (organic) treatments are not significantly different while the means are significantly different may be the result of the influence of outliers, which raise the mean in the conventional input treatment (Figure 141, Bottom). The influence of outliers on the mean and the reduction of influence of outliers on the median are the main difference between these two types of hypothesis testing, and is one reason that I favor the box plot comparisons over the more commonly used ANOVA approach.

It is worth noting that based on ANOVA the mean soil solution concentration of nitrate in the no-till system is significantly different and lower than in the conventional input, reduced input, or zero input (organic) treatments; whereas based on box plot comparisons the median soil solution concentration of nitrate in the no-till system is significantly lower than the conventional input and reduced input treatment only, but indistinguishable from the zero input (organic) treatment (Figure 142, Top).

Relative Leaching Losses

When attempting to evaluate nitrate concentrations as indicators of relative leaching losses among treatments, it is helpful to sum the data from each treatment because similar means and medians may not be indicative of relative leaching losses if the variances are markedly unequal between treatments, which is sometimes the case. When evaluating data this way, the relative ranking of nitrate concentrations from each treatment discussed above is as follows:

Conv. Input / Conv. Till > Reduced Input / Conv. Till > Conv. Input / No-Till > Zero Input (Organic) > Deciduous Forest > Coniferous Forest > Successional Forest

While the conclusions from the ranking are the same for most treatments as would be obtained through box plot comparisons, the lower overall potential for nitrate leaching losses of the zero input (organic) treatment becomes clearer when evaluating the data this way. Table 13 provides the numerical data upon which this relative ranking is based. Nevertheless, nitrate concentrations and thus leaching potential are still quite elevated in the zero input (organic) treatment compared to the unmanaged, natural vegetation treatments.

Relationship between Nitrogen and Other Cations in Solution

Across all treatments, higher concentrations of nitrate in soil solutions were positively correlated with concentrations of calcium ($r = 0.66$, $p = 0.000$), magnesium ($r = 0.45$, $p = 0.000$), potassium ($r = 0.42$, $p = 0.000$) and sodium ($r = 0.41$, $p = 0.000$) (Table 6).

The relationship between nitrate and other cations in solution such as calcium and magnesium is particularly striking when the median soil solutions of each treatment are plotted together (Figure 143). As the median concentration of nitrate in the soil solution increases, the median concentrations of calcium and magnesium also increase in a linear fashion ($r = 0.9$ and 0.8, respectively).

Perennial Systems (Alfalfa, Poplar, Successional Field)

Other treatments at the KBS LTER main experimental site include a perennial alfalfa treatment, a fast-growing perennial poplar treatment, and an herbaceous successional field. The median nitrate concentrations in these treatments were 16.00 mg-N/L (1.14 meq/L), 0.00 mg-N/L (0.00 meq/L), and 0.23 mg-N/L (0.017 meq/L), respectively (Table 1 and Table 5). The alfalfa had by far the highest nitrate concentrations of all of the treatments.

Discussion

Meyer and Turner (1992) assert that the expansion of agricultural land is widely recognized as one of the most significant alterations to the global environment, and that the total area of cultivated land worldwide has increased 466% from 1700 to 1980. Vitousek and Matson (1993) note that as of 1990, "80 million metric tons of N were produced in industrial N fixation each year, and another 40 million tons were fixed by crop plants carrying out biological N-fixation; together, these human-controlled inputs were equivalent to annual N inputs via natural processes." At least one study reported that up to 80% of the nitrogen supplied to agricultural systems becomes released to the surrounding air or water or is immobilized in the soil (Granstedt, 2000). Howarth et al., (1996) noted that nitrate concentrations in the major rivers of the northeastern United States have increased three- to tenfold since the early 1900s, which they attribute to fertilization as well as other human activities. This is consistent with a study by Kemp and Dodds (2001) that showed that nitrate concentrations in streams increased as the proportion of agriculture increased in watersheds in Kansas.

Furthermore, the response to decreases in fertilizer use can be slow. An 11-year study of a Latvian river system (Stalnackea et al., 2003) found that only 4 of 12 sites showed significant downward trends, even though the purchase of mineral fertilizers had decreased in the area by more than a factor of 15 over the same period. The results of this study are consistent with other studies performed in Europe (Gustafson et al, 1998; De Wit and Behrendt, 1999; Vagstad et al, 2000). This may be because changes in the mineralization and immobilization of nitrogen in soils delay and disproportionately reduce the impact of a reduction in the N surplus (Oenema and Roest, 1998) and also may reflect the slow turnover of groundwater reservoirs containing nitrate.

Given the important role nitrogen plays in the environment and the potentially slow recovery of ecosystems to elevated nitrate loading, it is important to understand the relative effects of vegetation and management practices on nitrate losses via leaching.

Forests

Soil solutions in all of the forested treatments were more ionically dilute than in the agronomic treatments, each with median soil solution conductivities below 100 (Figure 139, Bottom). The lower conductivities may result because base cations that contribute to conductivity are not released into the soil solution as much when nitrate concentrations are low. Compared to the deciduous and conifer forest systems, the successional forest treatment appeared to draw nitrate down to lower concentrations. This result is consistent with the theory put forth by Vitousek and Reiners (1975) that nitrate losses are expected to increase as stands age because ecosystem retention of limiting nutrients should decrease from strong retention in stands that are rapidly accumulating biomass to essentially no net retention in steady-state old growth systems. This theory is also supported by the low concentrations of nitrate in the soil solutions beneath the fast-growing perennial poplar system, where nitrate concentrations were generally below detectable levels. Interestingly, the herbaceous successional field treatment also had very low mean and median soil solution concentrations of nitrate. The low concentrations of nitrate in this treatment are likely related to the overall nutrient use efficiency of these systems, although published studies specific to nutrient use efficiency in successional fields could not be found. High nutrient use efficiency in successional fields might be explained by the hypotheses of differential resource limitation and micro-habitat differentiation (Braakhekke and Hooftman, 1999).

Agricultural ecosystems

The median soil solution concentration of nitrate in the conventional agroecosystem was nearly four times as great as that in the deciduous forest treatment. Increased soil solution concentrations of nitrate in the conventional agriculture treatment relative to the native deciduous forest treatment are not surprising given the nitrogen fertilizers and other amendments this agricultural system receives.

Despite additional nitrogen being added to the no-till system in 2000 in the form of ammonium sulfate, the conventional till system had significantly higher median soil solution concentrations of nitrate. The finding of higher nitrate beneath conventional till systems is consistent with a previous study performed in Georgia, U.S.A. (House et al., 1984). The reasons for increased soil solution concentrations of nitrate beneath conventional till may be increased uptake of nitrogen by weeds in the no-till system, and/or higher rates of N mineralization in conventional till systems due to stimulation by tillage (Stinner et al., 1984).

The reduced input treatment did not receive any ammonium sulfate, but otherwise received the same amendments as the conventional input treatment, but at a reduced level and/or frequency (Table 2). In addition, the reduced input treatment had a legume cover crop while the conventional input treatment did not. Despite the higher inputs of nitrogen fertilizer in the conventional input system, the median soil solution concentrations of nitrate were not significantly different between the reduced input and the conventional input treatments. In fact, the median soil solution concentration of nitrate was slightly higher in the reduced input system (Table 8, Figure 141, Top). This may be due to the differences in the N- mineralization potential of the treatments. In a previous study at the KBS LTER, Robertson et al., (2000) estimated the N-mineralization potential to be greatest in the reduced input treatment and lowest in the conventional till system. The greater N-mineralization potential in the reduced input treatment may be the result of fertilization combined with the presence of the winter legume cover crop which contributes both litter and nitrogen (via fixation) to the soil.

While the median soil solution concentrations of nitrate did not differ significantly between the conventional input and the zero input (organic) treatment, ANOVA indicated that the means differed significantly. In addition, the variance in the conventional input treatment was much greater than the variance in the zero input (organic) treatment, resulting in a greater relative leaching loss from the conventional input system. The higher variance of nitrate concentrations in the conventional input system may be the result of the pulsed inputs of fertilizer, which result in larger losses of nitrate via leaching (Matson, et al., 1997). As the variances are not equal among treatments, this also calls the ANOVA results into question.

The no-till system exhibited lower concentrations of nitrate than the conventional input and reduced input treatments, but high concentrations (and thus presumably greater leaching losses) than the zero input (organic) treatment. Relative to the zero input (organic) treatment, the advantages of the no-till system may be off-set by the high (conventional) inputs of nitrogen fertilizers.

Management Implications

In terms of reducing overall losses of nitrogen via leaching in agronomic systems, the data suggest that the zero input (organic) treatment results in the lowest losses of nitrate via leaching of all of the row-crop treatments examined. Reducing nitrate leaching may, however, come at the cost of an increased global warming potential. In a study conducted at the KBS LTER of the global warming potential of these same treatments, Robertson et al. (2000) found that the no-till treatment had a lower net global warming potential than the zero input (organic) treatment, while its annual net primary productivity was slightly higher. Reductions in nitrate losses via leaching is only one of the environmental impacts that must be considered when choosing among alternative agronomic management practices. It is clear that within the KBS LTER, conventional input / conventional till systems including particularly alfalfa are less environmentally desirable compared with other available management options.

REFERENCES

Allen, W.B., Miller, J.B., and Wood, W.W. 1972. Availability of water in Klamazoo County, Michigan. U.S. Geological Survey Water-Supply Paper 1973. 129 p

Aminot A, Kirkwood DS & Kérouel R. 1997. Determination of ammonia in seawater by the indophenol-blue method: Evaluation of the ICES NUTS I/C 5 questionnaire. Mar. Chem. 56: 59-75.

Andersson AJ, Mackenzie FT. 2004. Shallow-water oceans: A source or sink for atmospheric CO_2? Frontiers in Ecology and Evolution 2: 348-353.

Baron, J. S., M.D. Hartman, T.G. F. Kittel, L.E. Band, D. S. Ojima, and R. B. Lammers. 1998. Effects of land cover, water redistribution, and temperature on ecosystem processes in the South Platte Basin. Ecological Applications 8(4): 1307-1051.

Berner RA. 1999. A new look at the long-term carbon cycle. *GSA Today* 9:1-6.

Blette VL, Newton RM. 1996. Effects of watershed liming on the soil chemistry of Woods Lake, New York. Biogeochemistry 32: 175-194.

Böhlke JK. 2002. Groundwater recharge and agricultural contamination. Hydrogeology Journal 10:153-179.

Böhlke JK, Denver JM. 1995. Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. Water Resources Research 31: 2319-2339.

Box, G.E.P. 1954. Some theorems on quadratic forms applied in the study of analysis of variance problems, II. Effect of inequality of variances and correlation between errors in the two-way classification. Annals of Mathematical Statistics 25: 484-498.

Braakhekke, W. G. and D.A.P. Hooftman. 1999. The resource balance hypothesis of plant species diversity in grassland. Journal of Vegetative Science 10: 187-200.

Brady NC (1990) *The Nature and Properties of Soils, 10th ed.* Macmillan, New York, 621 pp.

Brady, N.C. and R.R. Weil. 1995. The nature and property of soils. 5th Edition. Prentice Hall, NJ.

Caldeira K, Morgan MG, Baldocchi D, Brewer PG, Chen CTA, Nabuurs GJ, Nakicenovic N, Robertson GP. 2004. A portfolio of carbon management options. In: The Global Carbon Cycle (eds Field CB, Raupach MR), pp. 103-130. Island Press, Washington, DC, USA

Cantrell KJ, Serkiz SM, Perdue EM., 1990. Evaluation of acid neutralizing capacity data for solutions containing natural organic acids. *Geochimica et Cosmochimica Acta* 54: 1247-1254.

CAST (Council for Agricultural Science and Technology). 2004. Climate Change and Greenhouse Gas Mitigation: Challenges and Opportunities for Agriculture. Task Force Report No. 141. Ames, Iowa, USA.120 pp.

Chambers, J.M. W.S. Cleveland, B. Kleiner, P.A. Tukey. 1983. Chapter 3: Comparing Data Distributions, in *Graphical methods for data analysis*, Duxbury Press, Boston.

Claassen, H.C., Halm, D.R., 1996. Estimates of evapotranspiration or effective moisture in Rocky Mountain watersheds from chloride ion concentrations in stream baseflow. Water Resour. Res. 32, 363–372.

Cole, D. W. and M. Rapp. 1981. Element cycling in forest ecosystems. Pp. 341-409. In D.E. Reichle (ed.), *Dynamic Properties of Forest Ecosystems.* Cambridge University Press, Cambridge.

Compton, J.E. and R.D. Boone. 2000. Long-term impacts of agriculture on soil carbon and nitrogen in New England forests. Ecology 81(8): 2314-2330.

Dahlgren, R.A., Ugolini, F.C., Shoji, S., Ito, T., Sletten, R.S., 1991. Soil-forming processes in Alic Melanudands under Japanese pampas grass and oak. Soil Sci. Soc. Am. J. 55, 1049– 1056.

Davidson EA, Ackerman IL, 1993. Changes in soil carbon inventories following cultivation of previously untilled soil. Biogeochemistry 20, 161-193.

De Wit, M., Behrendt, H., 1999. Nitrogen and phosphorus emissions from soil to surface water in the Rhine and Elbe basins. Water Science and Technology 39: 109–116.

Drees LR, Wilding LP, Nordt LC (2001) Reconstruction of soil inorganic and organic carbon sequestration across broad geoclimatic regions. In: Soil Carbon Sequestration and the Greenhouse Effect (ed Lal R), pp. 155-172. Soil Science Society of America, Special Publication No. 57, Madison, WI, USA.

Drift and Bedrock Aquifers, Barry County, Michigan, USA. Environ. Geol.

Evangelou, V.P., L.D. Whittig, and K.K. Tanji. 1984. An automated manometricmethod for quantitative determination of calcite and dolomite. Soil Sci. Soc. Am. J. 48: 1236-1239.

Falkengren-Grerup, U., DJ ten Brink, and J. Brunet. 2006. Land use effects on soil N, P, C and pH persist over 40-80 years of forest growth on agricultural soils. Forest Ecology and Management 225: 74-81.

Fan AM, Steinberg VE. 1996. Health implications of nitrate and nitrite in drinking water: an update on methemoglobinemia occurrence and reproductive and developmental toxicity. Regul Toxicol Pharmacol 23:35–43

Fenchel, T., G.M. King, and T.H. Blackburn. 1998. Bacterial biogeochemistry: The ecophysiology of mineral cycling. Second ed. Academic Press, San Diego. 307 p.

Fenn, M.E., M.A. Poth, J.D. Aber, J.S. Baron, B.T. Bormann, D.W. Johnson, A.D. Lemly, S.G. McNulty, D.F. Ryan and R. Stottlemyer. 1998. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. Ecological Applications 8(3): 706-733.

Fisher J, Diggle A, Bowden B. 2003. Quantifying the acid balance for broad-acre agricultural systems. In: Handbook of Soil Acidity (ed Rengel Z), pp. 117-133. Marcel-Dekker, New York.

Fisher J, Diggle A, Bowden B .2003. Quantifying the acid balance for broad-acre agricultural systems. In: *Handbook of Soil Acidity* (ed Rengel Z), pp. 117-133. Marcel-Dekker, New York.

Fisher, R.A. 1926. The arrangement of field experiments. Journal of the Ministry of Agriculture of Great Britain. 33:503-513.

Fisher, R.A. 1935. The design of experiments. Edinburgh: Oliver and Boyd.

Franzluebbers AJ, Steiner JL. 2002. Climatic influences on soil organic C storage with no tillage. In: Agriculture Practices and Policies for Carbon Sequestration in Soil (eds Kimble JM, Lal R, Follett RF), pp. 71-86. CRC Press, Boca Raton, Florida, USA.

Gaillardet J, Dupré B, Louvat P, Allègre CJ. 1999. Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. Chemical Geology 159: 3-30.

Golterman, H.L. and R.S. Clymo. 1969. Methods for chemical analysis of fresh waters. Blackwell, Oxford. 172 p.

Granstedt, A. 2000. Increasing the efficiency of plant nutrient recycling within the agricultural system as a way of reducing the load to the environment - experience from Sweden and Finland. Agriculture, Ecosystems and Environment 80:169–185

Grunzweig, J.M., S. Sparrow and F. S.T. Chapin III. 2003. Impact of forest conversion to agriculture on carbon and nitrogen mineralization in subarctic Alaska. Biogeochemistry 64: 271–296.

Gustafson, A., Fleischer, S., Joelsson, A., 1998. Decreased leaching and increased retention potential co-operative measures to reduce diffuse nitrogen load on a watershed level. Water Science and Technology 38:181–189.

Hagen-Thorn, A., Callesen, I., Armolaitis, K., Nihlgard, B., 2004. The impact of six European tree species on the chemistry of mineral topsoil in forest plantations on former agricultural land. For. Ecol. Manag. 195: 373–384.

Hamilton, S.K., A.L. Kurzman, C. Arango, L. Jin, and G.P. Robertson. *In review.* Evidence for carbon sequestration by agricultural liming. Global Change Biology.

Helyar KR, Porter WM. 1989. Soil acidification, its measurement and the processes involved. In: *Soil Acidity and Plant Growth* (ed Robson AD), pp. 61-101. Academic Press, Sydney.

Houghton, JT, Meira Filho LG, Lim B, Treanton K, Mamaty I, Bonduki Y, Griggs DJ, Callander BA. (eds). 1997. *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories*. Hadley Centre Meteorological Office, United Kingdom.

House, G.J., R.R. Stinner, D.A. Crossley, Jr., and E.P. Odum. 1984. Nitrogen cycling in conventional and no-tillage agro-ecosystems: analysis of pathways and processes. The Journal of Applied Ecology 21(3): 991-1012.

Howarth, R.W., D.P. Swaney, T.J. Butler, and R. Marino. 2000. Climatic control on eutrophication of the Hudson River estuary. Ecosystems 3: 210-215.

Ito, P.K. 1980. Robustness of ANOVA and MANOVA to test procedures. In *Handbook of Statistics*, Vol 1. (P.R. Krishnaiah, ed, Amsterdam: North-Holland), pp. 199-236.

Jackson, R.B., S.R. Carpenter, C.N. Dahm, D.M. McKnight, R.J. Naiman, S.L. Postel, and S.R. Running. 2001. Water in a changing world. Ecological Applications, 11(4): 1027-1045.

Jin, L, Williams EL, Szramek KJ, Walter LM, Hamilton SK .2006. Relative contributions of silicate versus carbonate mineral weathering in soils developed on Pleistocene glacial drift: An integrated study of soil and soil water geochemistry across an environmental gradient from the Upper- to Lower-Peninsulas of Michigan (U.S.A.). Geochimica et Cosmochimica Acta, in review.

Jobbagy, E.G., Jackson, R.B., 2003. Patterns and mechanisms of soil acidification in the conversion of grasslands to forests. Biogeochemistry 64, 205– 229.

Johnson-Maynard J.L., R.C. Grahamb, P.J. Shousec, S.A. Quideau. 2005. Base cation and silicon biogeochemistry under pine and scrub oak monocultures: implications for weathering rates. Geoderma 126: 353–365

Johnson-Maynard, J.L., McDaniel, P.A., Ferguson, D.E., Falen A.L., 1997. Chemical and mineralogical conversion of Andisols following invasion by bracken fern. Soil Sci. Soc. Am. J. 61: 549– 555.

KBS LTER Website: http://lter.kbs.msu.edu

Kehew, A.E. and Brewer, M.K. 1992. Groundwater Quality Variations in Glacial

Kemp, Melody J. and W.K. Dodds. 2001. Spatial and temporal patterns of nitrogen concentrations in pristine and agriculturally-influenced prairie streams. Biogeochemistry 53: 125–141.

Knops, J.M.H, and David Tilman. 2000. Dynamics of soil nitrogen and carbon accumulation for 61 years after agricultural abandonment. Ecology 81: 88-98.

Kuehl, R.O. 2000. Design of experiments: Statistical principles of research design and analysis. (2nd edition, Duxbury Press, Pacific Grove, CA).

Lajtha, K, Jarrell WM, Johnson DW, Sollins P. 1999. Collection of soil solution. In: *Standard Soil Methods for Long-Term Ecological Research* (eds Robertson GP, Bledsoe CS, Coleman DC, Sollins P), pp. 166-182. Oxford University Press, New York.

Lal, R, Kimble JM, Follett RF, Cole CV. 1999. The Potential of U.S. Cropland to Sequester Carbon and Mitigate the Greenhouse Effect. CRC Press, Boca Raton, FL, USA, 144 pp.

Lelong, F., Dupraz, C., Durand, P., Didon-Lescot, J.F., 1990. Effects of vegetation type on the biogeochemistry of small catchments (Mont Lozere, France). Journal of Hydrology 116: 125– 145.

Leydecker, A., and J.M. Melack. 2000. Estimating evaporation in seasonally snow-covered catchments in Sierra Nevada, California. Journal of Hydrology 236: 121-138.

Likens, G. E., F.H. Bormann, N.M. Johnson, D.W. Fisher, and R.S. Pierce. 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. Ecological Monographs 40: 23-47.

Loeppert, R.H.; Suarez, D.L. 1996 Carbonate and gypsum. Pp. 437-474 in: Methods of soil analysis. Part 3. Chemical methods. Soil Science Society of America, Madison.

Matson, P.A., W.J. Parton, A.G. Power, and M.J. Swift. 1997. Agricultural intensification and ecosystem properties. Science 227(5325): 504-509.

McGill, R., J. W. Tukey, and W. A. Larsen. 1978. Variations of Boxplots. *The American Statistician*, Vol. 32, 1978, pp.12-16.

Meyer, W.B. and B.L. Turner II. 1992. Annu. Rev Ecol. Syst. 23: 39.

Miller, H.G., M.H. Unsworth, I. Th. Rosenqvist, G. Abrahamsen. 1984. Deposition-plant-soil interactions [and discussion]. Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences, 305(1124): 339-352.

Milliman JD. 1993. Production and accumulation of calcium-carbonate in the ocean – budget of a nonsteady state. Global Biogeochemical Cycles 7: 927-957.

NADP/NTN. 1997. National Atmospheric Deposition Program (NRSP-3)/National Trends Network means of annual volume-weighted means for 1979-96 from the KBS station (MI26), downloaded 2 Dec 1997. NADP/NTN Coordination Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.

Nelson, L. S., "Evaluating Overlapping Confidence Intervals," *Journal of Quality Technology*, Vol. 21, 1989, pp. 140-141.

Nihlgard, B., 1971. Pedological influence of spruce planted on former beech forest soils in Scania, south Sweden. Oikos 22, 302– 314.

Oenema, O., Roest, C.W.J., 1998. Nitrogen and phosphorus losses from agriculture into surface water; the effects of policies and measures in the Netherlands. Water Science and Technology 37:19–30.

P.M. Vitousek and P.A. Matson. 1993. In *Biogeochemistry of Global Change: Radiatively Active Trace Gases.* R. Oremland, Ed. (Chapman & Hall, New York, 1993), pp 193-208.

Plummer LN, Parkhurst DL, Wigley TM. 1979. Critical review of the kinetics of calcite dissolution and precipitation. In: Chemical Modeling in Aqueous Systems, pp. 537-573. American Chemical Society Symposium 93.

Qualls, R.G., B.L. Haines, and W.T. Swank. 1991. Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. Ecology 72: 254-266.

Raven, J.A., B. Wollenweber, and L.L. Handley. 1992. A comparison of ammonium and nitrate as nitrogen sources for photolithotrophs. New Phytol. 121: 19-32.

Raymond PA, Cole JJ. 2003. Increase in the export of alkalinity from North America's largest river. Science 302: 88-91.

Reardon EJ, Allison GB, and Fritz P. 1979. Seasonal chemical and isotopic variations of soil CO_2 at Trout Creek, Ontario. Journal of Hydrology 43: 355-371.

Reardon EJ, Mozeto AA, Fritz P. 1980. Recharge in northern clime calcareous sandy soils: soil water chemical and carbon-14 evolution. Geochimica et Cosmochimica Acta 44: 1723-1735.

Reich, P.B., B.D. Kloepeel, D.S. Ellsworth, and M.B. Walters. 1995. Different photosynthesis-nitrogen relations in deciduous hardwood and evergreen coniferous tree species. Oecologia 104: 24-30.

Rheaume, S.J. 1990. Geohydrology and water quality of Kalamazoo County, Michigan, 1986-88. U.S. Geological Survey Water-Resources Investigations Report 90-4028. 102 p.

Richter, D.D., Markewitz, D., Wells, C.G., Allen, H.L., April, R., Heine, P.R., Urrego, B. 1994. Soil chemical change during three decades in an old-field loblolly pine (Pinus taeda L.) ecosystem. Ecology 75: 1463– 1473.

Robertson GP. 1997. Nitrogen use efficiency in row crop agriculture: crop nitrogen use and soil nitrogen loss. In: Ecology in Agriculture (ed Jackson L), pp. 347-365. Academic Press, New York.

Robertson, G.P., E.A. Paul, R.R. Harwood. 2000. Greenhouse Gases in Intensive Agriculture: Contributions of Individual Gases to the Radiative Forcing of the Atmosphere. Science 289: 1922-1925.

Sanchez JE, Harwood RR, Willson TC, Kizilkaya K, Smeenk J, Parker E, Paul EA, Knezek BD, Robertson GP (2004) Managing soil carbon and nitrogen for productivity and environmental quality. Agronomy Journal 96: 769-775.

Schabenberger, O. 1999. Course Pack: Statistical Methods for Biologists I. (STT 464). Virginia Tech University.

Schlesinger WH. 1997. Biogeochemistry: An Analysis of Global Change, 2nd ed. Academic, New York, 588 pp.

Schlesinger WH. 1999. Carbon sequestration in soils. *Science* 284: 2095.

Schlesinger WH. 2000. Carbon sequestration in soils: some cautions amidst optimism. Agriculture, Ecosystems, and Environment 82(1/3): 121-127.

Schnoor J, Stumm W. 1985. Acidification of aquatic and terrestrial systems. In: Chemical Processes in Lakes (ed Stumm W), pp.311-338. Wiley, New York.

Semhi K, Suchet PA, Clauer N, Probst JL. 2000. Impact of nitrogen fertilizers on the natural weathering-erosion processes and fluvial transport in the Garonne basin. Applied Geochemistry 15: 865-878.

Shroder, J.J., D. Scholefield, F. Cabraol and G. Hofman. 2004. The effects of nutrient losses from agriculture on ground and surface water quality: the position of science in developing indicators for regulation. Environmental Science and Policy 7: 15-23.

Sinsabaugh, R.L., R.K. Antibus, A. E. Linkins, C.A. McClaugherty, L. Rayburn, D. Repert, and T. Weiland. 1993. Wood decomposition: Nitrogen and phosphorus dynamics in relation to extracellular enzyme activity. Ecology 74: 1586-1593.

Stallard RF, Edmond JM. 1987. Geochemistry of the Amazon. 3. Weathering chemistry and limits to dissolved inputs. Journal of Geophysical Research 92(C8): 8293-8302.

Stalnackea, P., A. Grimvallb, C. Libisellerb, M. Laznikc, I. Kokorite. 2003. Trends in nutrient concentrations in Latvian rivers and the response to the dramatic change in agriculture. Journal of Hydrology 283: 184–205.

Stinner, B.R., D.A. Crossley, Jr., E.P. Odum, and R.L. Todd. 1984. Nutrient budgets and internal cycling of N, P, K, Ca, and Mg in conventional tillage, no-tillage, and old-field ecosystems on the Georgia Piedmont. Ecology 65(2): 354-369.

Stumm W, Morgan J. 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natura Waters, 3rd ed. Wiley, New York, 1022 pp.

Szramek K, Walter LM. 2004. Impact of carbonate precipitation on riverine inorganic carbon mass transport from a mid-continent, forested watershed. Aquatic Geochemistry 10, 99-137.

Tang C, Rengel Z. 2003. Role of plant cation/anion uptake ratio in soil acidification. In: Handbook of Soil Acidity (ed Rengel Z), pp. 57-81. Marcel-Dekker, New York.

Thoen, Gregory F., 1990. Soil survey of Barry County, Michigan / United States Department of Agriculture, Soil Conservation Service; in cooperation with Michigan Agricultural Experiment Station, Michigan Department of Agriculture, and Michigan Technological University.

Tilman D, Fargione J, Wolff B, D'Antonio C, Dobson A, Howarth R, Schindler D, Schlesinger WH, Simberloff D, and Swackhamer D. 2001. Forecasting agriculturally driven global environmental change. Science 292: 281-284.

Ugolini, F.C., Minden, R., Dawson, H., Zachara, J., 1977. An example of soil processes in the Abies amabilis zone of central cascades, Washington. Soil Sci. 124, 291–303.

Vagstad, N., Jansons, V., Loigu, E., Deelstra, J., 2000. Nutrient losses from agricultural areas in the Gulf of Riga drainage basin. Ecological Engineering 14: 435–441.

Velleman, P.F., and D.C. Hoaglin. 1981. *Applications, Basics, and Computing of Exploratory Data Analysis*, Duxbury Press.

Vitousek, P.M. and W.A. Reiners. 1975. Ecosystem succession and nutrient retention: a hypothesis. BioScience 25: 376-381.

Vos, J. and P.E.L. van der Putten. 2004. Nutrient cycling in a cropping system with potato, spring wheat, sugarbeet, oats and nitrogen catch crops. II.

Effect of catch crops on nitrate leaching in autumn and winter. Nutrient Cycling in Agroecosystems 70: 23–31.

West TO, Marland G. 2002. A synthesis of carbon sequestration, carbon emissions, and net carbon flux from agriculture: comparing tillage practices in the United States. Agriculture, Ecosystems, and Environment 91: 217-232.

West TO, McBride AC. 2005. The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions. Agriculture, Ecosystems and Environment 108: 145-154.

West TO, Post WM. 2002. Soil organic carbon sequestration rates by tillage and crop rotation: A global data analysis. Soil Science Society of America Journal 66: 1930-1946.

Wetzel, R.G. and G.E. Likens. 2000. Limnological analyses. 3rd ed. Saunders. 429 p.

Willson, T. 1998. Managing nitrogen mineralization and biologically active organic matter fractions in agricultural soils. Ph.D. Dissertation, Michigan State University, East Lansing, Michigan, USA.

Wright RF. 1984. Norwegian models for surface water chemistry: An overview. In: Modeling of total acid precipitation impacts (ed Schnoor JL), pp. 73-87. Butterworth Publishers, Boston, MA, USA.

CHANGES IN MAJOR SOLUTE CHEMISTRY AS WATER INFILTRATES SOILS: COMPARISONS BETWEEN MANAGED AGROECOSYSTEMS AND UNMANAGED VEGETATION

VOLUME II

By

Amanda Lord Kurzman

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Zoology

2006

APPENDICES

APPENDIX A

Tables

Tal
in T

Tre
T1
T2
T3
T4
T5
T6
T7
CF
DF
SF

Table 1: Summary of Treatments. Note: Cereal rye was used as a cover crop in T6 in 1999 and 2000.

Treatment	Community Type	Vegetation	Chemical Input / Tilling Practice	Managed / Unmanaged
T1	Annual Cropping system	Corn / Soybean / Wheat Rotation	Conventional Input / Conventional Till	Managed
T2	Annual Cropping system	Corn / Soybean / Wheat Rotation	Conventional Input / No-Till	Managed
T3	Annual Cropping system	Corn / Soybean / Wheat Rotation + Clover Cover Crop	Reduced Input / Conventional Till	Managed
T4	Annual Cropping system	Corn / Soybean / Wheat Rotation + Clover Cover Crop	Reduced Input Organic / Conventional Till	Managed
T5	Perennial Cropping System	Poplar Trees	Herbicide only / Conventional Till	Managed
T6	Perennial Cropping System	Alfalfa	Herbicide and Lime Only / Conventional Till	Managed
T7	Early Successional Community	Mixed herbaceous vegetation	No Input / Last tilled in 1989	Unmanaged
CF	Coniferous Forest	Conifer Plantation	No Input	Unmanaged
DF	Deciduous Forest	Mixed Hardwood	No Input	Unmanaged
SF	Successional Forests	Mixed Hardwood	No Input	Unmanaged

Tat

Dat
4 2
5 1
6 3
4
4 1
8 24
4 20
5 8
5 10
7 1
4 26
4 26
4 20
5 14
6 29
5 26
4 5
4 18
8 24
4 20
4 26
5 10
7 1
4 26
4 26
4/20
5 13
5 14
4 5
4 20
5/15
4/20
8 29

Table 2: Summary of Agronomic Inputs.

Date	Additive	Description	Amount	Amount	Replicate
	T1: Conventional Input / Conventional Till				
4/20/1999	Lime		0.5 tons/acre	1.12 Mg/ha	All
5/19/1999	28% urea ammonium nitrate		25 lbs/acre	28 kg/ha	All
6/30/1999	NH_4NO_3	34-0-0	78.3 lbs N/acre	87.7 kg/ha	All
4/5/2001	28% urea ammonium nitrate		12 gal/acre		All
4/18/2001	28% urea ammonium nitrate		12 gal/acre		All
8/24/2001	Ammonium sulfate		50 lbs/ 6 ha	8.33 lbs/ha	All
4/20/2002	Potash	0-0-60	125 lbs/acre		All
5/8/2002	Liq Starter Fertilizer	19-17-0	12 gal/acre		R2 / R3
5/10/2002	Liq Starter Fertilizer	19-17-0	12 gal/acre		R4
7/1/2002	28% urea ammonium nitrate		111 lbs N/acre		All
4/26/2003		11-52-0		146 lbs/ha	All
4/26/2003	Potash	0-0-60		311 lbs/ha	All
	T2: Conventional Input / No Till				
4/20/1999	Lime		0.8 tons/acre	1.7 Mg/ha	All
5/14/1999	28% urea ammonium nitrate		25 lbs/acre	28 kg/ha	All
6/29/1999	NH4NO3	34-0-0	78.3 lbs N/acre	87.7 kg/ha	All
5/26/2000	Ammonium sulfate		50 lbs/ 6 ha	8.33 lbs/ha	All
4/5/2001	28% urea ammonium nitrate		12 gal/acre		All
4/18/2001	28% urea ammonium nitrate		12 gal/acre		All
8/24/2001	Ammonium sulfate		50 lbs/ 6 ha	8.33 lbs/ha	All
4/20/2002	Potash	0-0-60	125 lbs/acre		All
4/26/2002	Ammonium sulfate		50 lbs/ 6 ha	8.33 lbs/ha	All
5/10/2002	Liq Starter Fertilizer	19-17-0	12 gal/acre		All
7/1/2002	28% urea ammonium nitrate		111 lbs N/acre		All
4/26/2003		11-52-0		146 lbs/ha	All
4/26/2003	Potash	0-0-60		311 lbs/ha	All
	T3: Reduced Input / Conventional Till				
4/20/1999	Lime		0.5 tons/acre	1.12 Mg/ha	All
5/13/1999	28% urea ammonium nitrate		25 lbs/acre	28 kg N/ha	R2
5/14/1999	28% urea ammonium nitrate		25 lbs/acre	28 kg N/ha	R3 / R4
4/5/2001	28% urea ammonium nitrate		14 gal/acre		All
4/20/2002	Potash	0-0-60	125 lbs/acre		All
5/15/2002	Liq Starter Fertilizer	19-17-0	12 gal/acre		All
	T6: Perennial / Alfalfa				
4/20/1999	Lime		0.5 tons/acre	1.12 Mg/ha	All
8/29/2001	Ammonium sulfate		2.5 lbs/acre		All

Tab
trea

Add
NH_4
NO_3
Ca^{2+}
Mg^{2+}
Cl^-
SO_4^-
K^+
P

Table 3: Summary of major ions and elements added to each agronomic treatment.

Addition	T1	T2	T3	T4	T6
NH_4^+	X	X	X		X
NO_3^-	X	X	X		
Ca^{2+}	X	X	X		X
Mg^{2+}	X	X	X		X
Cl^-	X	X	X		
SO_4^-	X	X			X
K^+	X	X	X		
P	X	X	X		

Table
There
"consta

Io
OH^-
HCO_3^-
½ CO_3
Cl-
NO_3^-
½ SO_4

Taken
Fresh
Scient

Table 4: Equivalent conductance of major ions in µS/cm per meq at 25°C. There are discrepancies of 1% to 5% in different reported values for these "constants".

Ion	µS/cm; 25°C	Ion	µS/cm; 25°C
OH^-	192	H+	350
HCO_3^-	44.5	½ Ca^{2+}	60.0
½ CO_3^{2-}	69.3	½ Mg^{2+}	53.0
Cl-	76.4	K^+	74
NO_3^-	71.5	Na^+	50.5
½ SO_4^{2-}	80	$NH4^+$	74
		Fe^{2+}	54

Taken from: Page 53, IBP Handbook No. 8, Methods for Chemical Analysis of Fresh Waters, H.L. Golterman and R.S. Clymo, 1969. Published by Blackwell Scientific Publications, Oxford and Edinburgh.

Table 5: Hydrochemical characterization of the soil solutions of ten treatments in the KBS LTER Network in southwest Michigan for sampling periods during March 1999 – June 2003. Values represent the number of samples (n), the first quartile (Q1), the median, and the third quartile (Q3) for each variable. Concentration units are given here in the most commonly used forms to facilitate comparisons with other sources of information. Dissolved organic carbon (DOC), Total Dissolved Phosphorus (TDP) and Ammonium-N measurements were made on samples from March 1999 – May 2000.

Treatment	pH				Conductance (µS/cm @ 25°C)				Alkalinity (mg HCO_3^-/L)				Ammonium-N (mg/L)			
	N	Q1	Median	Q3	n	Q1	Median	Q3	n	Q1	Median	Q3	n	Q1	Median	Q3
CF	104	5.67	6.05	6.60	105	68	90	118	100	5.34	14.01	24.56	42	0.008	0.021	0.046
DF	98	5.59	6.07	6.59	98	67	84	129	96	3.04	10.15	21.44	32	0.024	0.040	0.061
SF	118	6.47	6.72	7.03	119	34	41	49	115	6.30	15.89	31.43	54	0.011	0.019	0.039
T1	126	6.32	6.54	7.44	128	110	169	242	126	11.73	19.75	54.77	50	0.008	0.020	0.051
T2	126	7.33	7.59	8.01	128	128	192	482	128	38.33	56.36	244.92	49	0.006	0.016	0.037
T3	138	6.50	7.14	7.51	138	123	179	264	137	12.64	30.31	58.36	53	0.006	0.009	0.025
T4	126	6.41	6.70	7.86	126	73	134	310	126	10.28	19.69	182.22	50	0.005	0.009	0.033
T5	145	6.40	6.88	7.20	145	53	65	89	140	13.13	24.14	36.02	56	0.006	0.010	0.018
T6	96	6.37	6.90	7.52	94	129	249	392	91	12.46	28.33	144.17	50	0.022	0.039	0.140
T7	102	6.75	7.05	7.37	102	54	66	87	98	12.92	24.22	37.60	40	0.008	0.011	0.027

Treatment	Calcium (mg/L)				Chloride (mg/L)				DOC (mg C/L)				Magnesium (mg/L)			
	n	Q1	Median	Q3	n	Q1	Median	Q3	n	Q1	Median	Q3	n	Q1	Median	Q3
CF	105	6.99	11.70	17.05	106	1.35	1.88	3.20	26	2.27	4.46	15.91	105	1.29	1.78	2.64
DF	96	4.88	7.37	10.06	98	1.06	1.48	2.93	24	2.16	2.63	3.64	98	2.35	3.42	4.84
SF	116	3.24	4.32	5.47	119	0.27	0.49	0.79	26	1.96	2.66	3.17	118	0.71	0.98	1.31
T1	127	11.89	20.01	33.11	127	0.42	0.90	2.21	26	2.09	3.00	5.43	127	1.86	2.56	3.98
T2	129	17.70	24.96	70.31	130	0.47	1.00	2.81	25	2.22	2.45	3.87	129	2.81	4.50	17.54
T3	137	11.48	21.35	34.54	138	0.31	1.19	3.78	27	2.13	3.72	4.23	137	2.23	3.39	4.77
T4	126	8.42	13.54	38.64	127	0.27	0.64	0.95	28	2.43	2.87	4.16	126	1.90	3.05	8.82
T5	145	4.52	7.31	11.01	145	0.43	0.56	1.10	29	2.03	2.29	3.93	144	1.23	1.84	2.88
T6	97	16.89	34.33	56.82	98	0.60	1.89	8.77	26	2.66	3.35	6.01	98	2.72	7.00	11.74
T7	102	5.77	8.10	11.06	103	0.21	0.57	1.57	23	2.48	3.07	5.63	103	0.84	1.16	2.04

Treatment	Nitrate-N (mg/L)				Potassium (mg/L)				Silica (mg Si/L)			
	n	Q1	Median	Q3	n	Q1	Median	Q3	n	Q1	Median	Q3
CF	106	0.82	2.17	5.26	106	0.14	0.36	0.98	106	7.90	9.58	11.35
DF	98	0.38	3.46	9.96	98	0.23	0.40	0.84	98	6.60	9.08	15.44
SF	119	0.02	0.08	0.40	119	0.15	0.23	0.41	119	3.99	6.13	8.94
T1	128	5.57	11.29	21.88	128	1.72	5.45	6.85	128	3.74	4.81	8.05
T2	130	3.70	7.25	11.95	130	0.70	1.59	2.45	129	6.19	9.38	14.84
T3	138	3.37	12.53	23.14	138	2.83	5.44	7.96	138	4.70	5.80	7.47
T4	126	2.61	8.33	13.39	127	1.18	1.79	2.92	127	4.06	5.31	10.01
T5	145	0.00	0.00	0.01	145	0.39	1.82	2.24	143	4.46	5.77	7.58
T6	98	1.98	16.00	33.25	98	0.62	1.04	2.19	96	6.56	8.88	13.68
T7	103	0.07	0.23	1.15	103	1.88	2.44	4.27	101	3.24	4.57	5.86

Treatment	Sodium (mg/L)				Sulfate (mg/L)				TDP (mg/L)			
	n	Q1	Median	Q3	n	Q1	Median	Q3	n	Q1	Median	Q3
CF	106	1.83	2.14	2.55	106	14.23	17.35	20.35	42	0.006	0.010	0.016
DF	98	1.51	2.04	2.46	98	9.71	13.69	17.40	32	0.005	0.007	0.014
SF	119	1.12	1.31	1.65	119	6.17	8.44	11.48	54	0.007	0.014	0.021
T1	128	1.23	1.58	2.12	128	7.34	10.52	13.51	50	0.010	0.024	0.044
T2	130	1.47	2.00	2.75	130	3.70	6.33	8.52	49	0.015	0.048	0.086
T3	138	1.31	1.78	2.47	138	3.56	6.70	9.68	53	0.012	0.022	0.037
T4	127	1.49	1.88	2.33	127	4.64	6.78	8.87	50	0.005	0.009	0.023
T5	145	1.34	1.53	1.76	145	13.42	17.65	21.26	56	0.007	0.011	0.017
T6	98	1.42	2.13	3.16	98	1.88	4.21	6.35	50	0.010	0.020	0.050
T7	102	1.25	1.47	1.89	103	7.52	9.37	12.80	40	0.009	0.021	0.031

Table 6: Pearson pairwise correlation matrix for the hydrochemical data from all treatments combined. Coefficients are shown together with Bonferroni-corrected probabilities. Significant ($P < 0.05$) correlations are bolded.

	Conductivity	pH	TDP	Si	DOC	Dilution Factor	% Ion Diff	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4-N	Cl^-	SO_4^{2-}	NO_3-N
Conductivity	1.000															

	Conductivity	pH	TDP	Si	DOC	Dilution Factor	% Ion Diff	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4-N	Cl^-	SO_4^-	NO_3-N
Conductivity	1.000															
Probability	0.000															
pH	**0.416**	1.000														
Probability	**0.000**	0.000														
TDP	0.147	0.140	**1.000**													
Probability	0.170	0.274	**0.000**													
Si	**0.429**	**0.209**	0.178	1.000												
Probability	**0.000**	**0.000**	0.010	0.000												
DOC	-0.089	-0.157	0.005	0.104	**1.000**											
Probability	1.000	1.000	1.000	1.000	**0.000**											
Dilution Factor	0.087	**0.125**	0.035	**0.199**	**0.258**	1.000										
Probability	0.342	**0.002**	1.000	**0.000**	**0.003**	0.000										
% Ion Diff	0.099	**0.182**	0.003	**0.152**	0.009	0.056	**1.000**									
Probability	0.096	**0.000**	1.000	**0.000**	1.000	1.000	**0.000**									
HCO_3^-	**0.554**	**0.625**	0.100	**0.615**	-0.032	**0.167**	0.094	1.000								
Probability	**0.000**	**0.000**	1.000	**0.000**	1.000	**0.000**	0.194	0.000								
Ca^{2+}	**0.957**	**0.478**	0.137	**0.473**	0.025	**0.121**	**0.163**	**0.670**	1.000							
Probability	**0.000**	**0.000**	0.287	**0.000**	1.000	**0.003**	**0.000**	**0.000**	0.000							
Mg^{2+}	**0.839**	**0.379**	0.079	**0.559**	0.022	**0.147**	**0.205**	**0.723**	**0.851**	1.000						
Probability	**0.000**	**0.000**	1.000	**0.000**	1.000	**0.000**	**0.000**	**0.000**	**0.000**	0.000						
Na^+	**0.480**	0.050	**0.258**	**0.408**	0.116	**0.159**	**0.150**	**0.118**	**0.396**	**0.445**	1.000					
Probability	**0.000**	1.000	**0.000**	**0.000**	1.000	**0.000**	**0.000**	**0.006**	**0.000**	**0.000**	0.000					
K^+	**0.303**	**0.157**	0.105	**-0.174**	-0.034	0.040	0.035	-0.076	**0.232**	0.063	**0.246**	1.000				
Probability	**0.000**	**0.000**	1.000	**0.000**	1.000	1.000	1.000	1.000	**0.000**	1.000	**0.000**	0.000				
NH_4-N	0.151	0.034	**0.604**	0.159	0.106	0.141	-0.028	0.021	0.125	0.078	**0.291**	0.101	1.000			
Probability	0.124	1.000	**0.000**	0.054	1.000	0.215	1.000	1.000	0.699	1.000	**0.000**	1.000	0.000			
Chloride	**0.590**	0.053	0.069	-0.018	0.007	0.018	-0.019	-0.028	**0.520**	**0.386**	**0.347**	**0.277**	0.143	1.000		
Probability	**0.000**	1.000	1.000	1.000	1.000	1.000	1.000	1.000	**0.000**	**0.000**	**0.000**	**0.000**	0.192	0.000		
SO_4^-	**-0.296**	**-0.334**	-0.117	0.071	0.202	-0.066	0.068	**-0.212**	**-0.294**	**-0.219**	-0.016	**-0.234**	-0.093	**-0.211**	1.000	
Probability	**0.000**	**0.000**	1.000	1.000	0.109	1.000	1.000	**0.000**	**0.000**	**0.000**	1.000	**0.000**	1.000	**0.000**	0.000	
NO_3-N	**0.746**	0.030	0.107	0.026	-0.090	0.001	-0.090	-0.033	**0.660**	**0.449**	**0.415**	**0.421**	0.151	**0.595**	**-0.297**	1.000
Probability	**0.000**	1.000	1.000	1.000	1.000	1.000	0.251	1.000	**0.000**	**0.000**	**0.000**	**0.000**	0.098	**0.000**	**0.000**	0.000

Tabl
and
stati
and

Table 7: Correlation (and associated probability) between nitrate concentrations and calcium plus magnesium concentrations. The relationship is positive and statistically significant in all replicates, with the exception of Replicate T2-R3 and T4-R3.

Treatment-Replicate	r-value	p-value
T1-R2	0.971	0.000
T1-R3	0.89	0.000
T1-R4	0.979	0.000
T2-R2	0.925	0.000
T2-R3	-0.247	0.130
T2-R4	0.896	0.000
T3-R2	0.937	0.000
T3-R3	0.865	0.000
T3-R4	0.967	0.000
T4-R2	0.949	0.000
T4-R3	-0.066	0.711
T4-R4	0.964	0.000
T6-R2	0.861	0.000
T6-R3	0.424	0.000
T6-R4	0.935	0.000

Table 8: Statistics for soil solution concentrations of nitrate (meq-N/L) in samples collected from lysimeters located in managed agroecosystems and unmanaged forests and fields at the KBS LTER site. All values are calculated on the basis of n samples; each treatment consists of 3 replicates. [illegible]

Table 8: Statistics for soil solution concentrations of nitrate (meq-N/L) in samples collected from lysimeters located in managed agroecosystems and unmanaged forests and fields at the KBS LTER site. All values are calculated on the basis of *n* samples; each treatment consists of 3 replicates. Forested treatments share general vegetative characteristics and soil types, but have notable differences among replicates. The remaining treatments are located in a contiguous 42-hectare site and the 1-hectare replicates are arranged in a randomized complete block design consisting of six blocks and seven treatments; lysimeters were placed in each replicate of Blocks 2, 3, and 4. S.D. = standard deviation; C.V. = coefficient of variation.

					Range				
Treatment	Mean	Median	S.D.	C.V. (%)	Min	Max	Skewness	Kurtosis	n
Deciduous Forest	0.454	0.247	0.549	1.21	0	2.43	1.60	2.40	98
Coniferous Forest	0.318	0.155	0.425	1.34	0	2.48	2.61	8.37	107
Successional Forest	0.025	0.006	0.053	2.15	0	0.44	5.25	34.71	119
Conventional Input / Conventional Till	1.399	0.806	2.14	1.53	0	12.55	3.78	15.16	128
Conventional Input / No-Till	0.952	0.518	1.606	1.69	0	11.25	4.35	22.35	130
Reduced Input / Conventional Till	1.240	0.895	1.314	1.06	0.001	5.92	1.66	2.54	138
Zero Input / Conventional Till	0.678	0.595	0.576	0.85	0	2.84	0.98	0.71	126
Perennial Poplar	0.001	0.000	0.002	2.48	0	0.01	5.20	29.22	145
Perennial Alfalfa	1.401	1.142	1.279	0.91	0.001	4.58	0.69	-0.49	98
Successional Field	0.069	0.017	0.112	1.63	0	0.61	2.38	6.14	103

Table 9: Statistics for soil solution concentrations of chloride (meq /L) in samples collected from lysimeters located in managed agroecosystems and unmanaged forests and fields at the KBS LTER site. All values are calculated on the basis of n samples; each treatment consists of 3 replicates.

Table 9: Statistics for soil solution concentrations of chloride (meq /L) in samples collected from lysimeters located in managed agroecosystems and unmanaged forests and fields at the KBS LTER site. All values are calculated on the basis of n samples; each treatment consists of 3 replicates. Forested treatments share general vegetative characteristics and soil types, but have notable differences among replicates. The remaining treatments are located in a contiguous 42-hectare site and the 1-hectare replicates are arranged in a randomized complete block design consisting of six blocks and seven treatments; lysimeters were placed in each replicate of Blocks 2, 3, and 4. S.D. = standard deviation; C.V. = coefficient of variation.

Treatment	Mean	Median	S.D.	C.V. (%)	Range Min	Range Max	Skewness	Kurtosis	n
Deciduous Forest	0.06	0.042	0.046	0.778	0.001	0.295	2.085	6.392	98
Coniferous Forest	0.075	0.054	0.057	0.761	0.008	0.305	1.912	3.846	107
Successional Forest	0.022	0.014	0.029	1.325	0.001	0.165	3.399	12.646	119
Conventional Input / Conventional Till	0.176	0.025	0.487	2.772	0.001	2.671	3.853	14.518	127
Conventional Input / No-Till	0.299	0.028	0.786	2.628	0.002	4.791	3.63	13.8	130
Reduced Input / Conventional Till	0.116	0.034	0.216	1.87	0.001	1.325	3.219	11.712	138
Zero Input / Conventional Till	0.024	0.018	0.04	1.629	0	0.381	6.792	55.446	127
Perennial Poplar	0.025	0.016	0.022	0.878	0.002	0.169	3.203	14.857	145
Perennial Alfalfa	0.347	0.053	0.635	1.829	0.001	2.994	2.327	4.947	98
Successional Field	0.037	0.016	0.052	1.413	0	0.283	2.57	7.222	103

Table 10: Results of Fisher's (protected) Least Significant Different (LSD) test for significant differences among mean chloride concentrations. Following a significant analysis of variance F-test (p = 0.000), Fisher's (protected) LSD test was performed. Bolded values indicate significant differences between means

Table 10: Results of Fisher's (protected) Least Significant Different (LSD) test for significant differences among mean chloride concentrations. Following a significant analysis of variance *F*-test ($p = 0.000$), Fisher's (protected) LSD test was performed. Bolded values indicate significant differences between means.

	CF	DF	SF	Conv. Input	No-Till	Red. Input	Zero Input	Poplar	Alfalfa	Field
Coniferous Forest (CF)	1.000									
Deciduous Forest (DF)	0.764	1.000								
Successional Forest (SF)	0.271	0.442	1.000							
Conv. Input / Conv. Till	**0.035**	**0.018**	**0.001**	1.000						
Conv. Input / No-Till	**0.000**	**0.000**	**0.000**	**0.007**	1.000					
Reduced Input / Conv. Till	0.385	0.245	**0.039**	0.180	**0.000**	1.000				
Zero Input / Conv. Till	0.290	0.471	0.951	**0.001**	**0.000**	**0.042**	1.000			
Perennial Poplar	0.282	0.467	0.938	**0.001**	**0.000**	**0.036**	0.988	1.000		
Perennial Alfalfa	**0.000**	**0.000**	**0.000**	**0.000**	0.324	**0.000**	**0.000**	**0.000**	1.000	
Successional Field	0.450	0.658	0.752	**0.004**	**0.000**	0.097	0.794	0.799	**0.000**	1.000

Table 11: Median conductivity and median concentrations of major cations (meq/L) and nitrate (meq-N/L) in samples collected from lysimeters located in unmanaged managed agroecosystems and unmanaged forests and fields at the KBS LTER site. All values are calculated on the basis of *n* samples (see Table 1); each treatment consists of 3 replicates. n.d. = not detectable.

Treatments	Calcium	Magnesium	Sodium	Potassium	Nitrate-N
Deciduous Forest	0.368	0.282	0.089	0.01	0.247
Coniferous Forest	0.585	0.148	0.093	0.01	0.155
Successional Forest	0.216	0.081	0.057	0.006	0.006
Conventional Input / Conventional Till	0.999	0.211	0.069	0.139	0.806
Conventional Input / No-Till	1.245	0.37	0.087	0.041	0.518
Reduced Input / Conventional Till	1.065	0.279	0.077	0.139	0.895
Zero Input / Conventional Till	0.676	0.251	0.082	0.046	0.595
Perennial Poplar	0.365	0.151	0.067	0.047	n.d.
Perennial Alfalfa	1.713	0.576	0.093	0.026	1.142
Successional Field	0.404	0.095	0.064	0.062	0.017

*Table 12: **Results of Fisher's (protected) Least Significant Different (LSD) test** for significant differences among mean nitrate concentrations. Following a significant analysis of variance F-test (p = 0.000), Fisher's (protected) LSD test was performed. Bolded values indicate significant differences bet*

Table 12: Results of Fisher's (protected) Least Significant Different (LSD) test for significant differences among mean nitrate concentrations. Following a significant analysis of variance *F*-test ($p = 0.000$), Fisher's (protected) LSD test was performed. Bolded values indicate significant differences between means.

	CF	DF	SF	Conv. Input	No-Till	Red. Input	Zero Input	Poplar	Alfalfa	Field
Coniferous Forest (CF)	1.000									
Deciduous Forest (DF)	0.369	1.000								
Successional Forest (SF)	**0.044**	**0.004**	1.000							
Conv. Input / Conv. Till	**0.000**	**0.000**	**0.000**	1.000						
Conv. Input / No-Till	**0.000**	**0.001**	**0.000**	**0.001**	1.000					
Reduced Input / Conv. Till	**0.000**	**0.000**	**0.000**	0.235	**0.030**	1.000				
Zero Input / Conv. Till	**0.012**	0.238	**0.000**	**0.000**	**0.044**	**0.000**	1.000			
Perennial Poplar	**0.023**	**0.001**	0.859	**0.000**	**0.000**	**0.000**	**0.000**	1.000		
Perennial Alfalfa	**0.000**	**0.000**	**0.000**	0.990	**0.002**	0.264	**0.000**	**0.000**	1.000	
Successional Field	0.098	**0.012**	0.765	**0.000**	**0.000**	**0.000**	**0.000**	0.629	**0.000**	1.000

Table 13: Sum of concentrations of nitrate (meq-N/L) in samples collected from lysimeters located in managed agroecosystems and unmanaged forests and fields at the KBS LTER site. Values are calculated on the basis of *n* samples; each treatment consists of 3 replicates. Values are not meant to represent total fluxes and are meant to be used as a basis for relative ranking only. Note that data are not corrected for differences in the number of samples collected; however, based on a review of the data, such correction is not expected to impact the relative ranking of the treatments.

Treatments	*n*	Sum (meq/L)
Conventional Input / Conventional Till	128	179.076
Conventional Input / No-Till	130	123.705
Reduced Input / Conventional Till	138	171.159
Zero Input / Conventional Till	126	85.375
Deciduous Forest	98	44.523
Coniferous Forest	107	33.978
Successional Forest	119	2.95

Table 14: Relative global warming potentials (GWP) for different management systems based on soil carbon sequestration, agronomic inputs, and trace gas fluxes (in part from Robertson et al. 2000). Units are CO2-equivalents (g *m-2 y-1) based on IPCC conversion factors. Negative GWP indicates a global warming mitigation potential.*

Table 14: Relative global warming potentials (GWP) for different management systems based on soil carbon sequestration, agronomic inputs, and trace gas fluxes (in part from Robertson *et al.* 2000). Units are CO2-equivalents (g m-2 y-1) based on IPCC conversion factors. Negative GWP indicates a global warming mitigation potential. Net GWP is calculated based on the alternative assumptions that lime acts as either a CO2 source or sink proportional to its carbon content (Hamilton et al, *in review)*.

	CO_2 equivalents						Net GWP:	Net GWP:
Ecosystem	Soil -	N-	Lime[1]	Fuel	N_2O	CH_4	lime as	lime as
Management	C	fertil.					source[2]	sink[3]
Annual Crops (corn/soy/wheat):								
Conventional	0	27	23	16	52	-4	114	68
No-Till	-110	27	34	12	56	-5	14	-54
Low input with legume cover	-40	9	19	20	60	-5	63	25
Organic with legume cover	-29	0	0	19	56	-5	41	41
Perennial crops:								
Alfalfa	-161	0	80	8	59	-6	-20	-180
Poplar	-117	5	0	2	10	-5	-105	-105

[1] Equivalent CO_2 in lime amendments, which were applied following standard best management practices

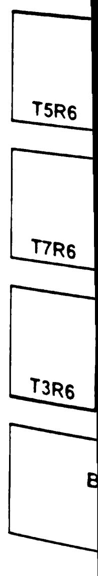
[2] Calculated by Robertson et al. (2000), assuming all carbon in lime becomes CO_2.

[3] Calculated with the alternative assumption that all lime dissolves via carbonic weathering.

APPENDIX B

Figures

T1: Con
T2: Con
T3: Red
T4: Zero
T5: Pere
T6: Pere
T7: Earl
R1 - 6 R
L = Lysi



F

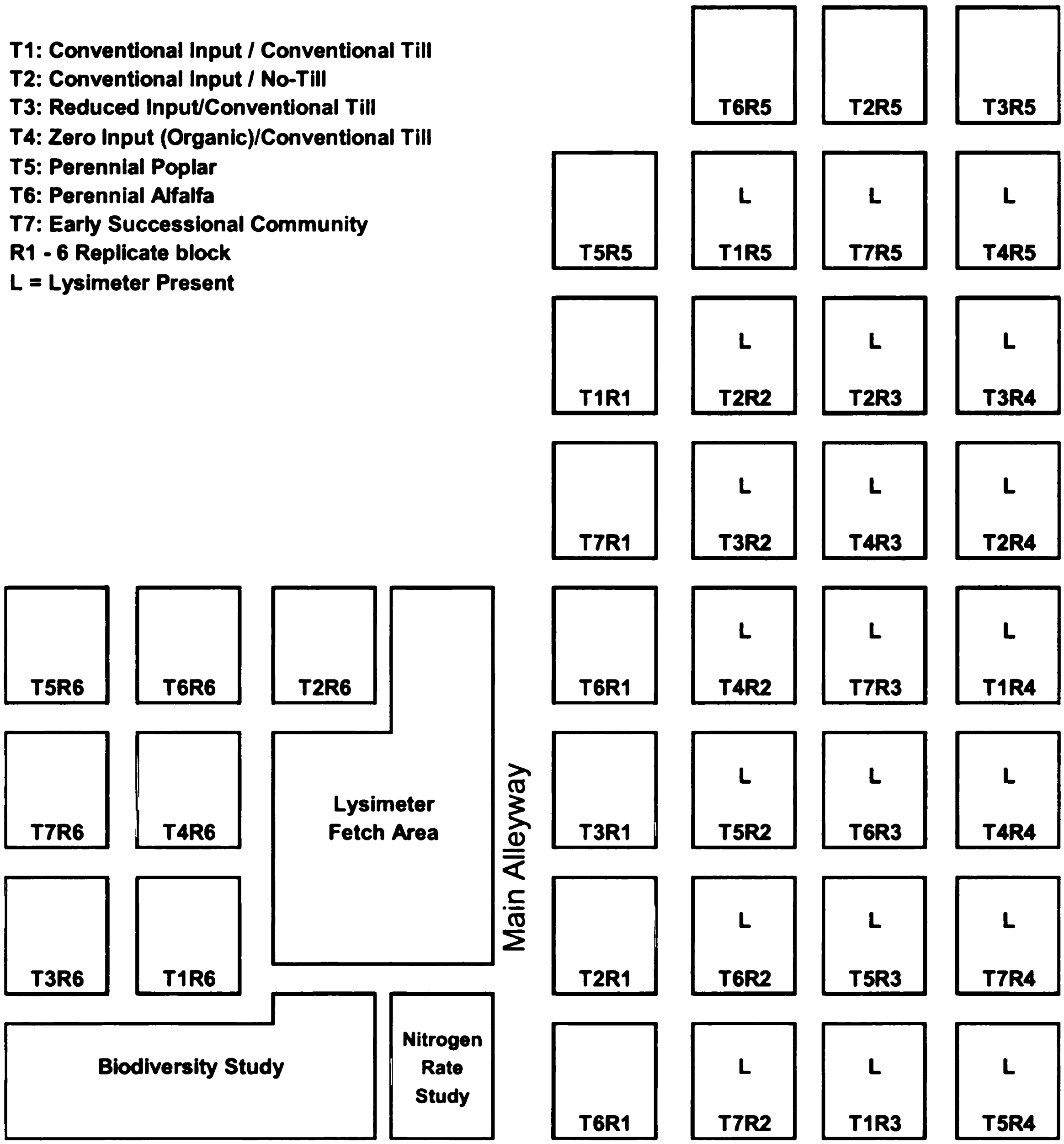


Figure 1: KBS LTER Main Site Layout in 2003 (row crops are rotated annually).

Figure 2

Figure 3:
generate
collection

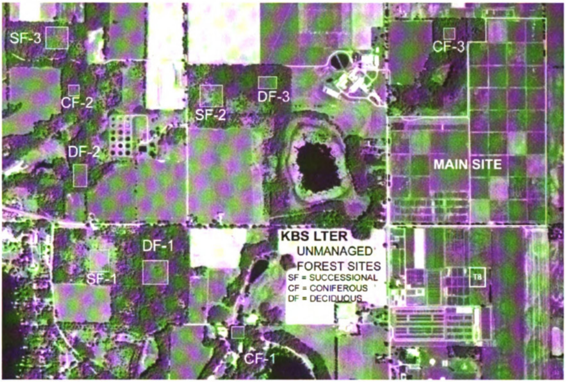


Figure 2: KBS LTER Unmanaged Forest Sites

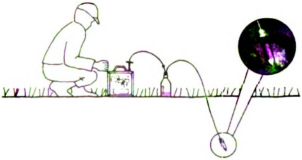


Figure 3: Representative diagram of soil solution sampler. A portable vacuum is used to generate low-tension suction on the lysimeter and draw soil pore water into the sample collection vial. [Source: www.prenart.dk]

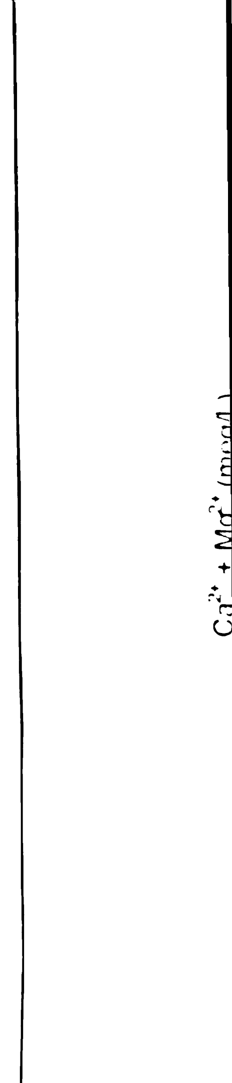


Figure 4
the expe
The soli
Hypothe
meq L-1
consum
is –60%

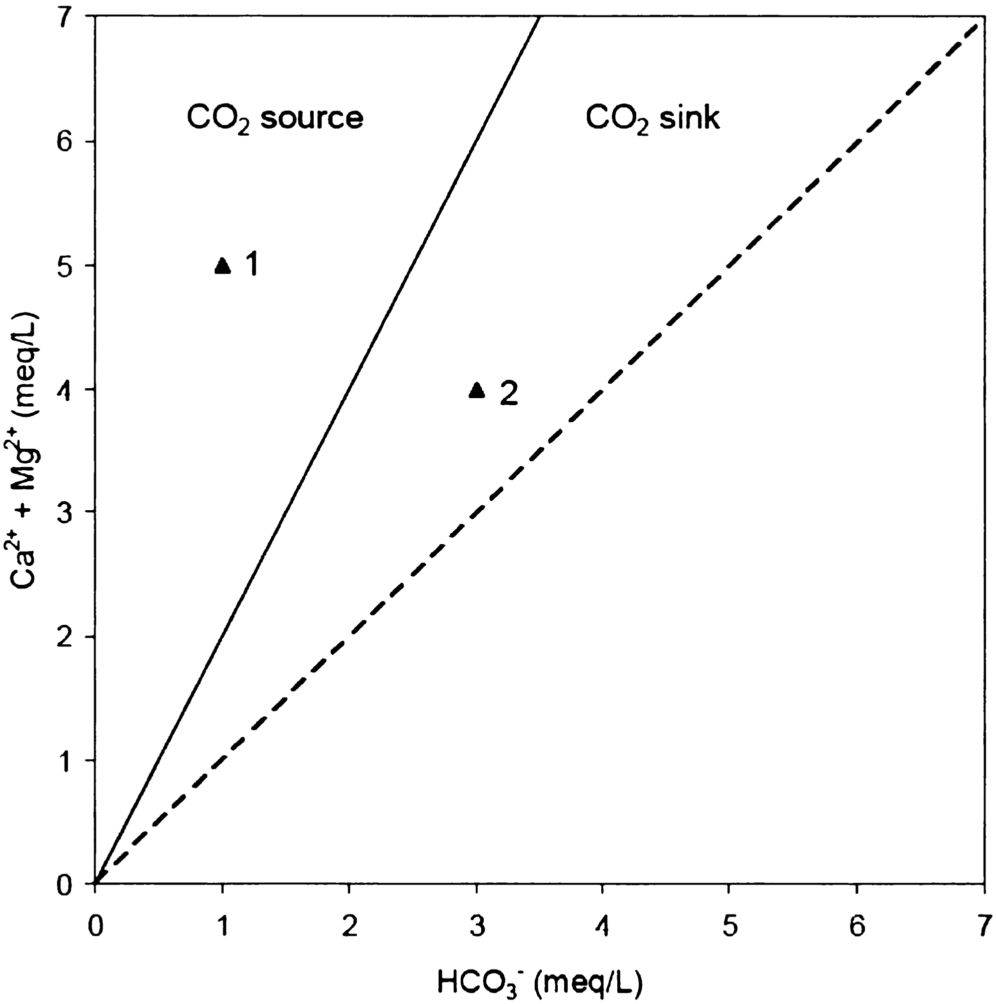


Figure 4: Conceptual model for carbonate mineral dissolution in soils. The dashed line depicts the expected 1:1 ratio of dissolved Ca^{2+} + Mg^{2+} to HCO_3^- produced by carbonic acid weathering. The solid line represents the elemental stoichiometry in the lime (calcite or dolomite). Hypothetical sample 1 demonstrates a case in which the lime has yielded CO_2 equivalent to 1.5 meq L-1, or 60% of its C content, thereby serving as a source of soil CO_2. Sample 2 has consumed soil CO_2 equivalent to 1 meq L-1, or 50% of its C content. The "CO_2-C sink strength" is –60% for Sample 1 (i.e., a CO_2 source) and +50% for Sample 2 (a CO_2 sink).

Figure
and Aq
differen
for in A

Figure
of the c
concern
conduc
uniden

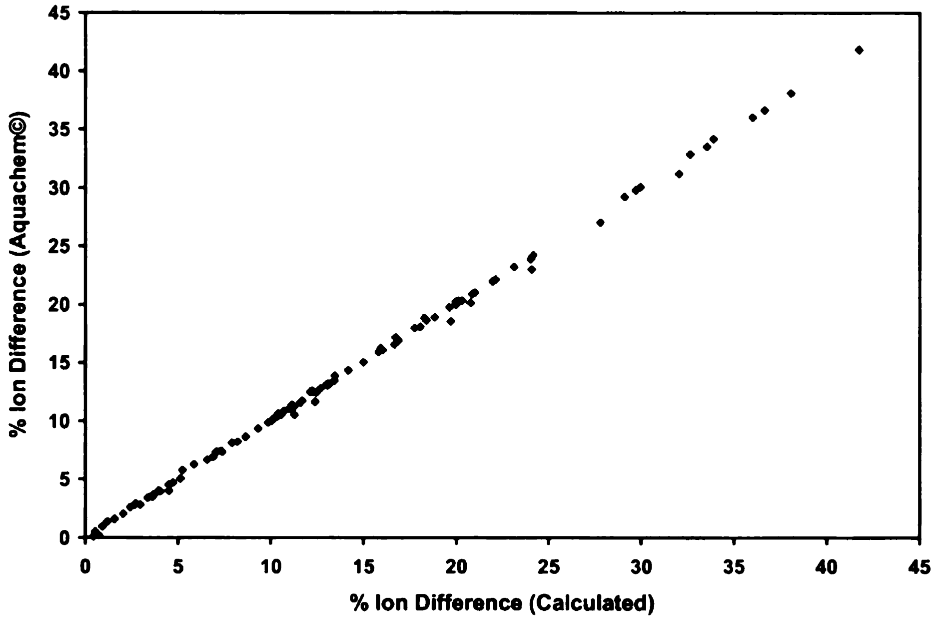
Figure 5
conduc
the sum
deficit)
than the
charge
overall
deficit a

Figure 5, Top: Ion charge balances for soil solutions were calculated in Microsoft Excel (X-axis) and Aquachem. An excellent agreement was obtained between the two methods, and the slight differences between the two methods can be attributed to ion base pairing which is accounted for in Aquachem, but not in Excel. This example is from the Coniferous Forest Treatment.

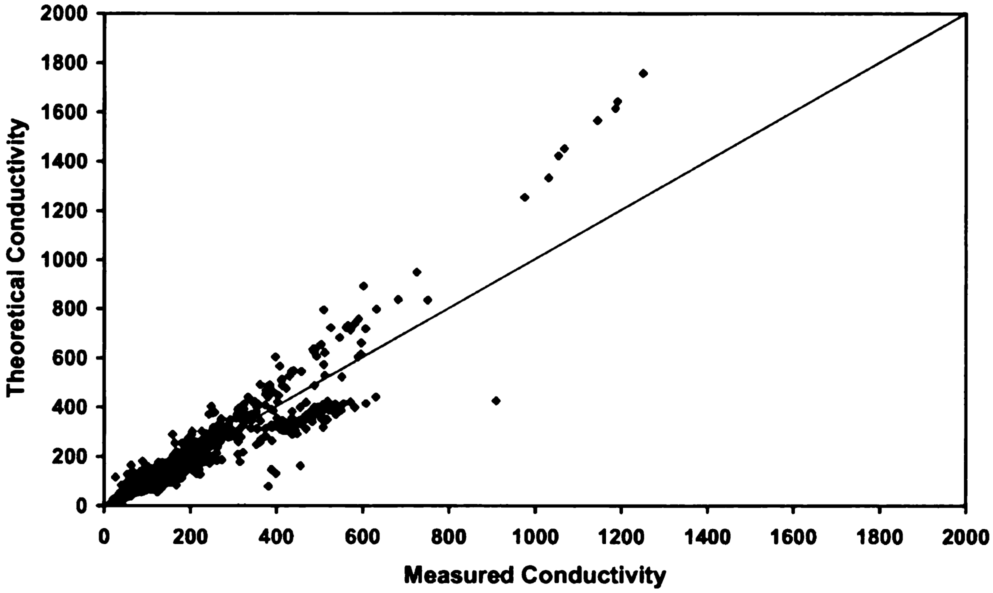
Figure 5, Middle: Theoretical conductance was plotted against measured conductance as part of the quality assurance investigation. The deviation from the one-to-one line raised some concerns regarding data quality. Points above the one-to-one line indicate that the measured conductance was greater than the theoretical conductance, indicating the potential that an unidentified ion is present in the solution.

Figure 5, Bottom: Percent ion difference was plotted against the measured specific conductance. As water is electrically neutral, the points plotting above the zero line indicate that the sum of cations (meq/L) is greater than the sum of anions (meq/L) (a cation surplus/anion deficit). Points plotting below the zero line indicate that the sum of anions (meq/L) is greater than the sum of cations (meq/L) (anion surplus/cation deficit). This graph indicates that ion charge imbalances occur at greater frequency in dilute (low conductance) samples, and that overall conductance ranges, the points tend to fall below the zero line indicating a cation deficit/anion surplus.

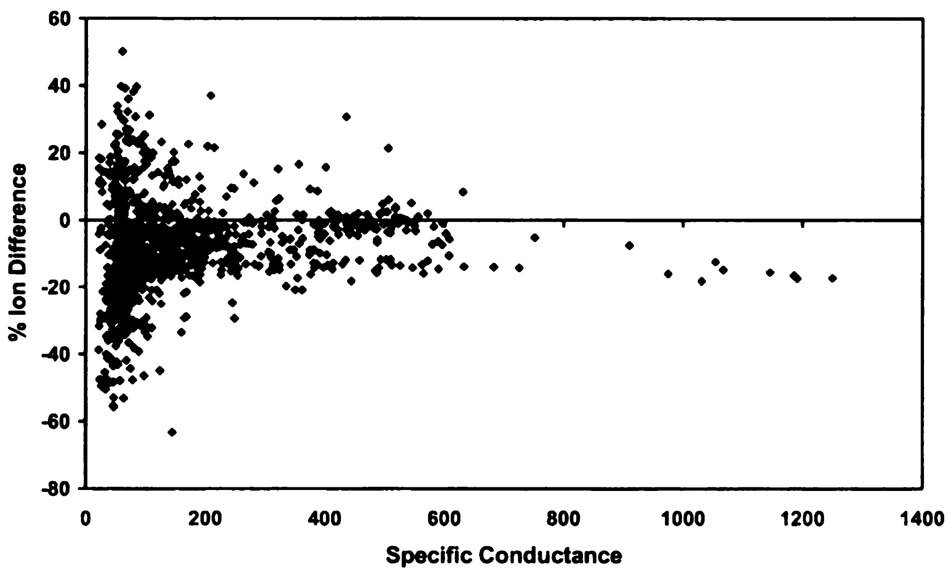

% Ion Difference
Theoretical Conductivity



% Ion Difference (Aquachem©)
% Ion Difference (Calculated)



Theoretical Conductivity
Measured Conductivity



% Ion Difference
Specific Conductance

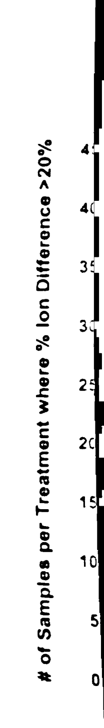
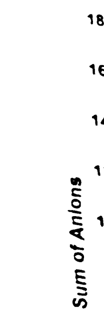


Figure 6
of the s
where t



Figu
the
anic
Mo

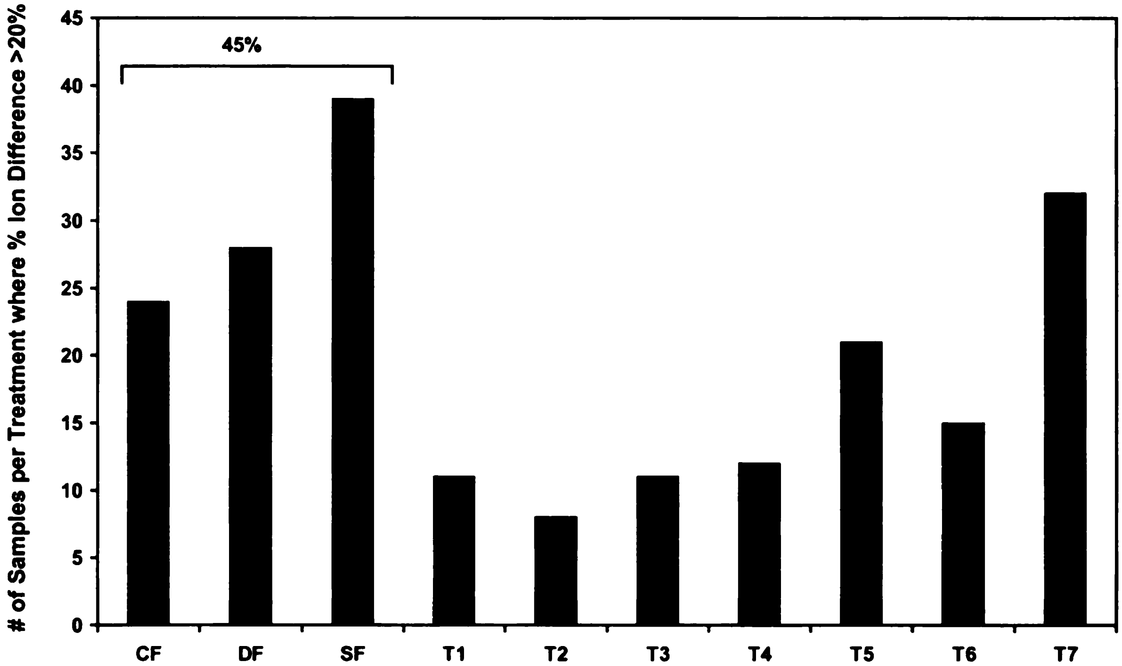


Figure 6, Top: Percent Ion Difference (cations vs. anions) by Treatment. While less than 30% of the samples collected came from forested sites, forested sites represent 45% of the samples where the percent ion difference is greater than 20%.

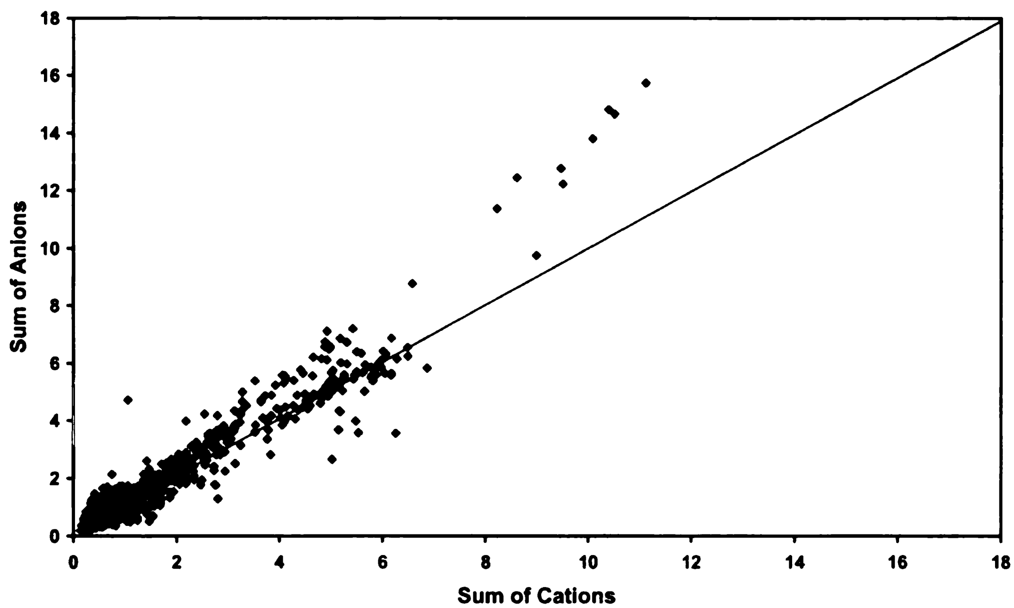


Figure 6, Bottom: Comparison of the sum of anions and cations (meq/L) for all samples where the complete suite of major ions were measured. Points above the line indicate a sample rich in anions (cation deficit). Points below the line indicate a sample rich in cations (anion deficit). Most samples are anion rich.

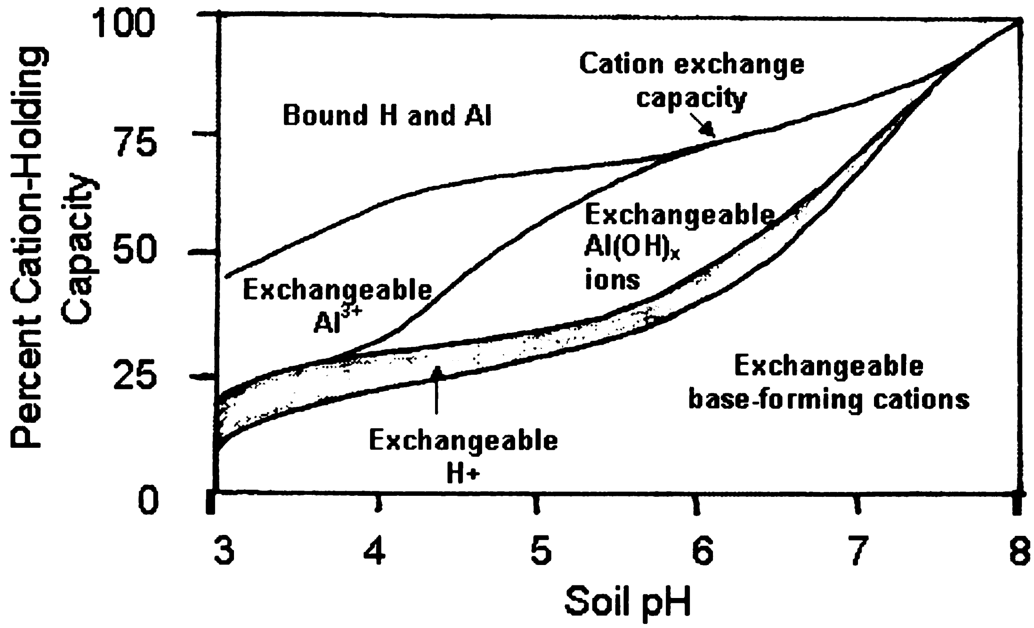


Figure 7: General relationship between soil pH and exchangeable aluminum hydroxy ions. The cation exchange capacity line is estimated using average data from 60 Wisconsin soils from Helling et al. (1964). At intermediate pH, aluminum hydroxy ions such as $Al(OH)^{2+}$ are prominent. This diagram shows typical conditions; any particular soil would likely give a modified distribution (Brady, 1995).

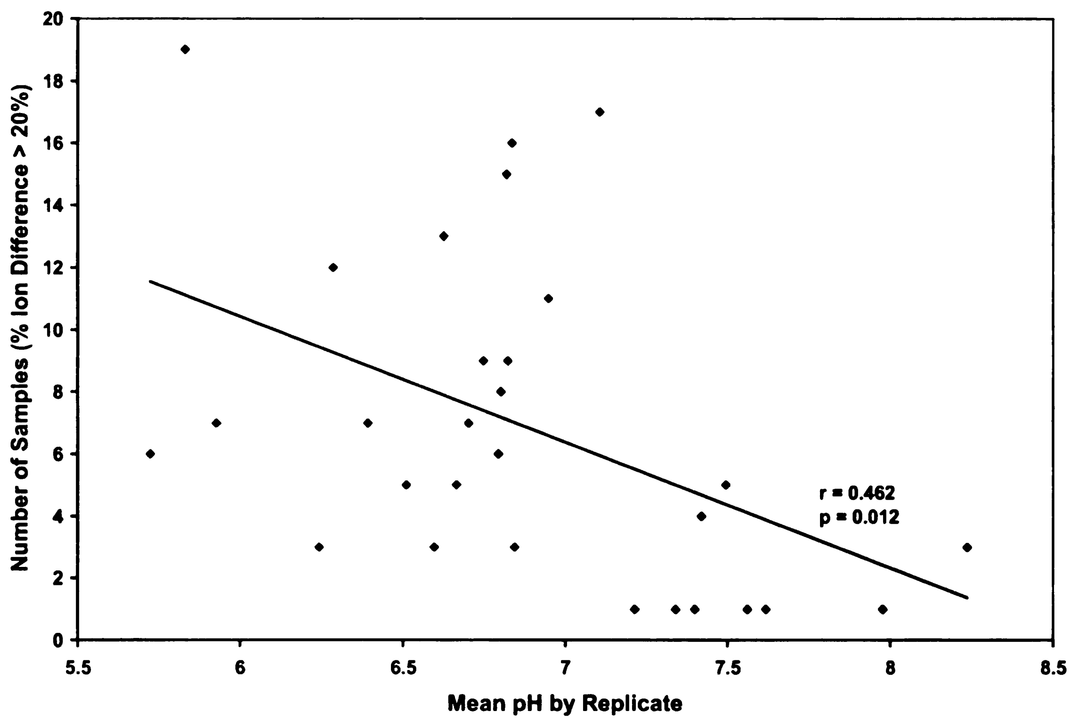
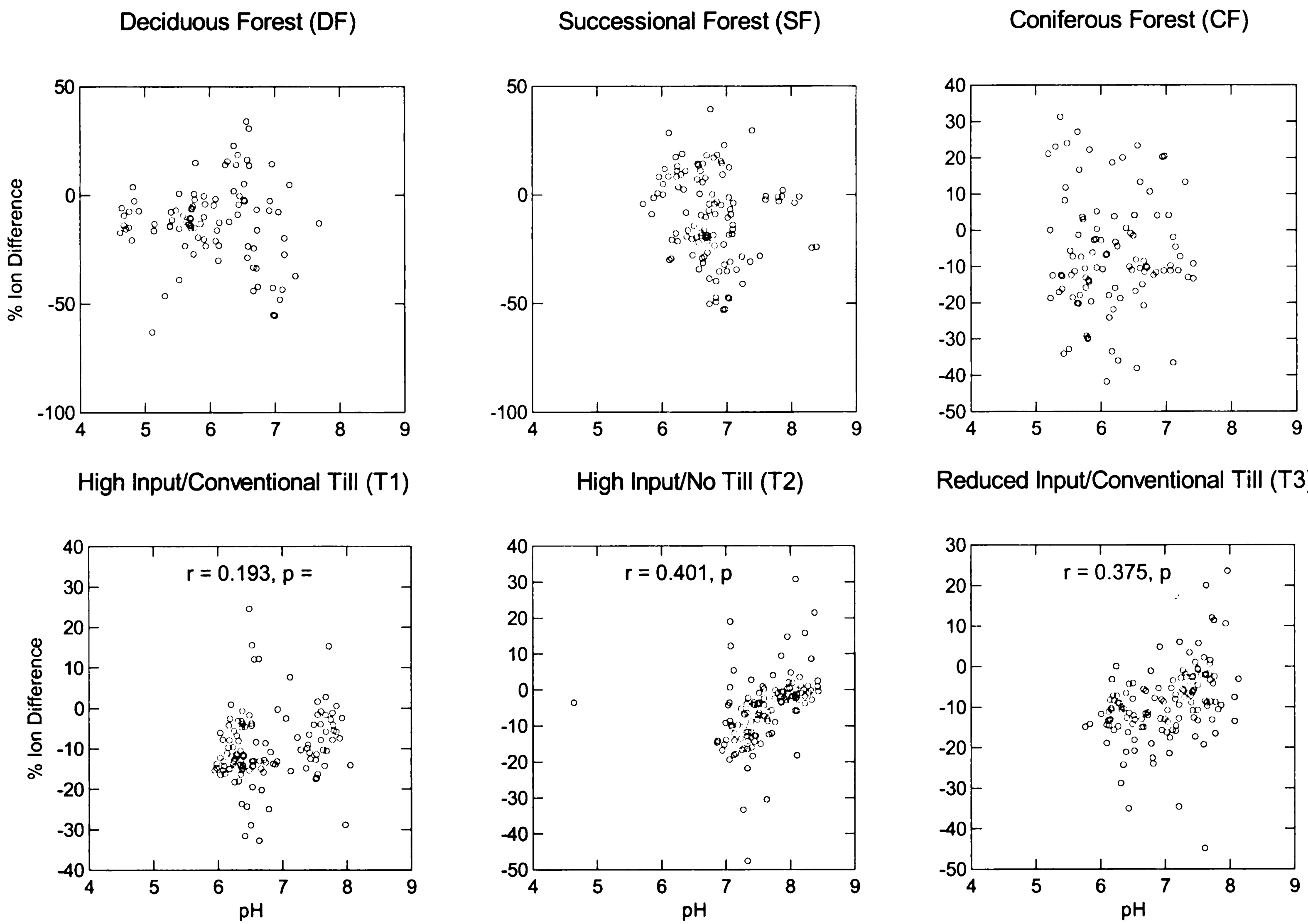
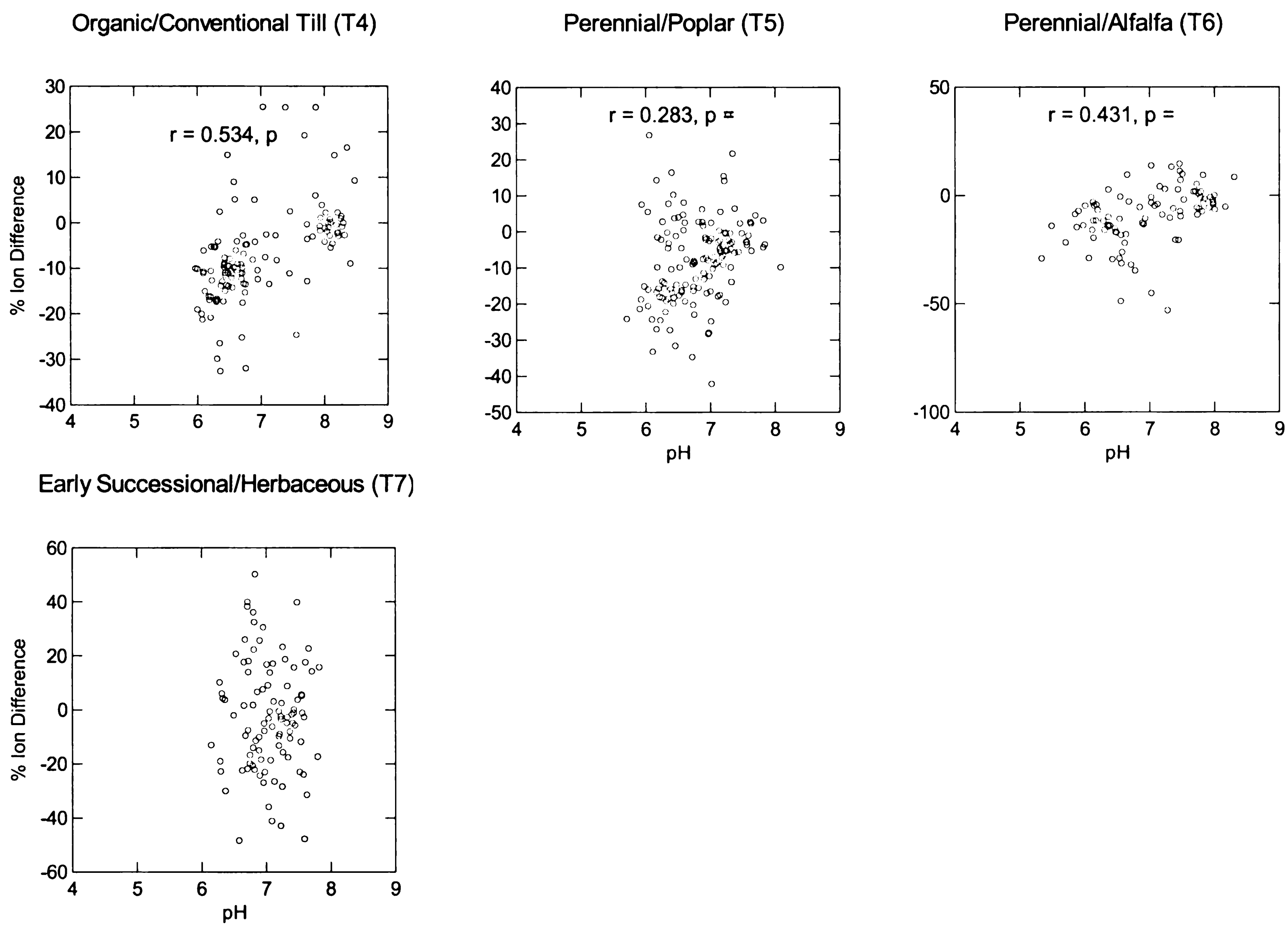


Figure 8: Mean pH versus percent ion difference by replicate, in cases where the % ion difference is greater than 20%. As the mean pH increases, the number of samples with a percent ion difference greater than 20% decreases.

Figure 9: pH versus percent ion difference for all ten treatments. Significant ($p<0.05$) correlations were observed in Treatments 1, 2, 3, 4, 5, and 6. The relationship in these treatments indicates that as the pH approaches 8.0, the percent ion difference declines. The other treatments where a significant relationship is not evident span a pH range where the presence of aluminum hydroxy ions is relatively constant, explaining the lack of a significant relationship.


Deciduous Forest (DF)
Successional Forest (SF)
Coniferous Forest (CF)
High Input/Conventional Till (T1)
High Input/No Till (T2)
Reduced Input/Conventional Till (T3)
r = 0.193, p =
r = 0.401, p
r = 0.375, p
% Ion Difference
pH


Organic/Conventional Till (T4)
r = 0.534, p
% Ion Difference
Perennial/Poplar (T5)
r = 0.283, p =
pH
Perennial/Alfalfa (T6)
r = 0.431, p =
pH
Early Successional/Herbaceous (T7)
% Ion Difference
pH

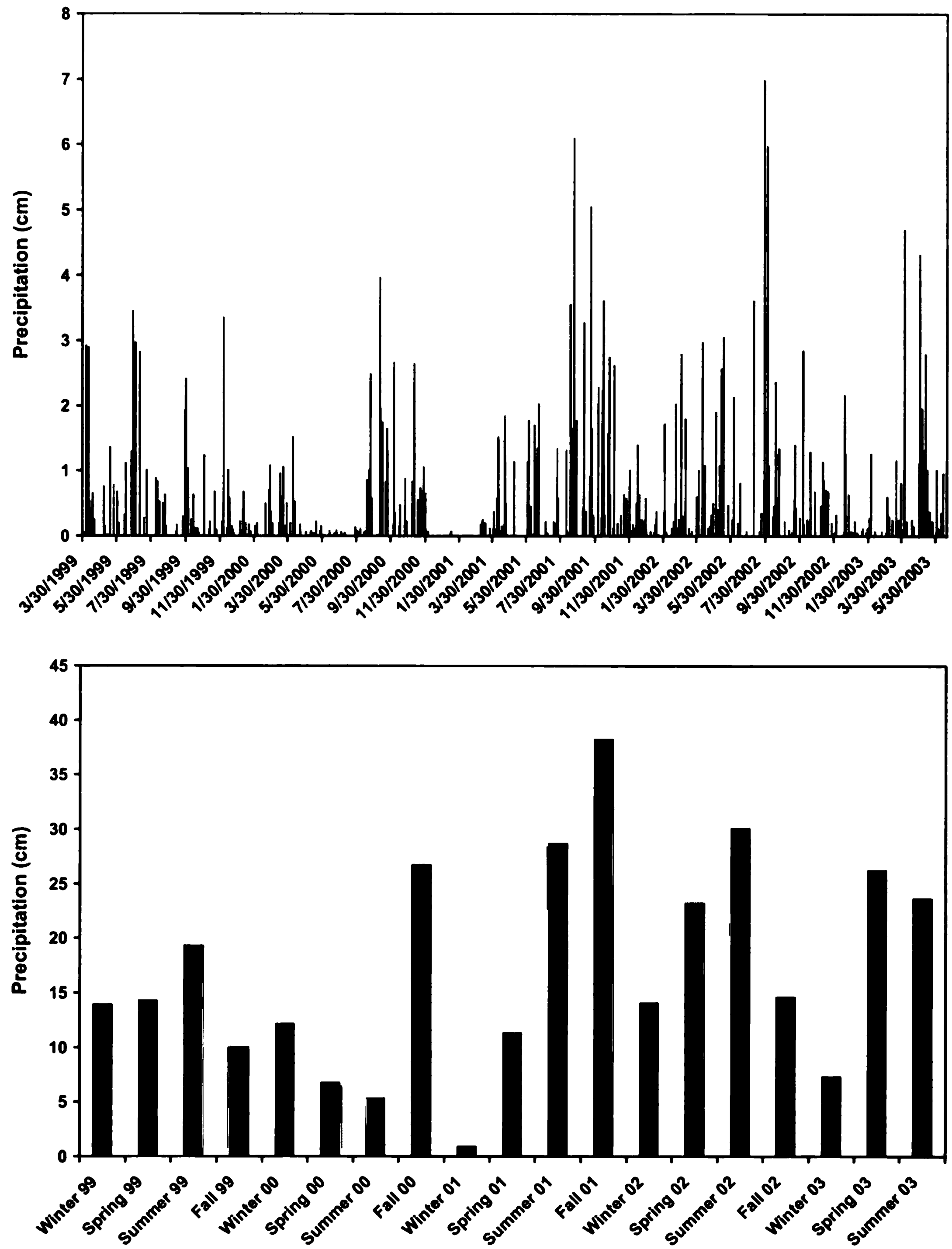


Figure 10: Daily and seasonal precipitation patterns. National Atmospheric Deposition Program (NRSP-3)/National Trends Network, KBS station (MI26), 1999-2003. Missing precipitation data were replaced using KBS National Weather Station Data.

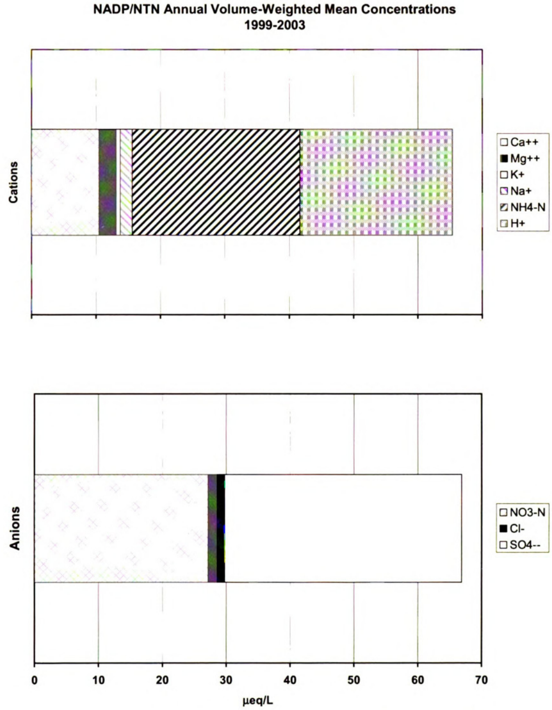


Figure 11: Annual volume-weighted mean concentrations of major ions in precipitation. The dominant cation is ammonium and the dominant anion is sulfate.

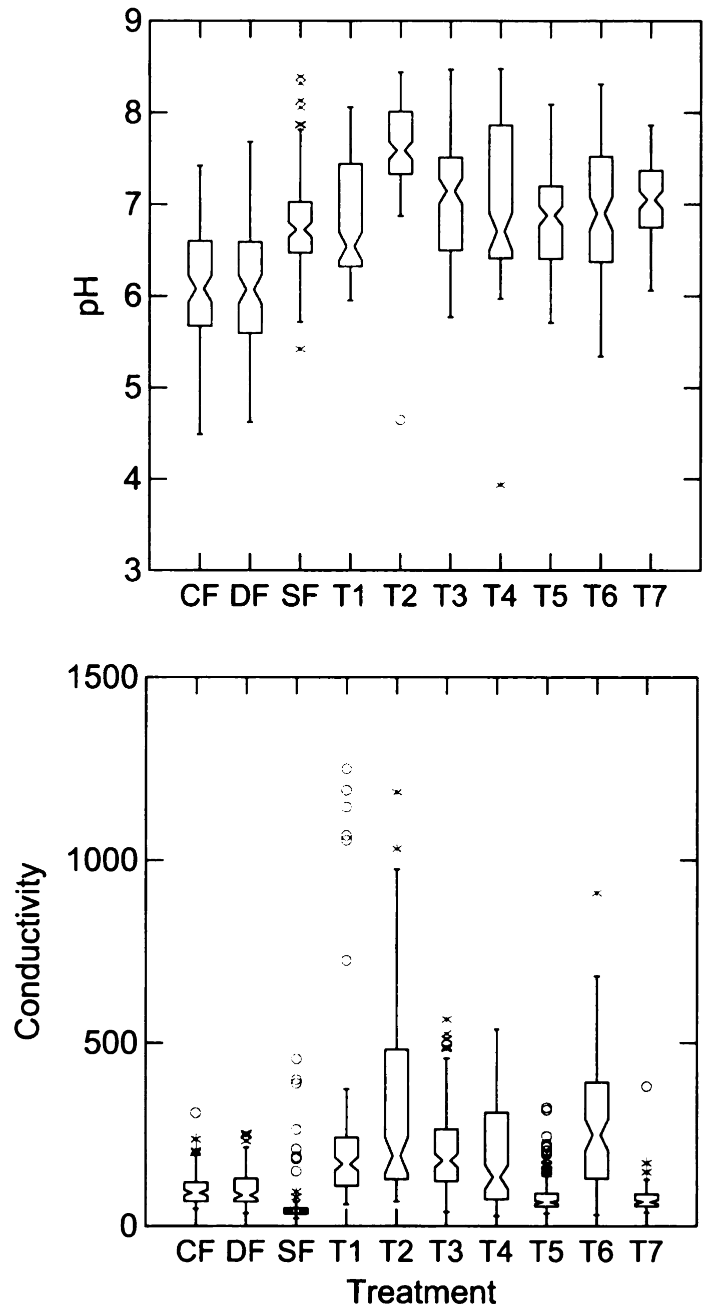


Figure 12: Notched box plots for pH and specific conductance (µS/cm at 25ºC.) across all treatments. The notches indicate the approximate 95% confidence intervals around the median.

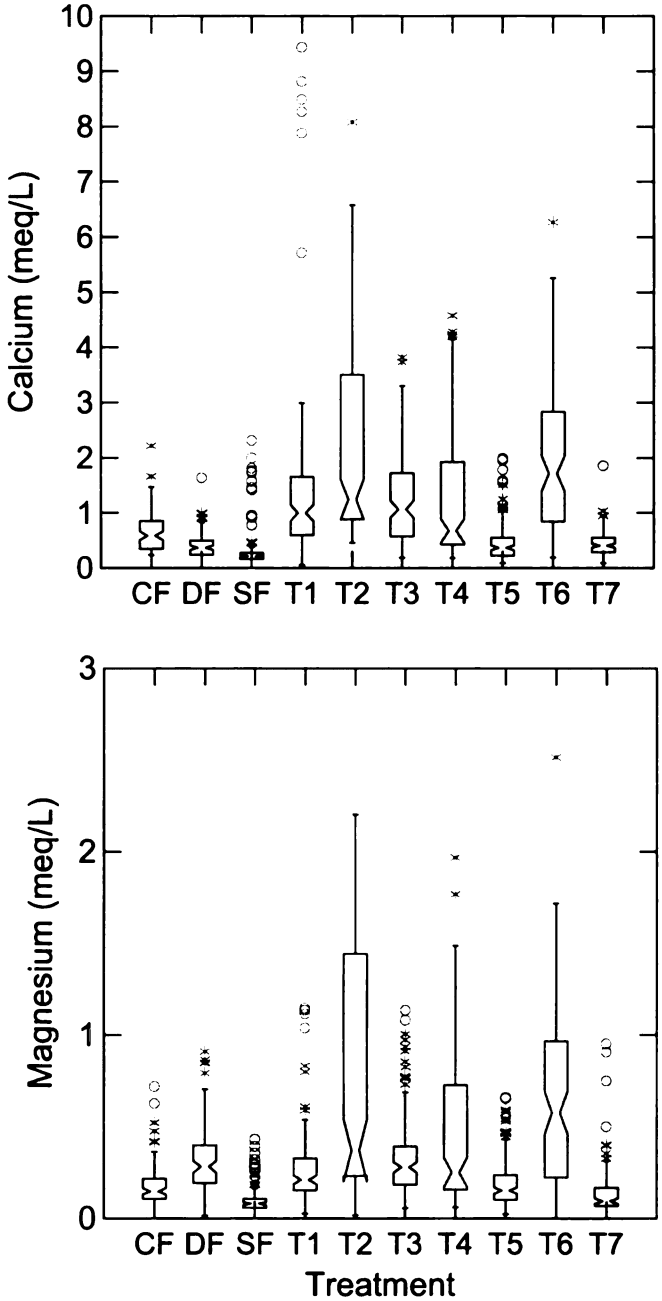


Figure 13: Notched box plots for calcium and magnesium across all treatments. The notches indicate the approximate 95% confidence intervals around the median.

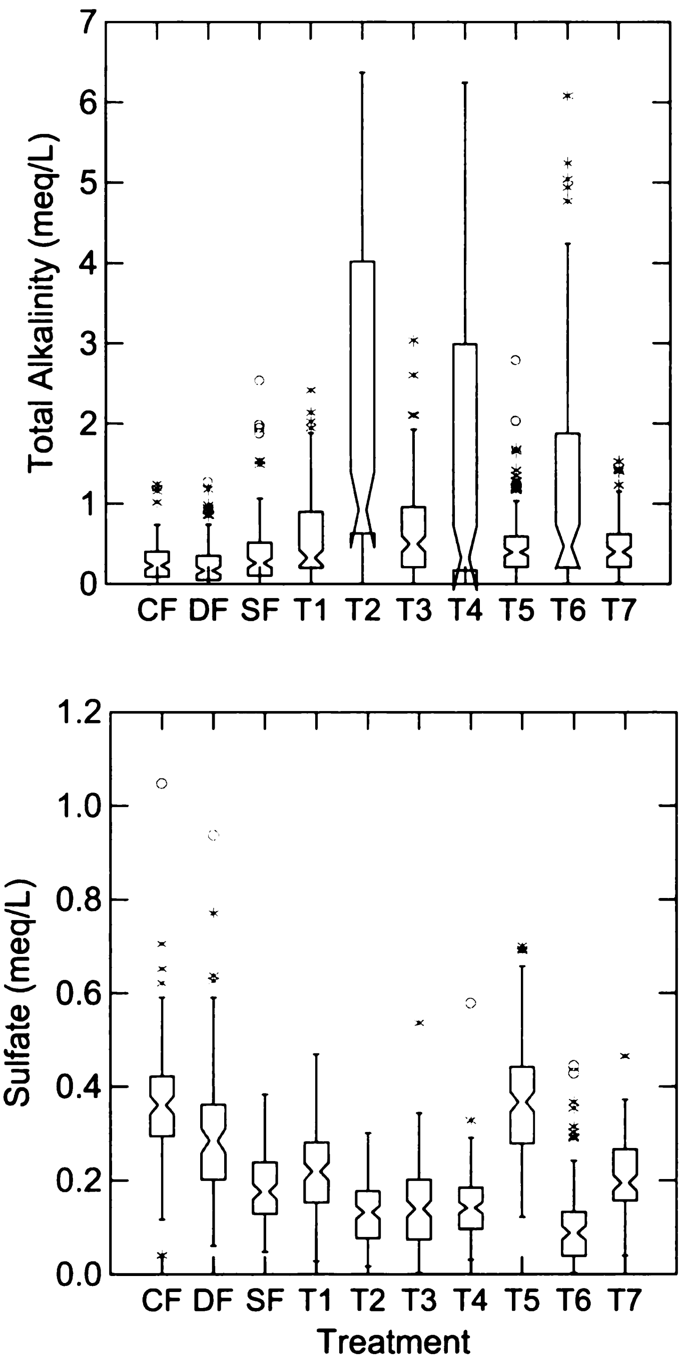
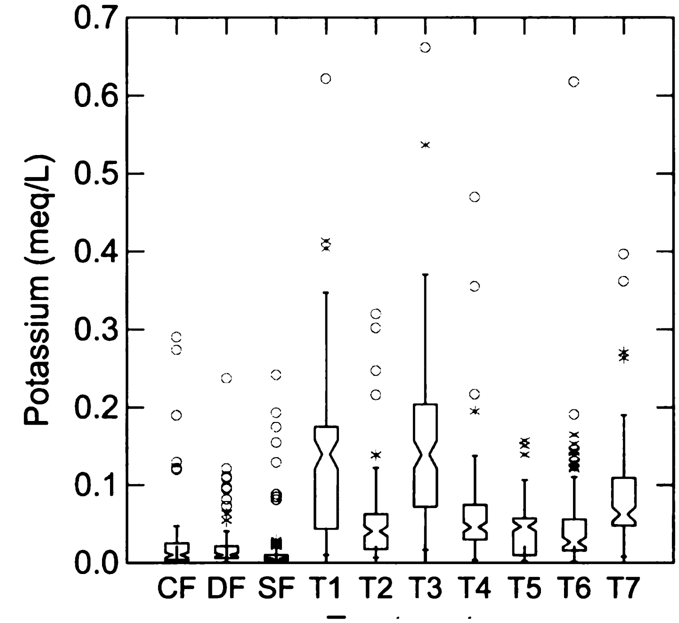


Figure 14: Notched box plots for total alkalinity and sulfate across all treatments. The notches indicate the approximate 95% confidence intervals around the median.



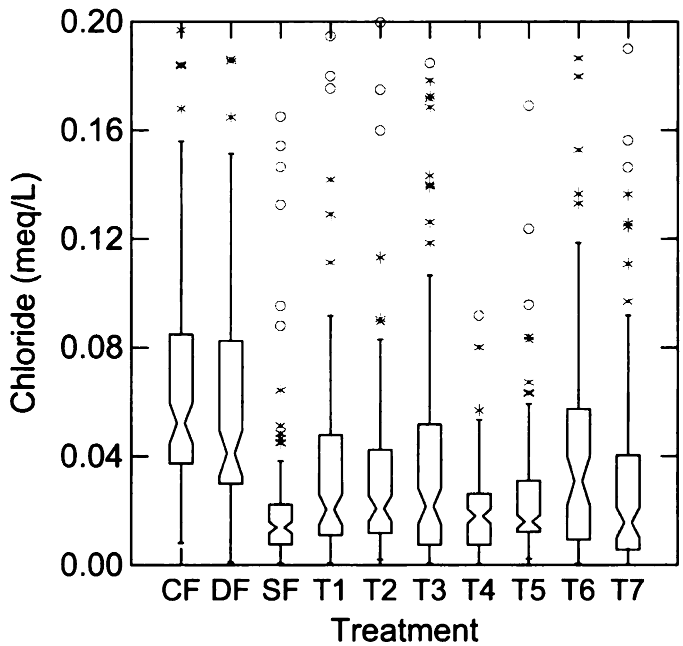


Figure 15: Notched box plots for potassium and chloride across all treatments. The notches indicate the approximate 95% confidence intervals around the median.

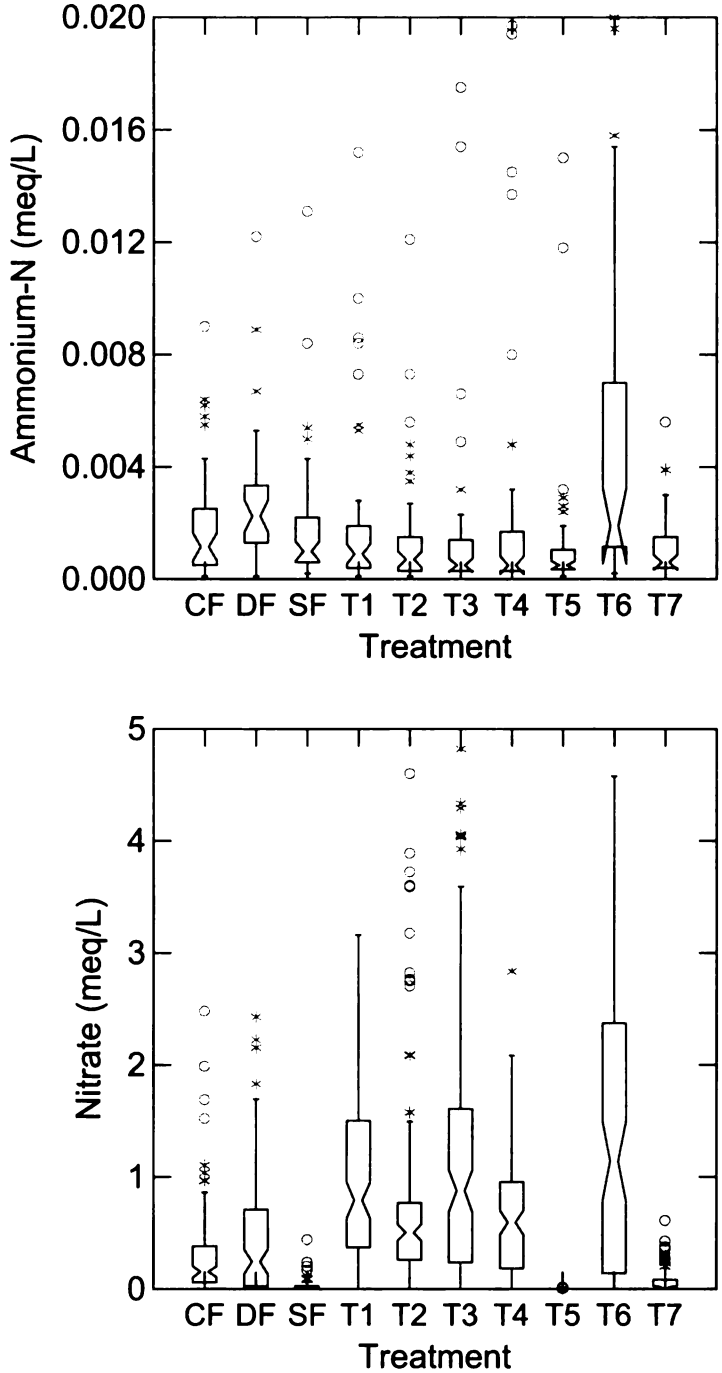


Figure 16: Notched box plots for ammonium and nitrate across all treatments. The notches indicate the approximate 95% confidence intervals around the median.

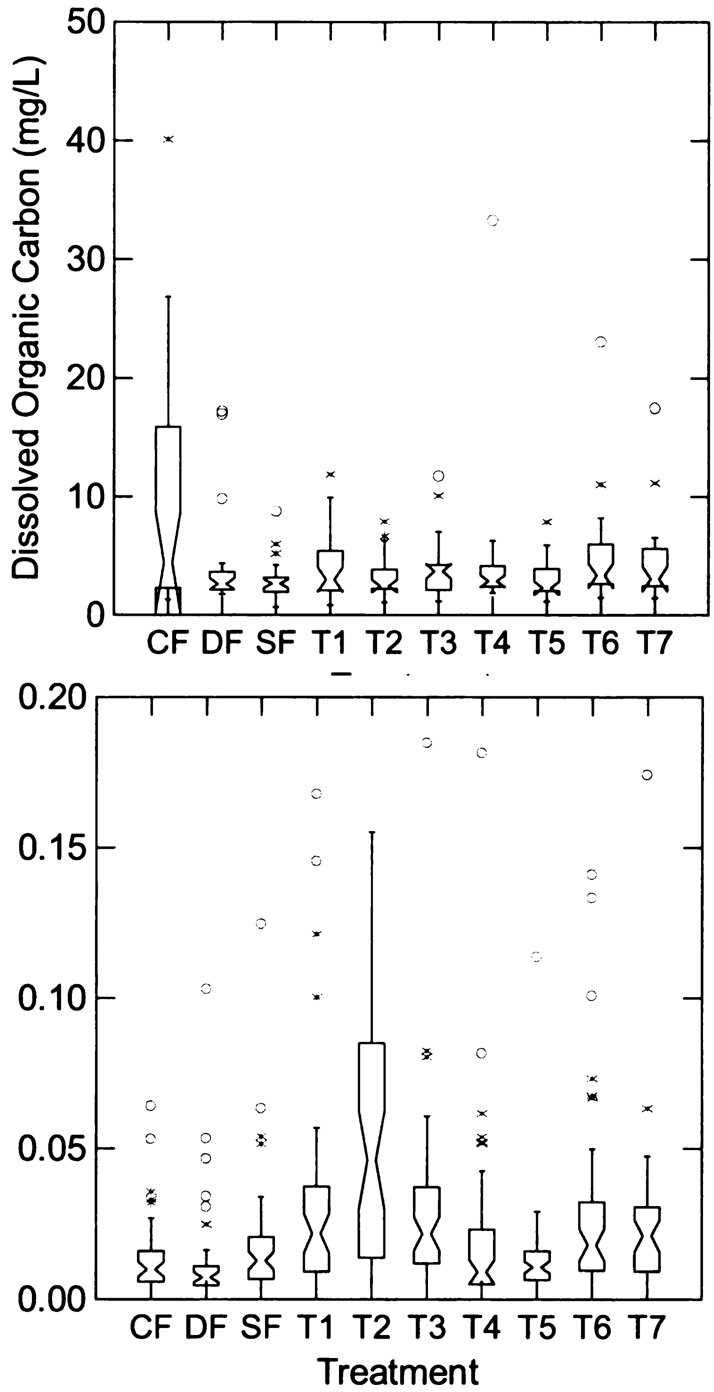


Figure 17: Notched box plots for dissolved organic carbon and total dissolved phosphorus across all treatments. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 1198 cases, 14 were excluded by making the TDP graph range less than data range.

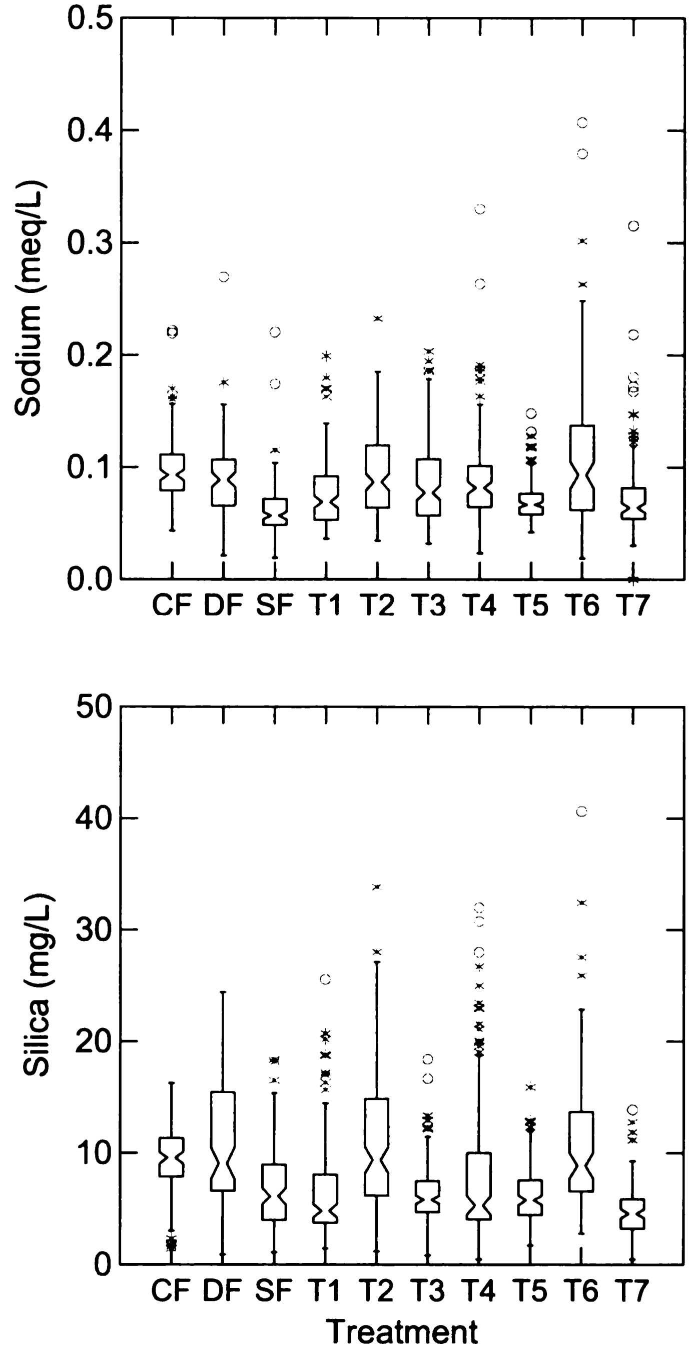


Figure 18: Notched box plots for sodium and silica across all treatments. The notches indicate the approximate 95% confidence intervals around the median.

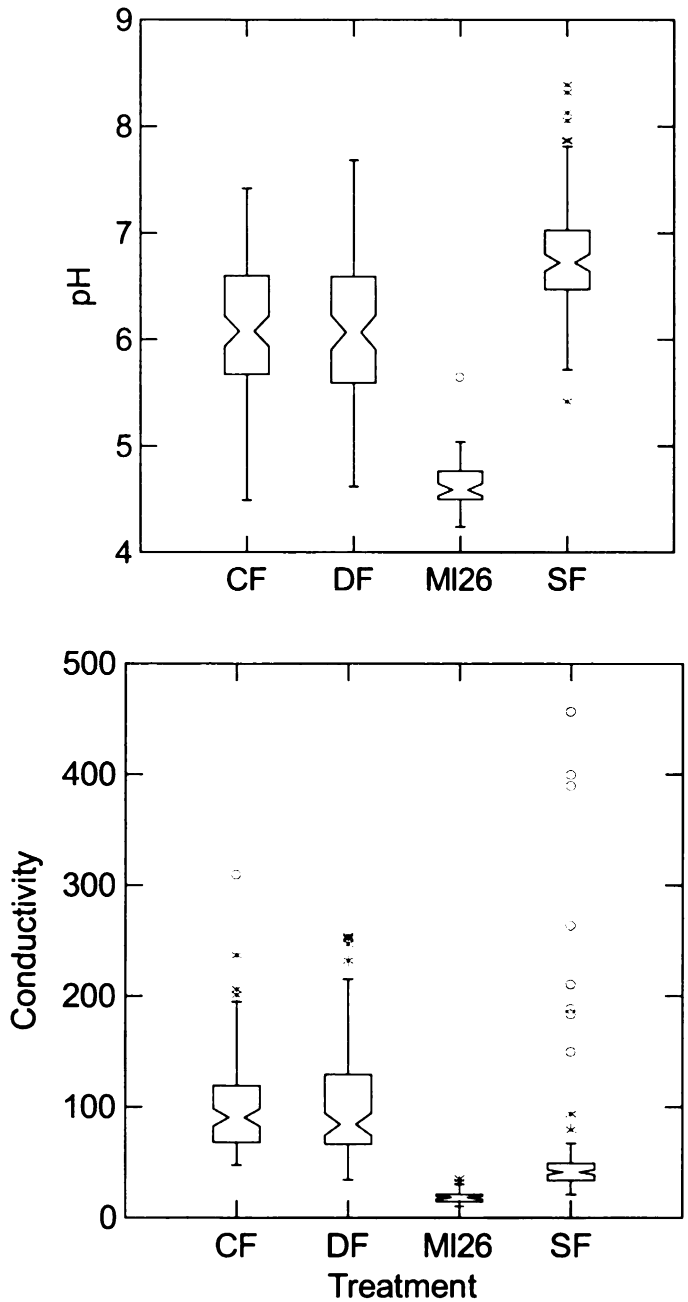


Figure 19: Notched box plots for pH and conductance (µS/cm at 25°C in Treatments CF, DF, and SF. Precipitation is included for comparison; MI 26 is the NADP/NTN precipitation collection site located near the KBS LTER sites. The notches indicate the approximate 95% confidence intervals around the median.

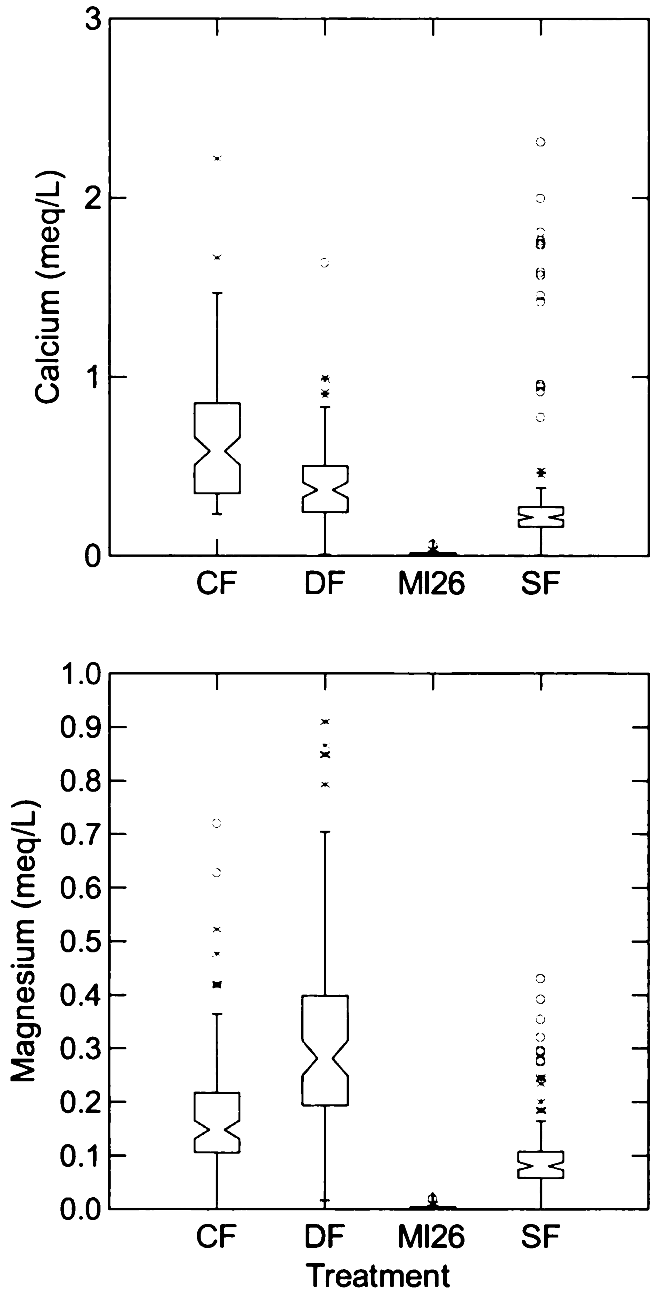


Figure 20: Notched box plots for calcium and magnesium in Treatments CF, DF, and SF. MI 26 is the NADP/NTN precipitation collection site located at the KBS LTER. The notches indicate the approximate 95% confidence intervals around the median.

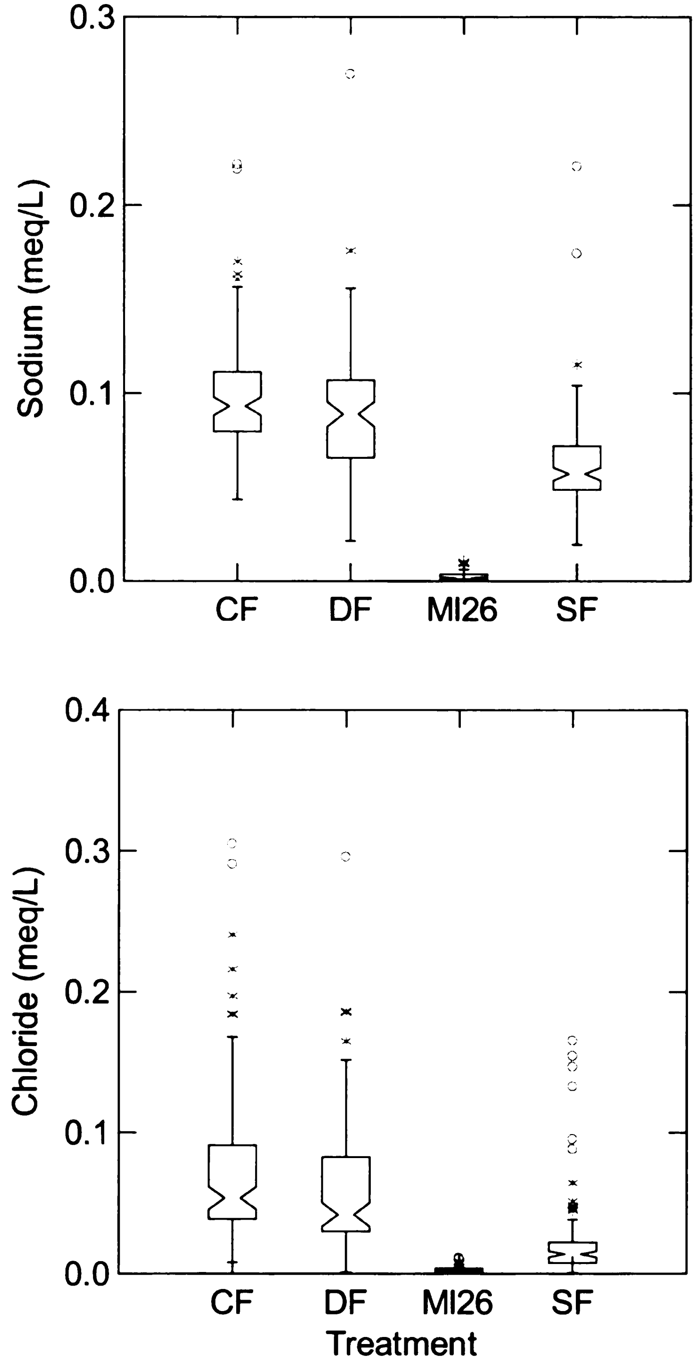
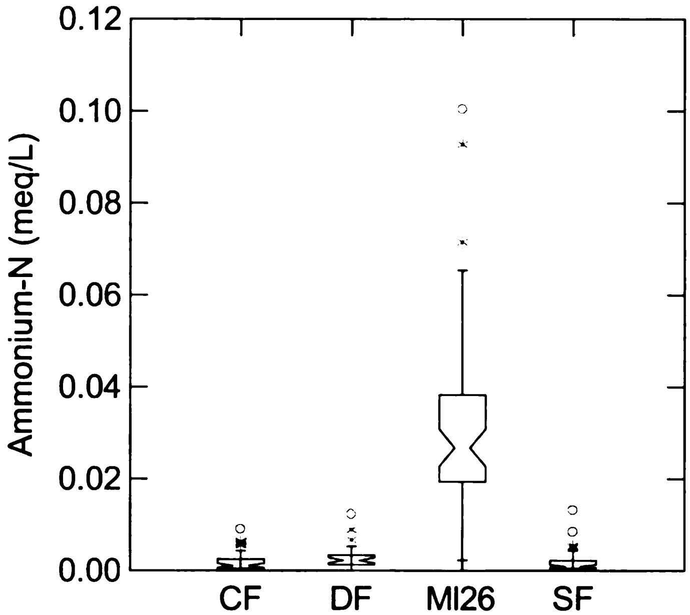


Figure 21: Notched box plots for sodium and chloride in Treatments CF, DF, and SF. MI 26 is the NADP/NTN precipitation collection site located at the KBS LTER. The notches indicate the approximate 95% confidence intervals around the median.



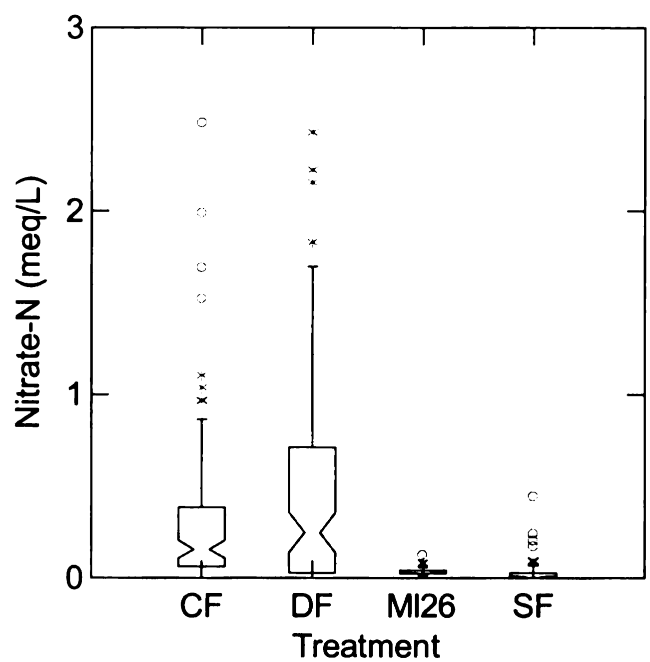


Figure 22: Notched box plots for ammonium and nitrate in Treatments CF, DF, and SF. MI 26 is the NADP/NTN precipitation collection site located at the KBS LTER. The notches indicate the approximate 95% confidence intervals around the median.

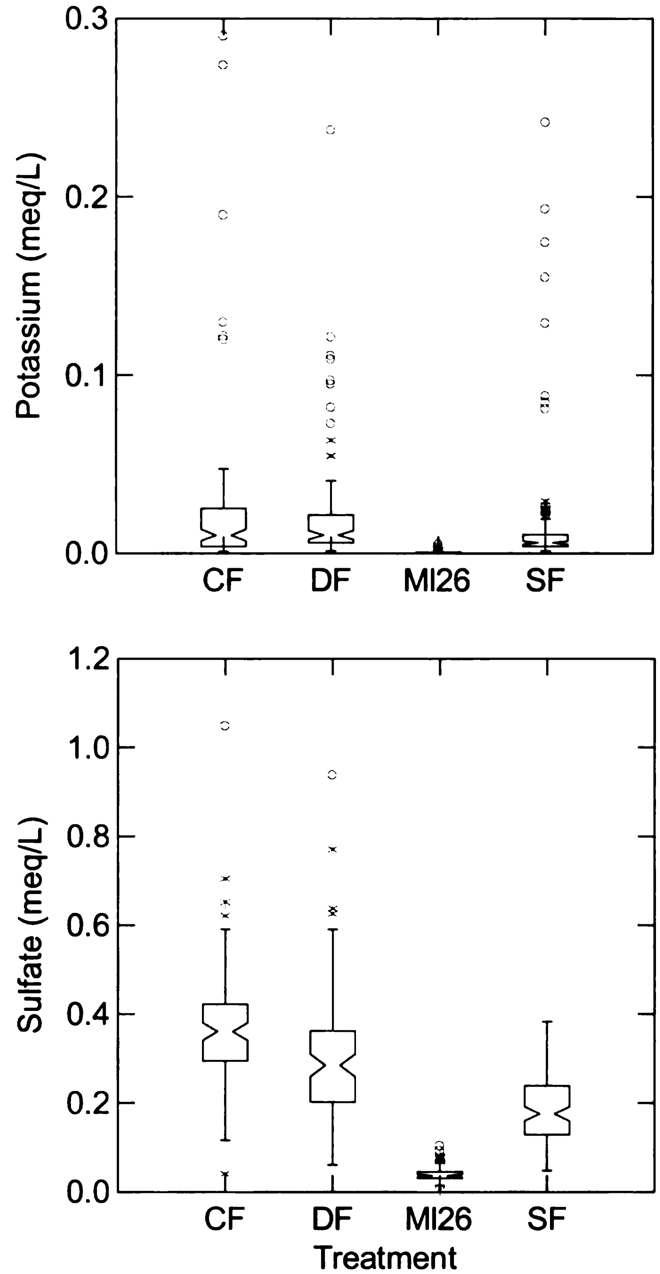


Figure 23: Notched box plots for potassium and sulfate in Treatments CF, DF, and SF. MI 26 is the NADP/NTN precipitation collection site located at the KBS LTER. The notches indicate the approximate 95% confidence intervals around the median.

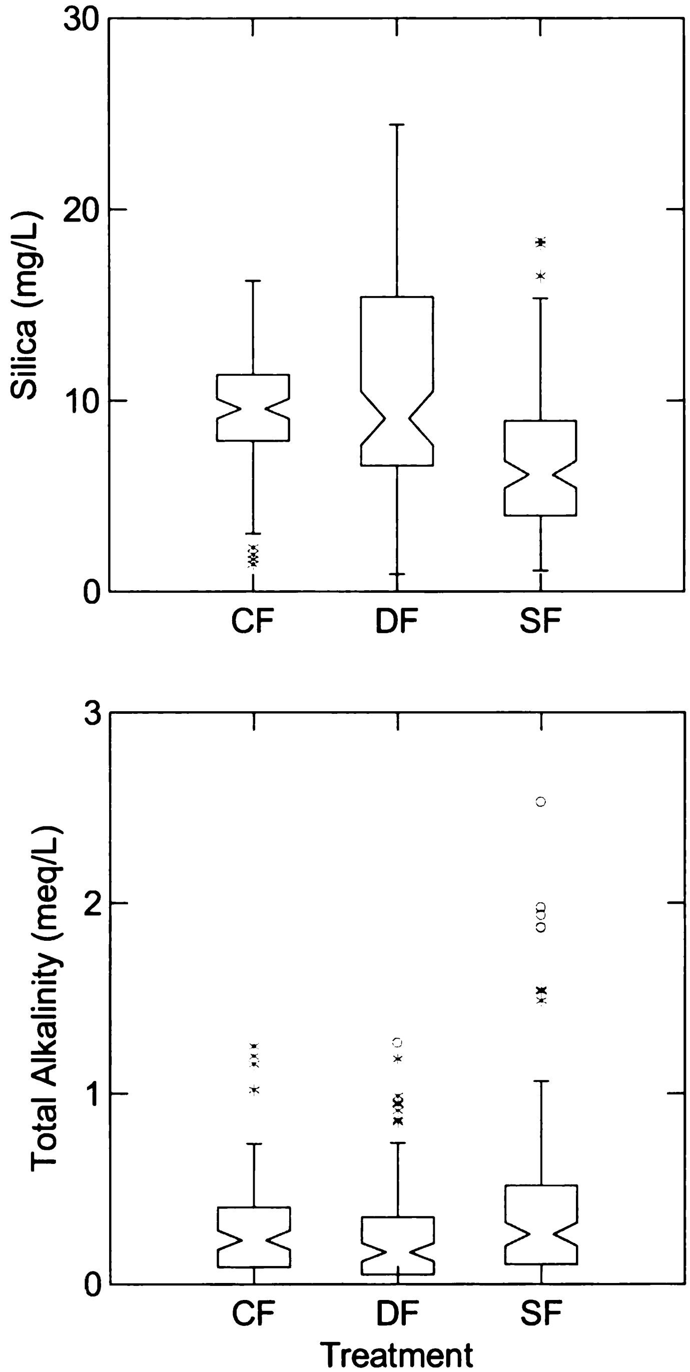


Figure 24: Notched box plots for silica and total alkalinity in Treatments CF, DF, and SF. Precipitation data on these variables were not available but in general precipitation contains negligible concentrations of these solutes. The notches indicate the approximate 95% confidence intervals around the median.

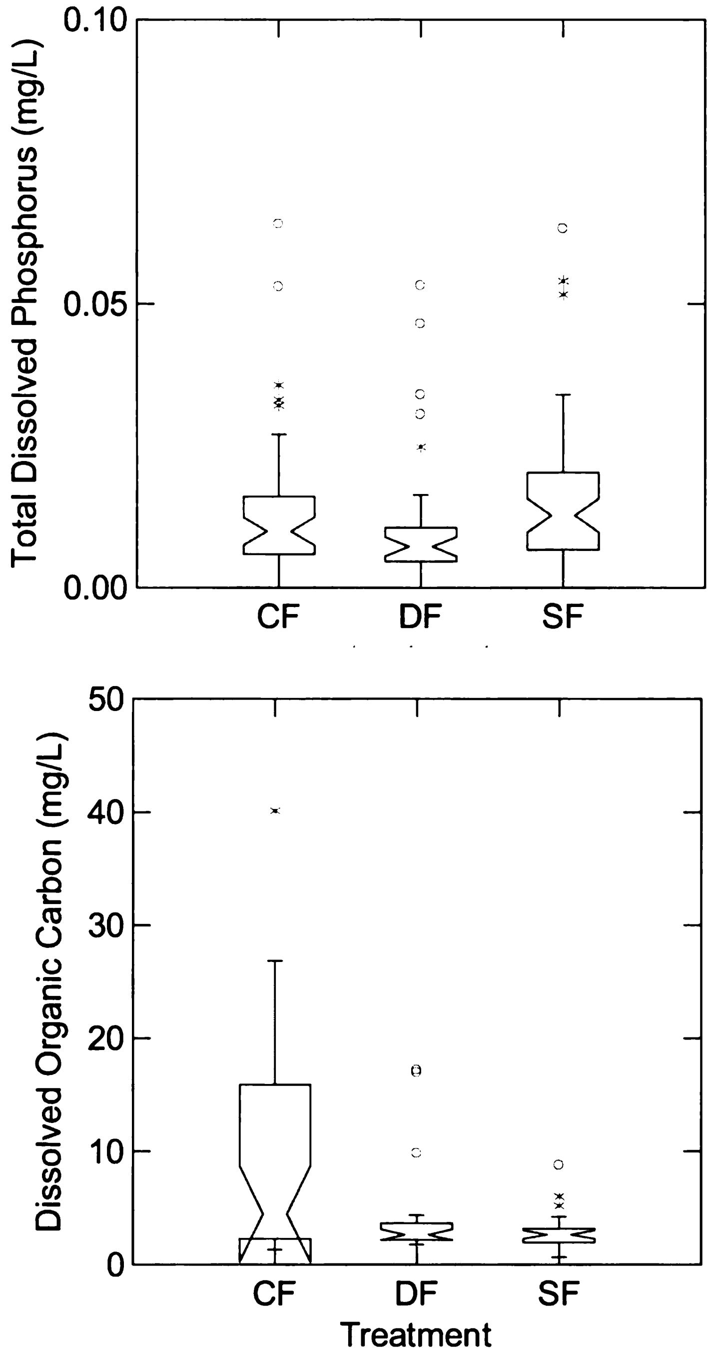


Figure 25: Notched box plots for total dissolved phosphorus and dissolved organic carbon in Treatments CF, DF, and SF. Precipitation data on these variables were not available for the KBS site, but a USGS study at a nearby location reported a mean annual concentration of TDP of 0.03 mg/L (Rheaume 1990). The notches indicate the approximate 95% confidence intervals around the median.

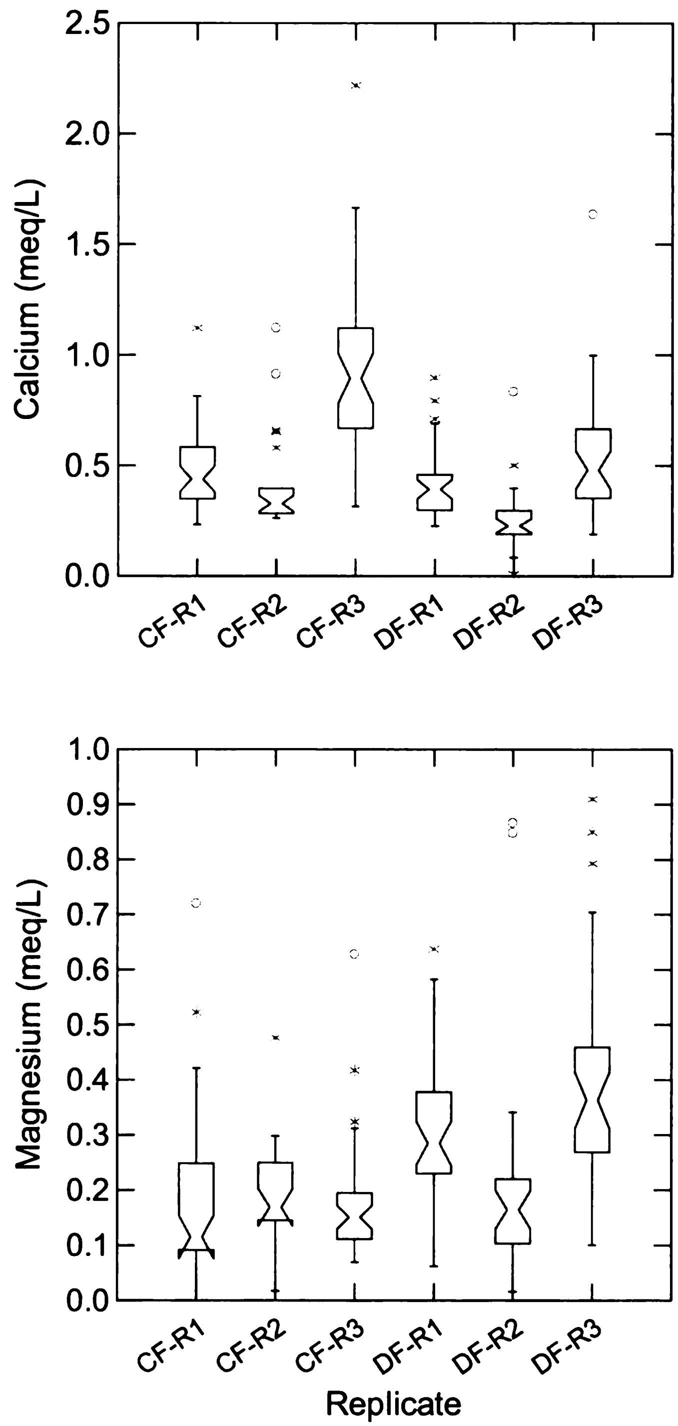


Figure 26: Notched box plots for calcium and magnesium in Replicates from Treatments CF and DF. The notches indicate the approximate 95% confidence intervals around the median.

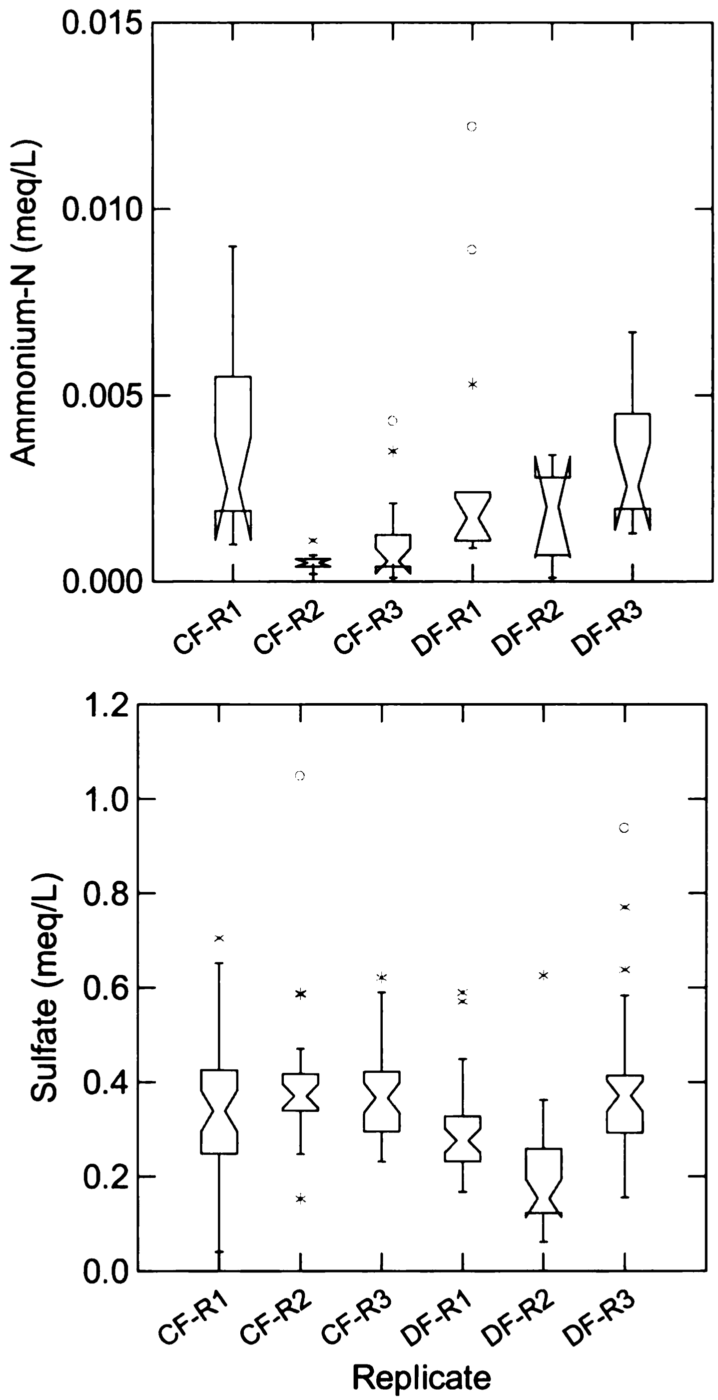


Figure 27: Notched box plots for ammonium and sulfate in replicates from Treatments CF and DF. The notches indicate the approximate 95% confidence intervals around the median.

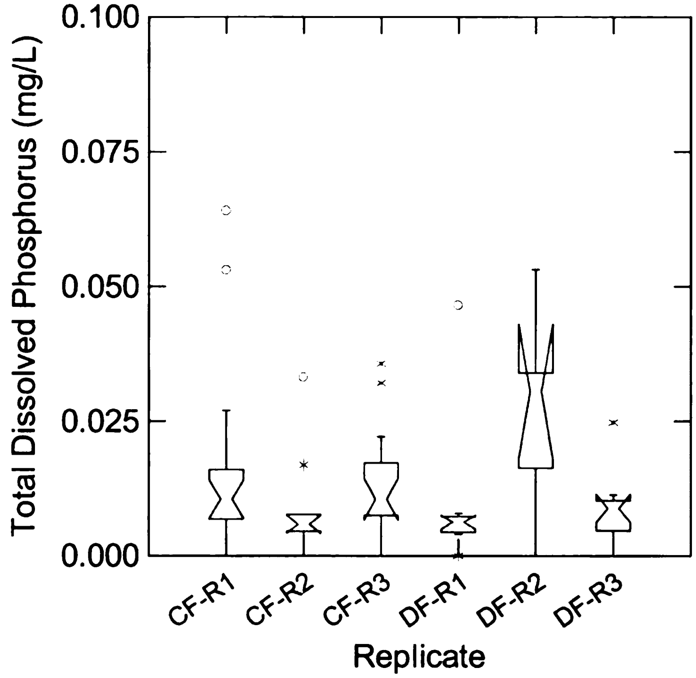


Figure 28: Notched box plots for total dissolved phosphorus in replicates from Treatments CF and DF. The notches indicate the approximate 95% confidence intervals around the median. Of 393 cases, 2 were excluded by making the TDP graph range less than data range.

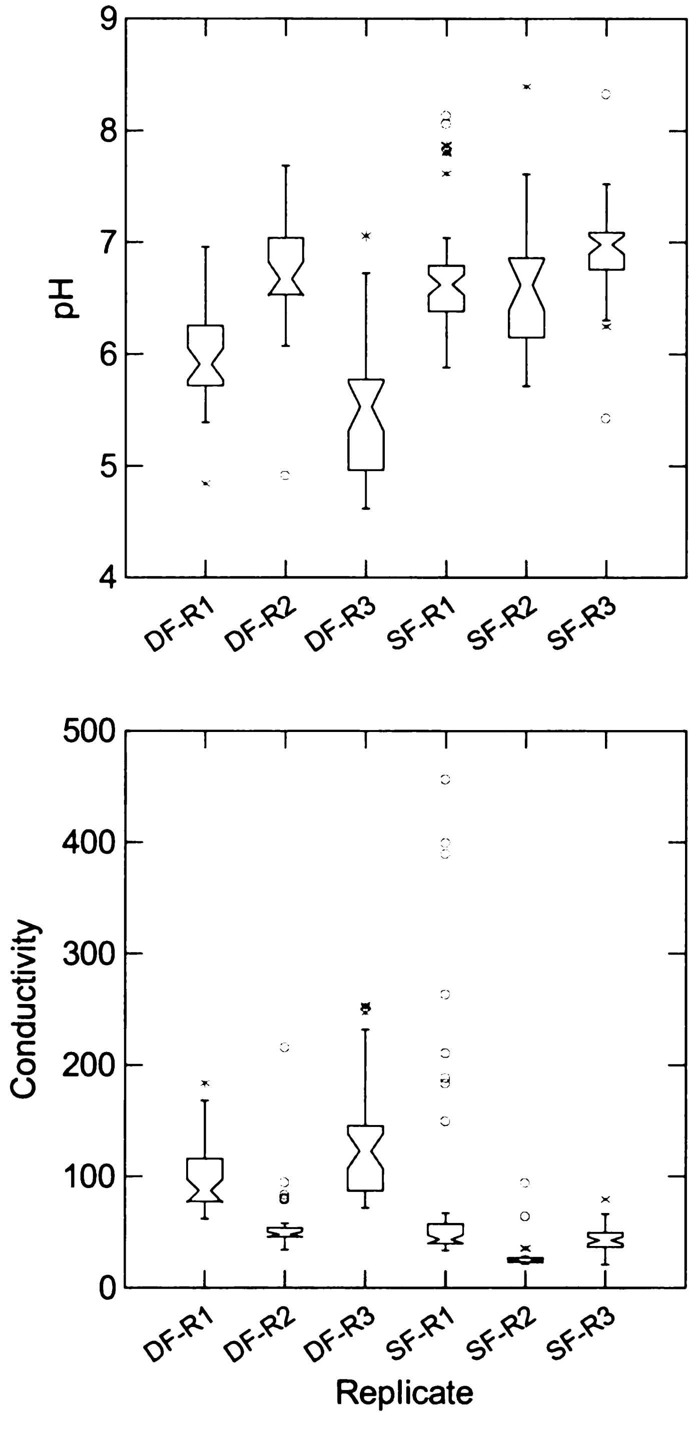


Figure 29: Notched box plots for pH (air-equilibrated) and conductance (μS/cm@25°C) in replicates from Treatments DF and SF. The notches indicate the approximate 95% confidence intervals around the median.

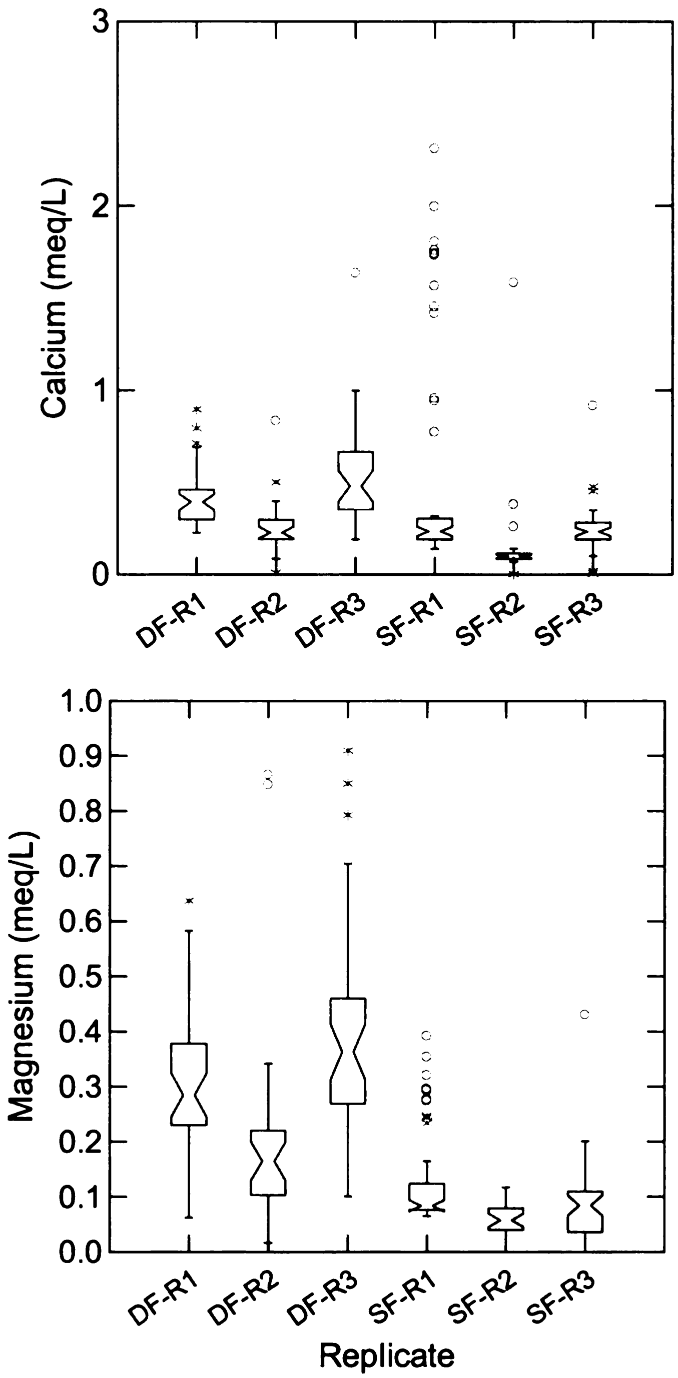


Figure 30: Notched box plots for calcium and magnesium in replicates from Treatments DF and SF. The notches indicate the approximate 95% confidence intervals around the median.

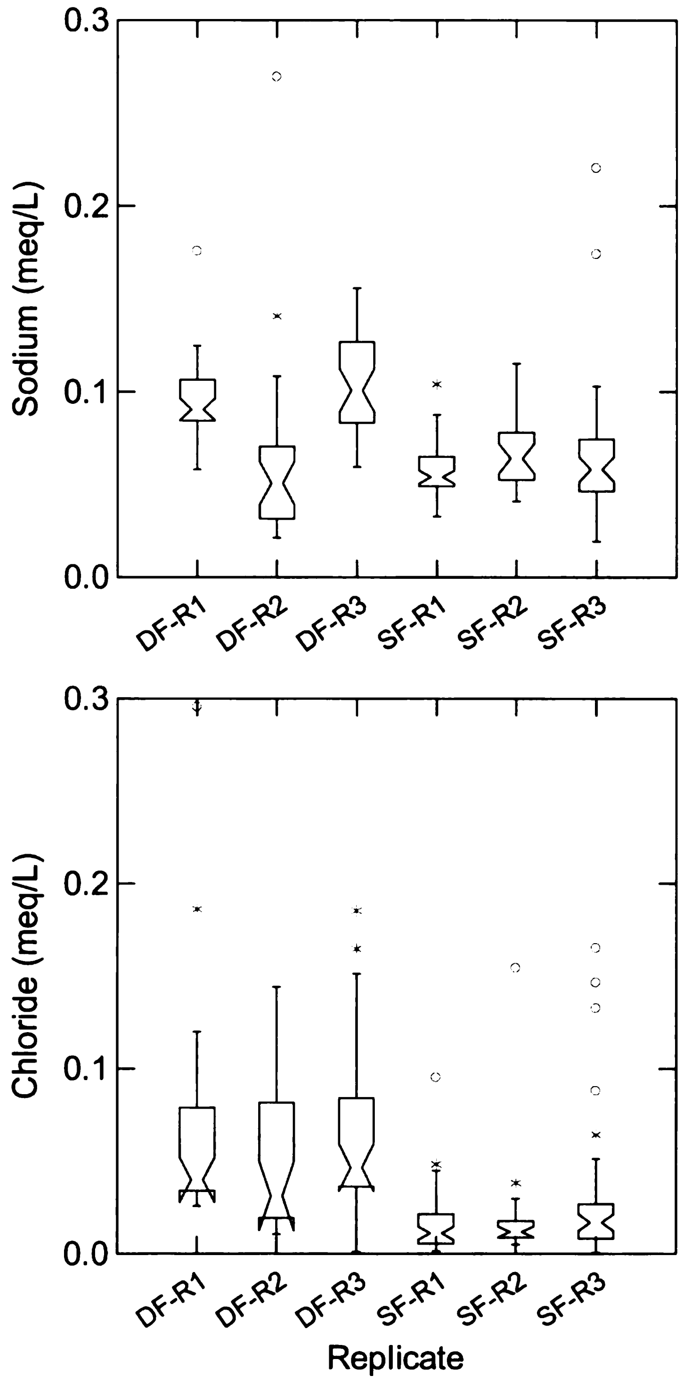


Figure 31: Notched box plots for sodium and chloride in replicates from Treatments DF and SF. The notches indicate the approximate 95% confidence intervals around the median.

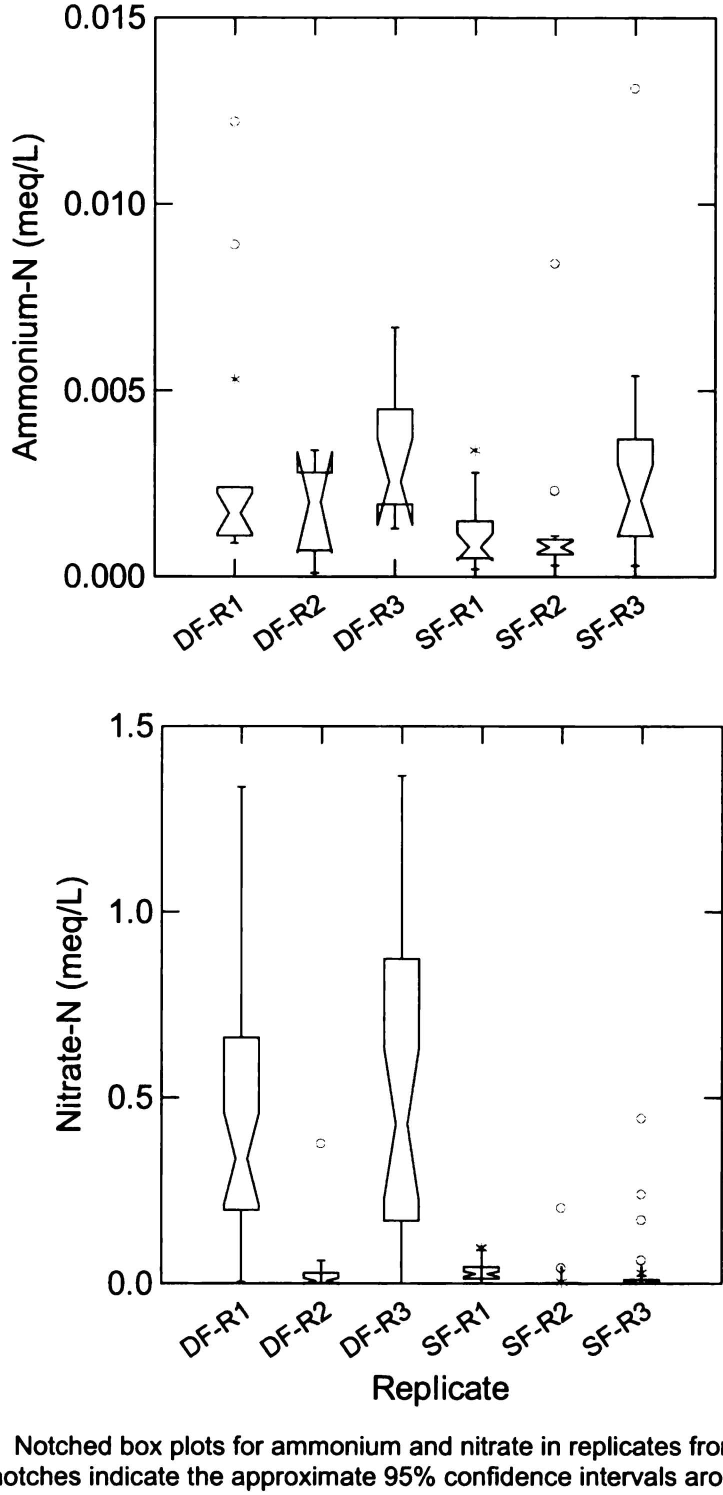


Figure 32: Notched box plots for ammonium and nitrate in replicates from Treatments DF and SF. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases, 6 were excluded by making the nitrate-N graph range less than data range.

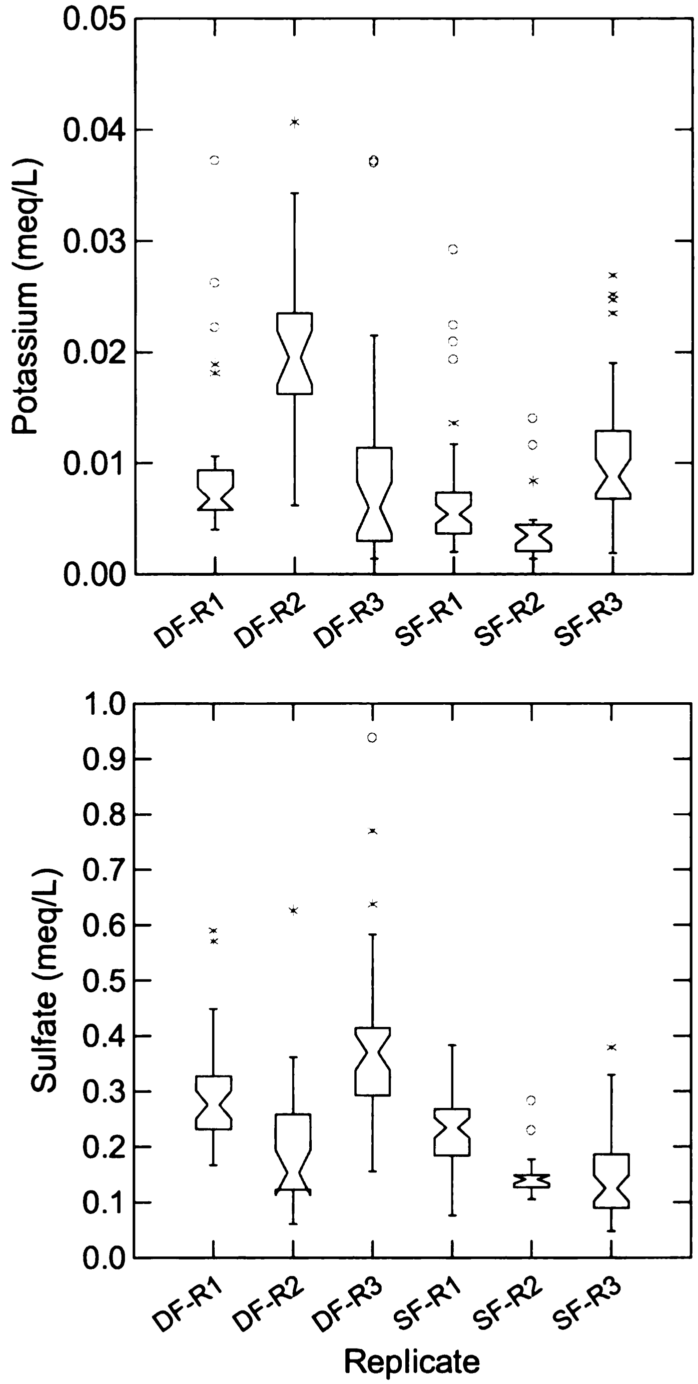


Figure 33: Notched box plots for potassium and sulfate in replicates from Treatments DF and SF. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases 19 were excluded making the potassium graph range less than data range.

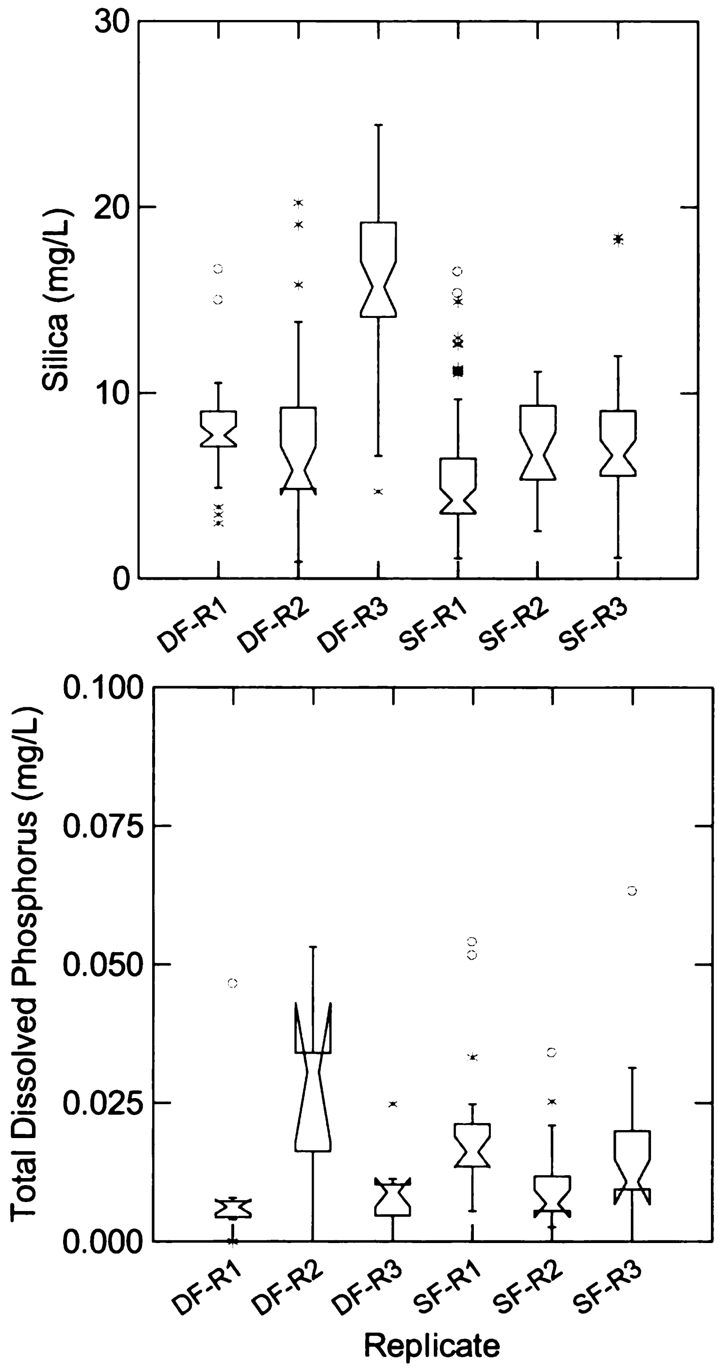


Figure 34: Notched box plots for silica and total dissolved phosphorus in replicates from Treatments DF and SF. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases, 4 were excluded by making the TDP graph range less than data range.

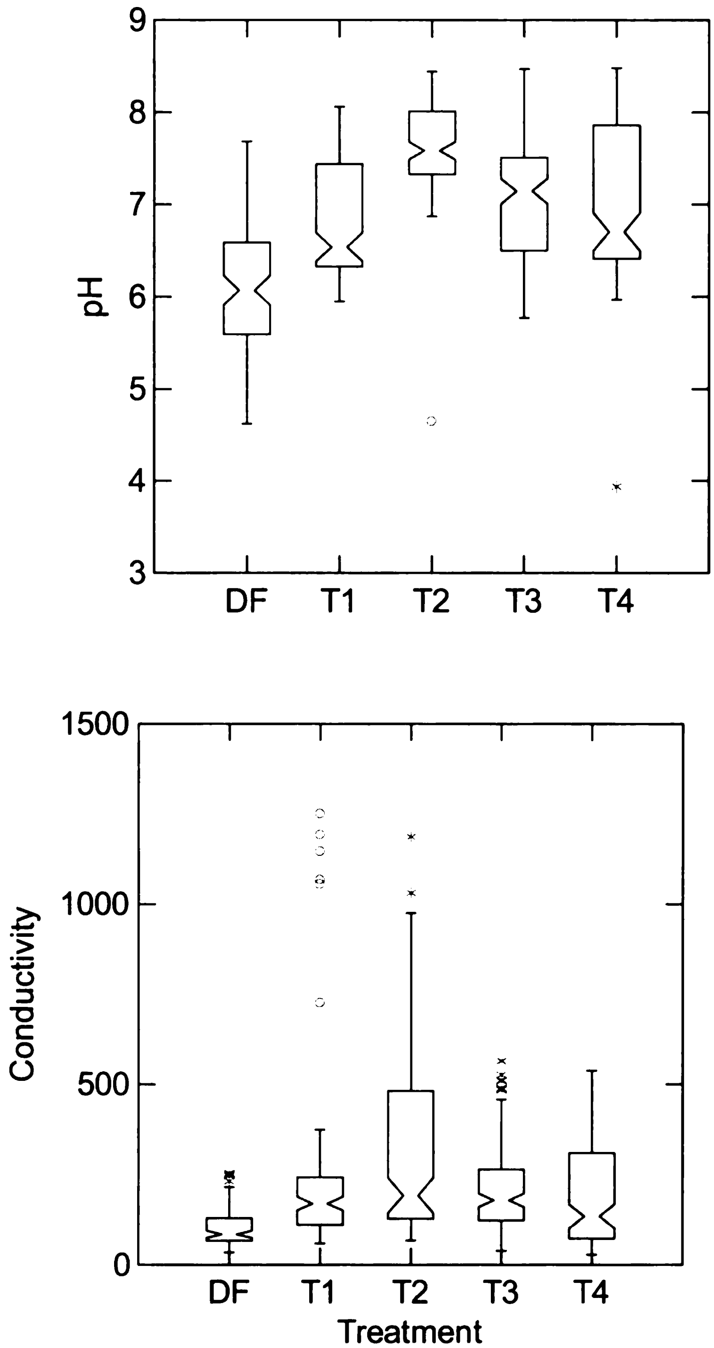


Figure 35: Notched box plots for pH (air-equilibrated) and conductance, Treatments DF, T1, T2, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median.

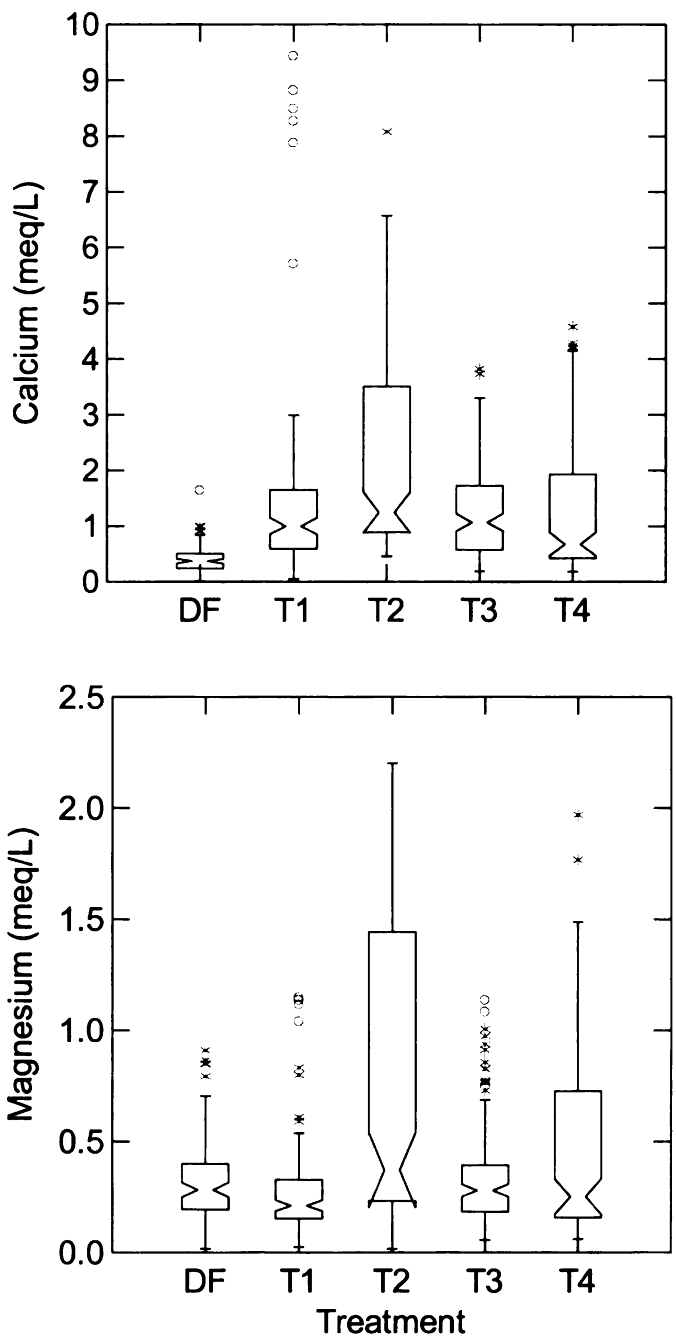


Figure 36: Notched box plots for calcium and magnesium, Treatments DF, T1, T2, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median.

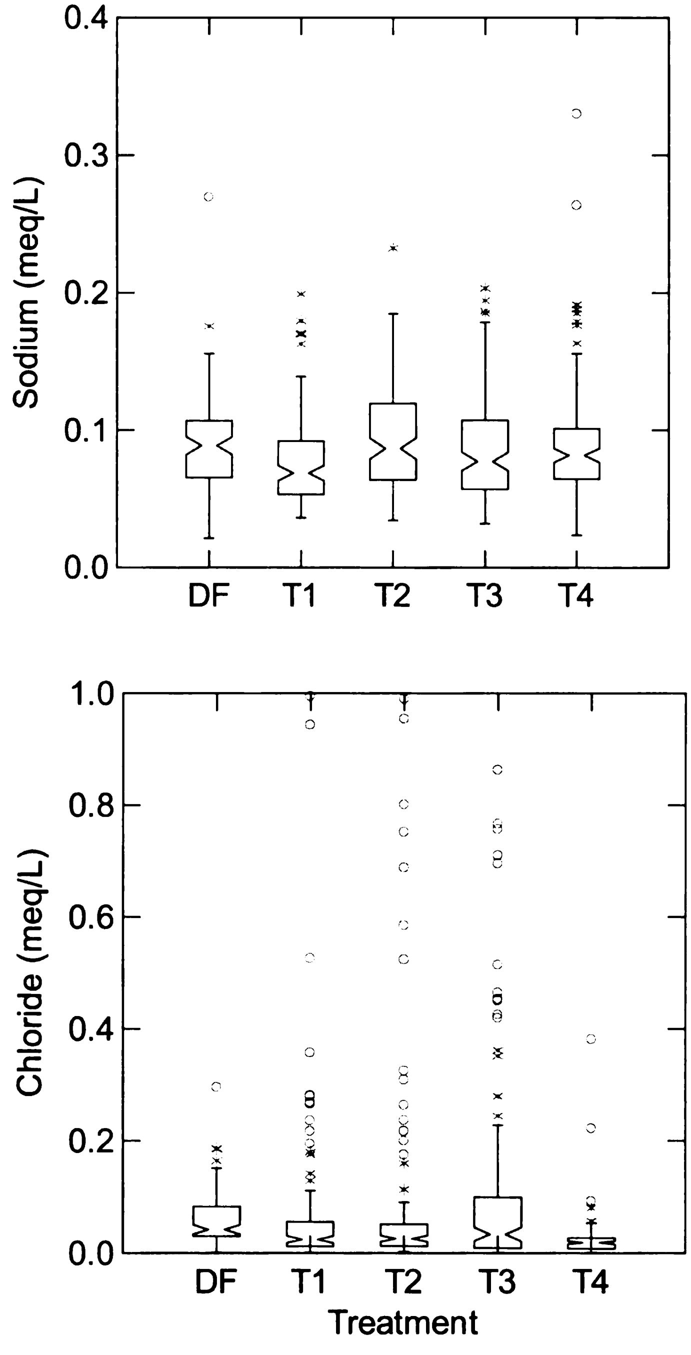
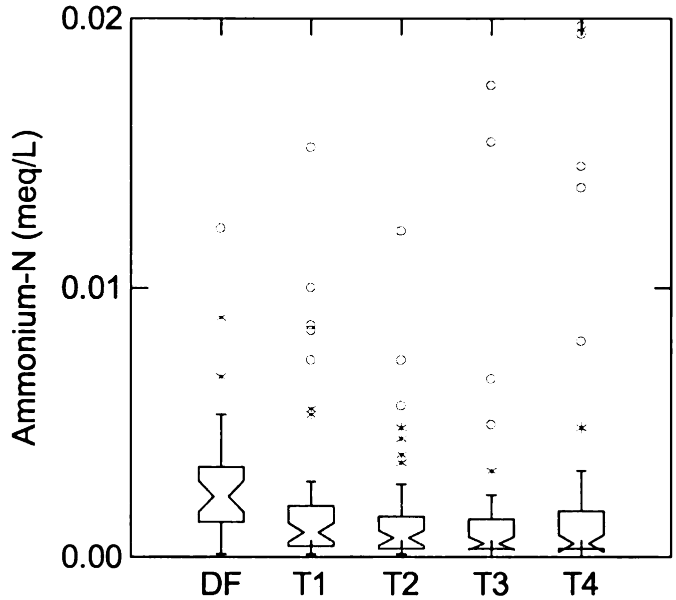


Figure 37: Notched box plots for sodium and chloride, Treatments DF, T1, T2, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 621 cases, 20 were excluded by making the chloride graph range less than data range.



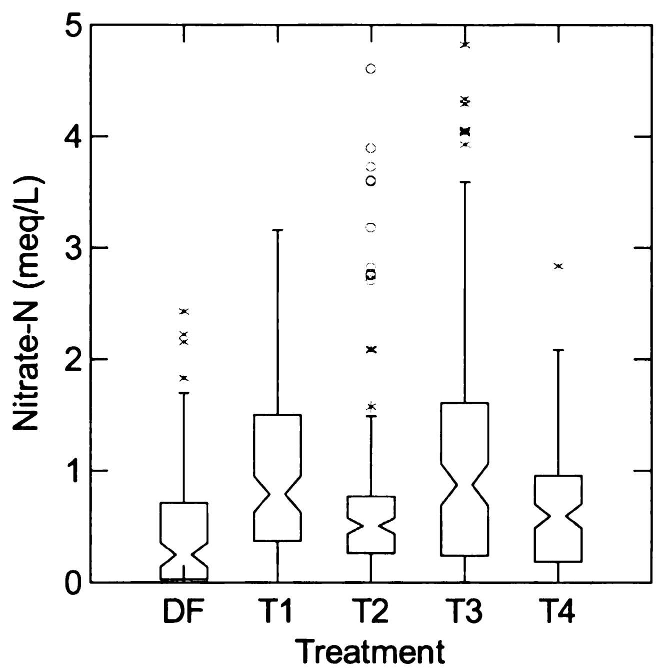
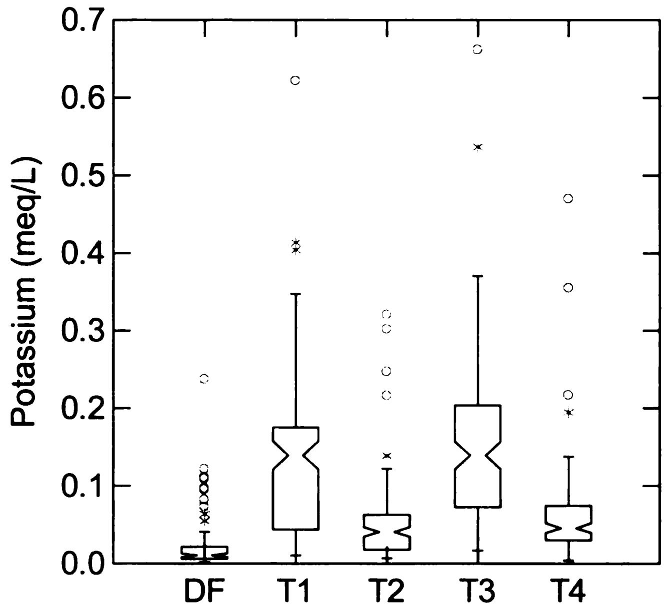


Figure 38: Notched box plots for ammonium and nitrate, Treatments DF, T1, T2, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 621 cases, 8 and 13 were excluded, respectively, by making the ammonium and nitrate graph ranges less than the data range.



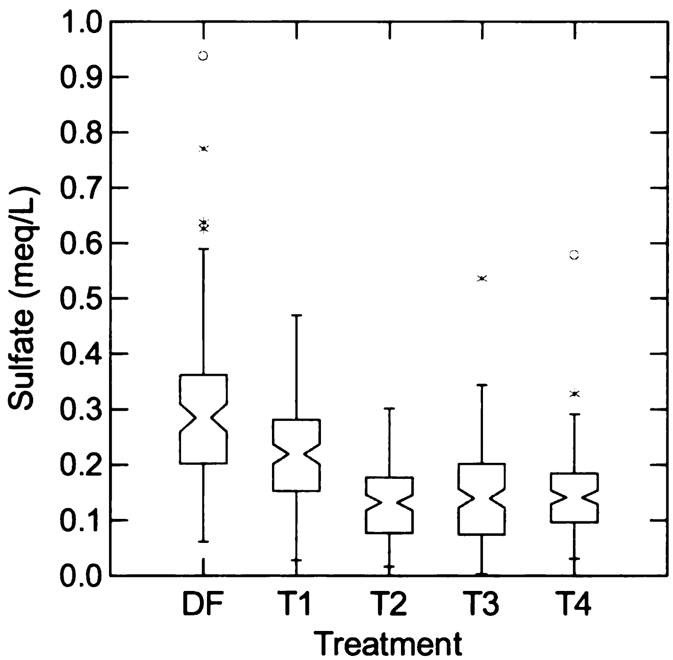


Figure 39: Notched box plots for potassium and sulfate, Treatments DF, T1, T2, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median.

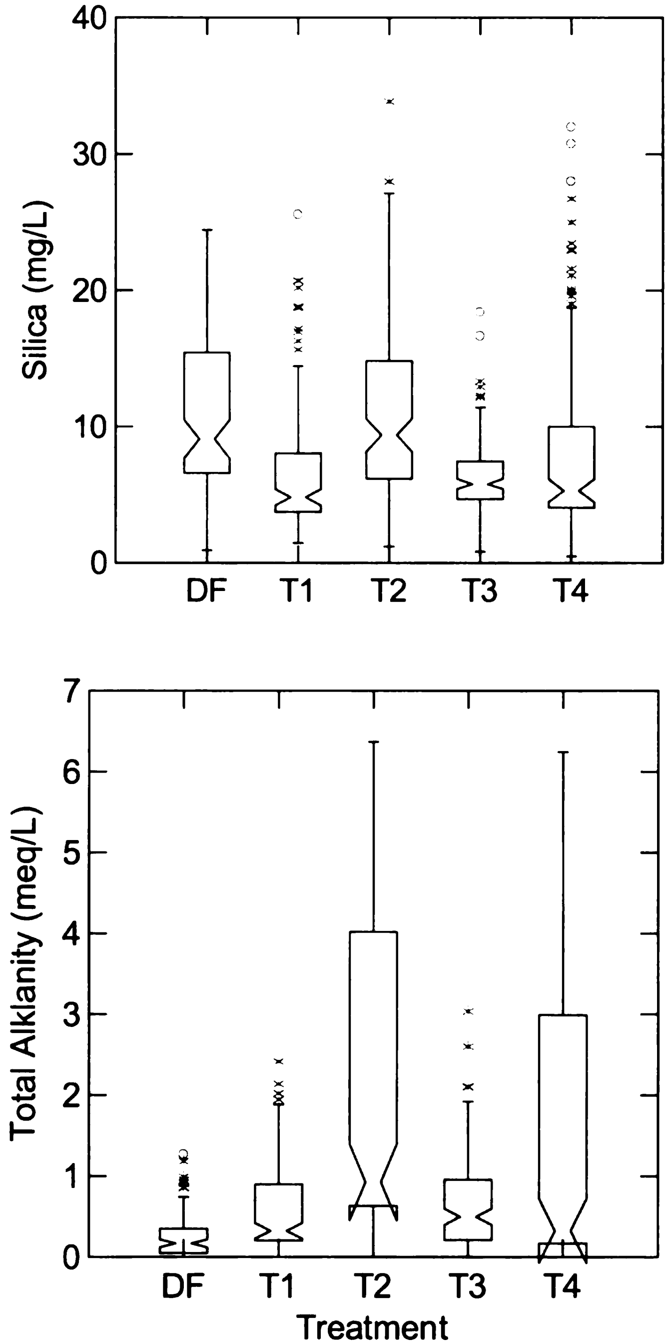


Figure 40: Notched box plots for silica and alkalinity, Treatments DF, T1, T2, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median.

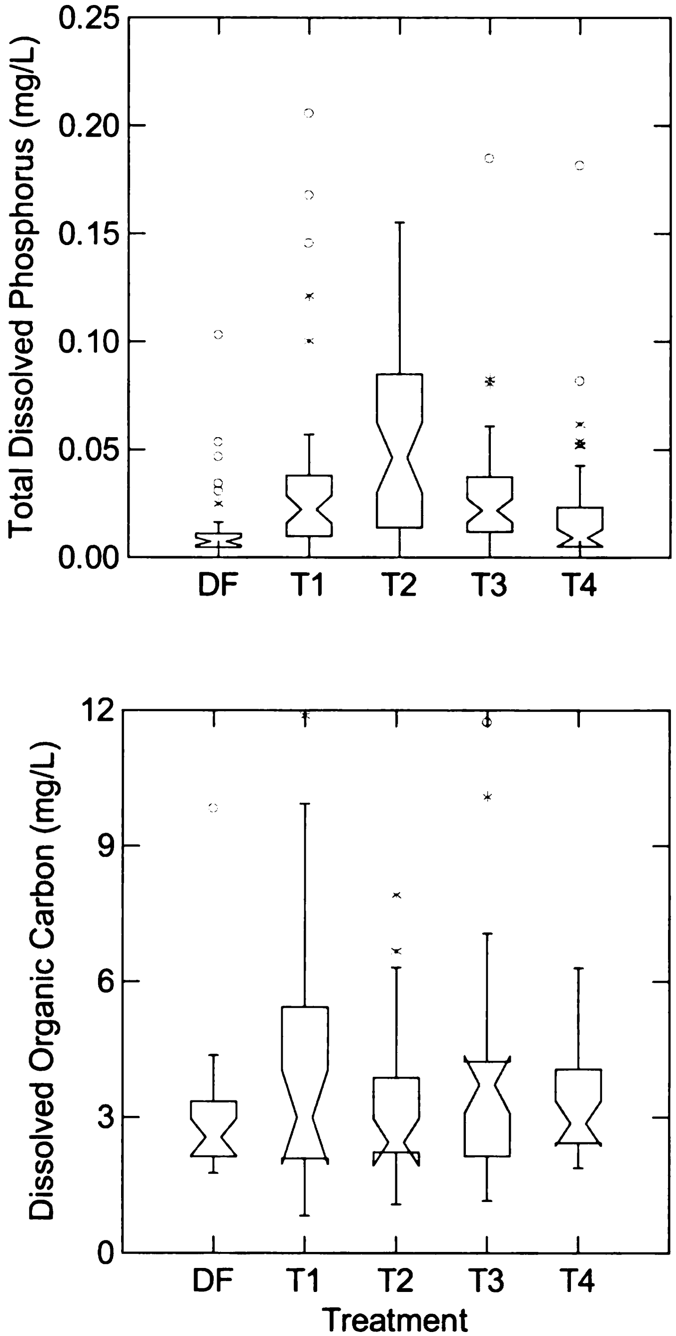


Figure 41: Notched box plots for total dissolved phosphorus and dissolved organic carbon, Treatments DF, T1, T2, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 621 cases, 5 and 3, respectively, were excluded in making the TDP and DOC graph range less than the data range.

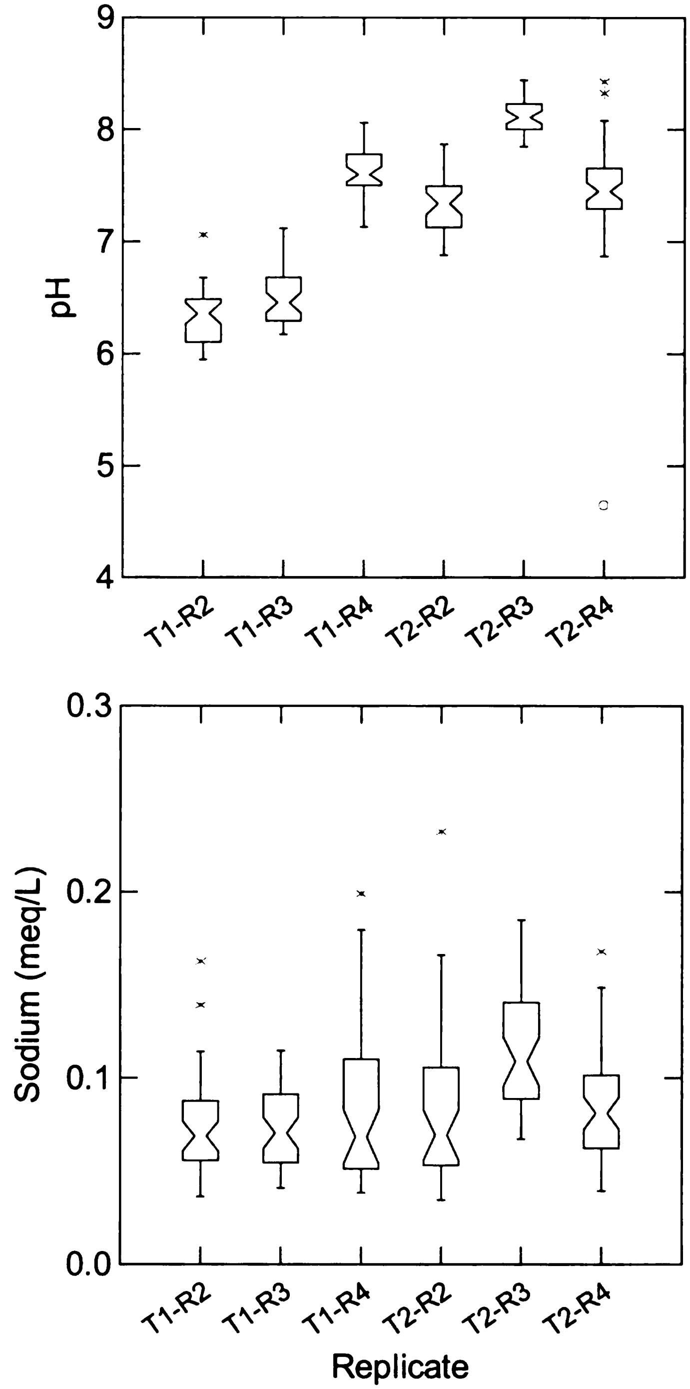


Figure 42: Notched box plots for pH and sodium by replicate for Treatments T1 and T2. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 621 cases, 3 were excluded in making the sodium graph range less than the data range.

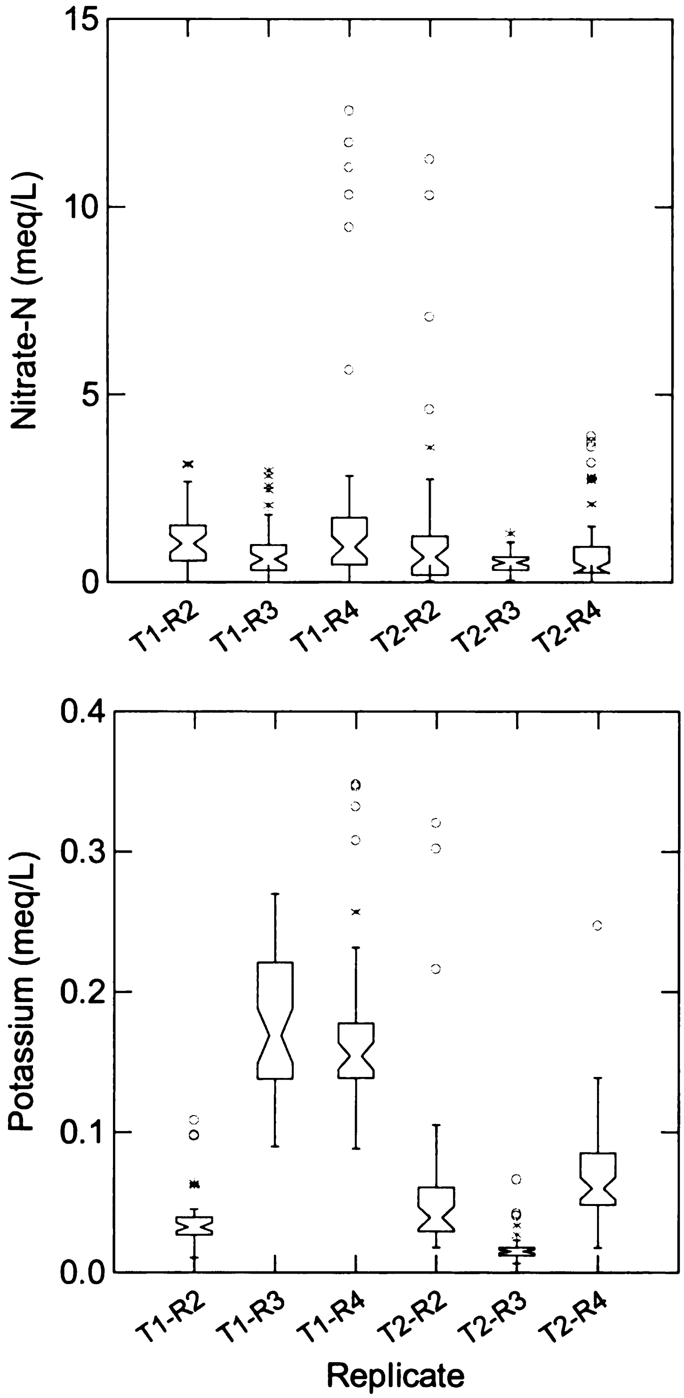


Figure 43: Notched box plots for nitrate and potassium by replicate for Treatments T1 and T2. The notches indicate the approximate 95% confidence intervals around the median.

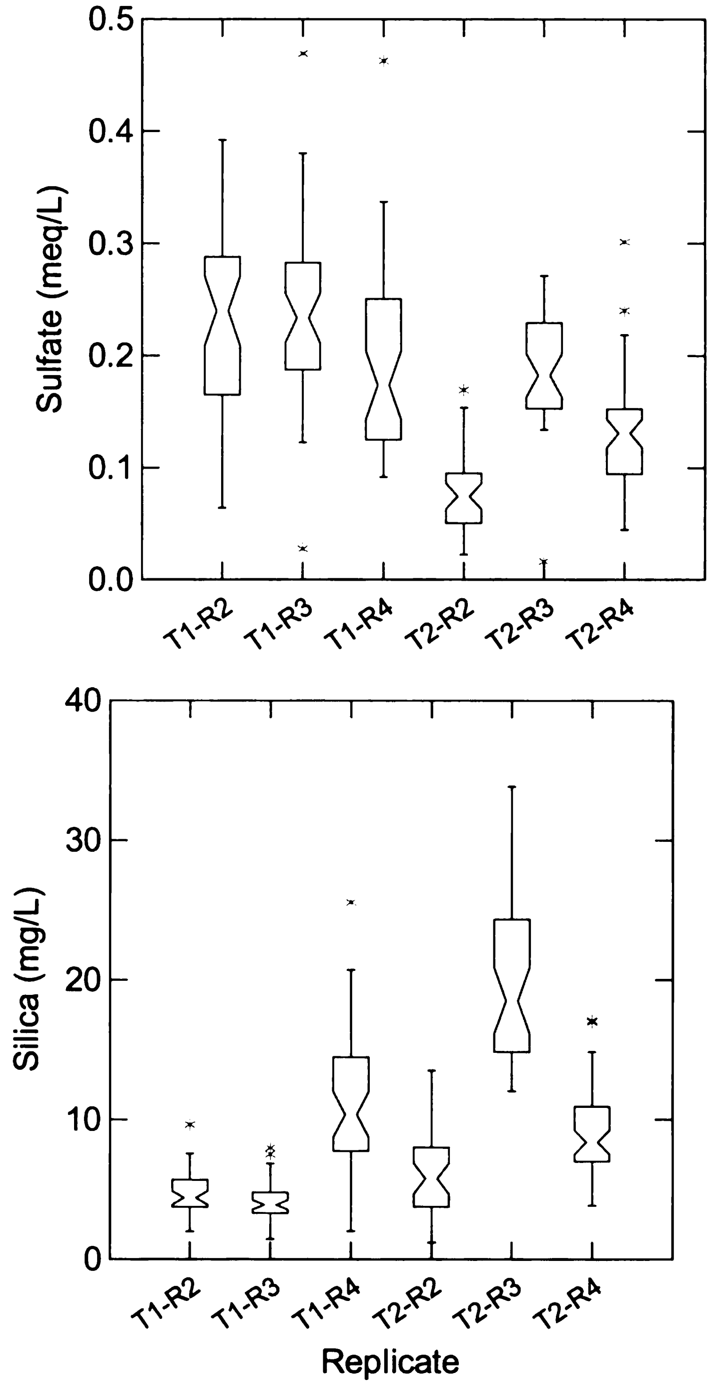


Figure 44: Notched box plots for sulfate and silica by replicate for Treatments T1 and T2. The notches indicate the approximate 95% confidence intervals around the median.

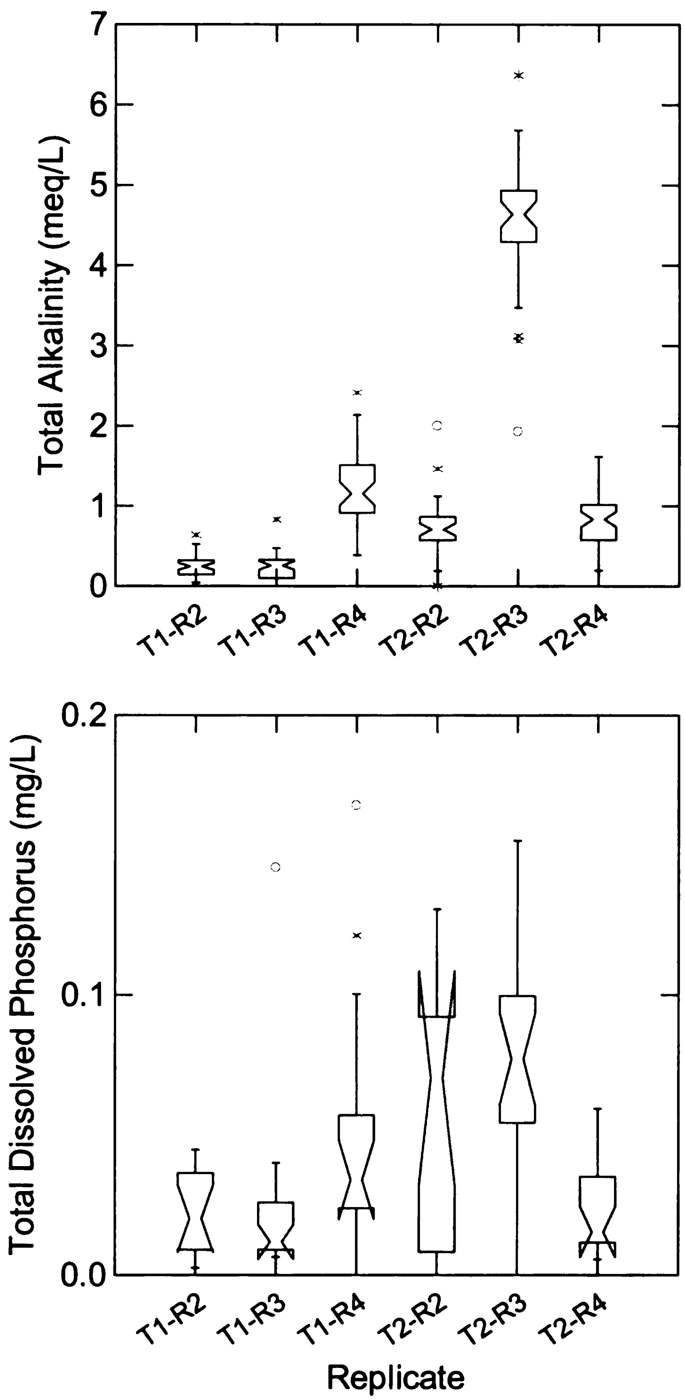


Figure 45: Notched box plots for total alkalinity and total dissolved phosphorus by replicate for Treatments T1 and T2. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases, 5 were excluded by making the TDP graph range less than data range.

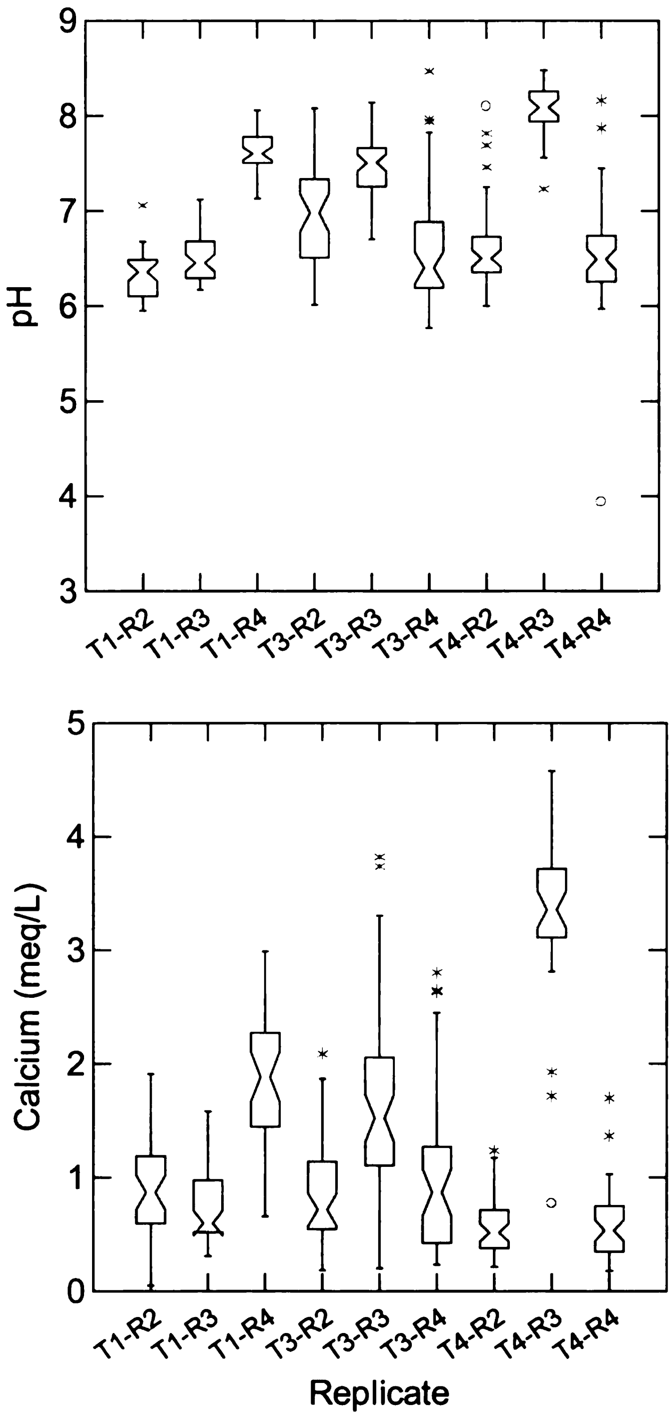


Figure 46: Notched box plots for pH and calcium by replicate for Treatments T1, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases, 6 were excluded by making calcium graph range less than data range.

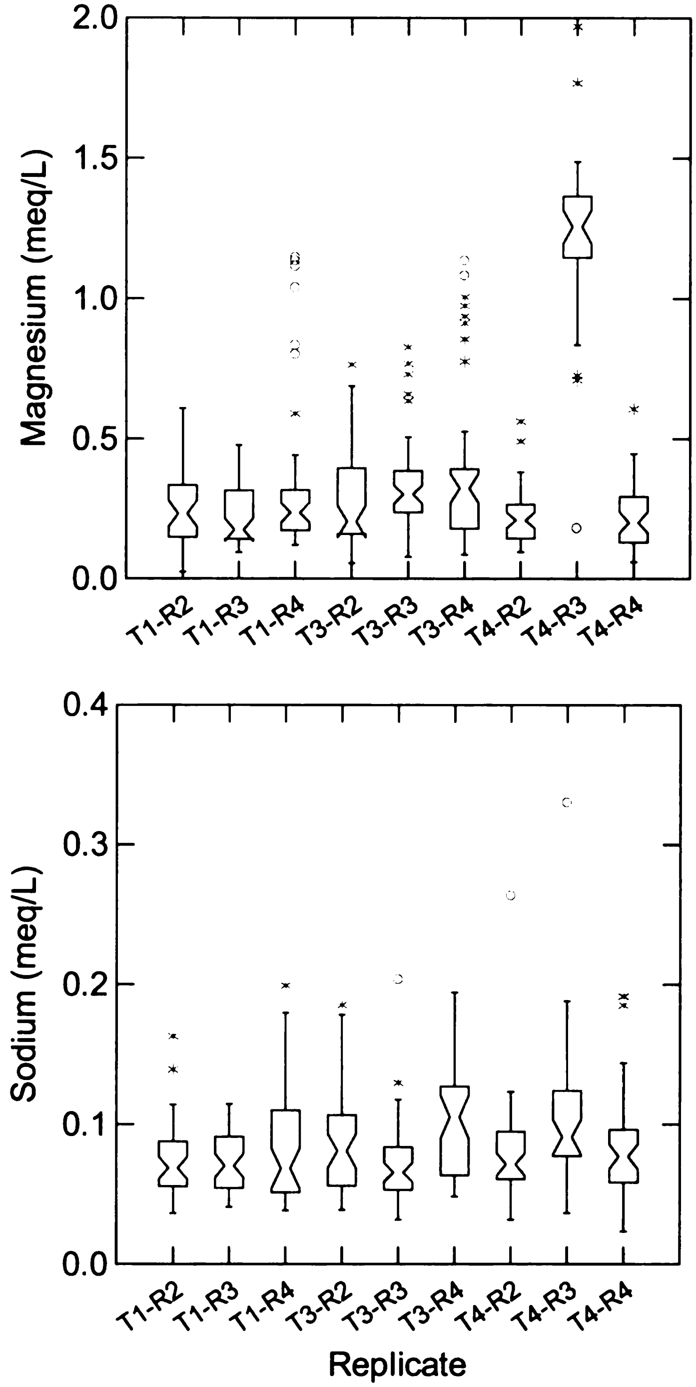


Figure 47: Notched box plots for magnesium and sodium by replicate for Treatments T1, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median.

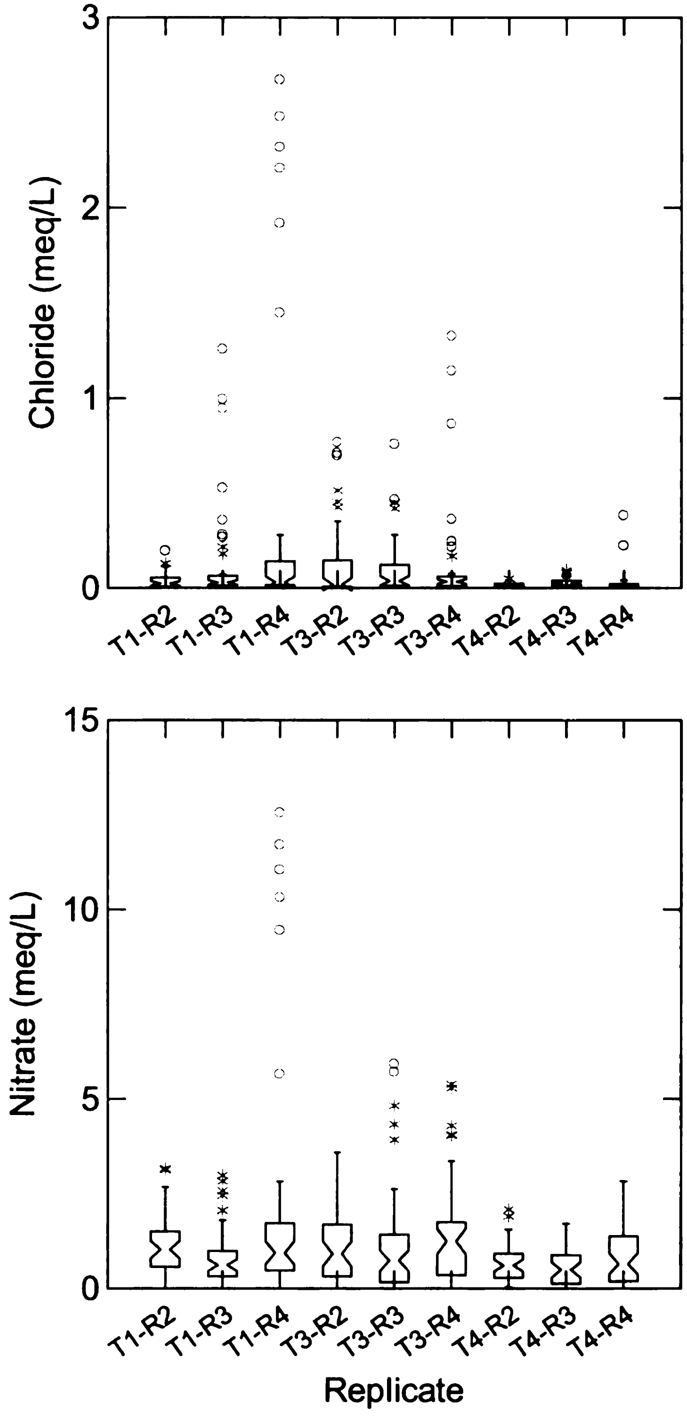


Figure 48: Notched box plots for chloride and nitrate by replicate for Treatments T1, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median.

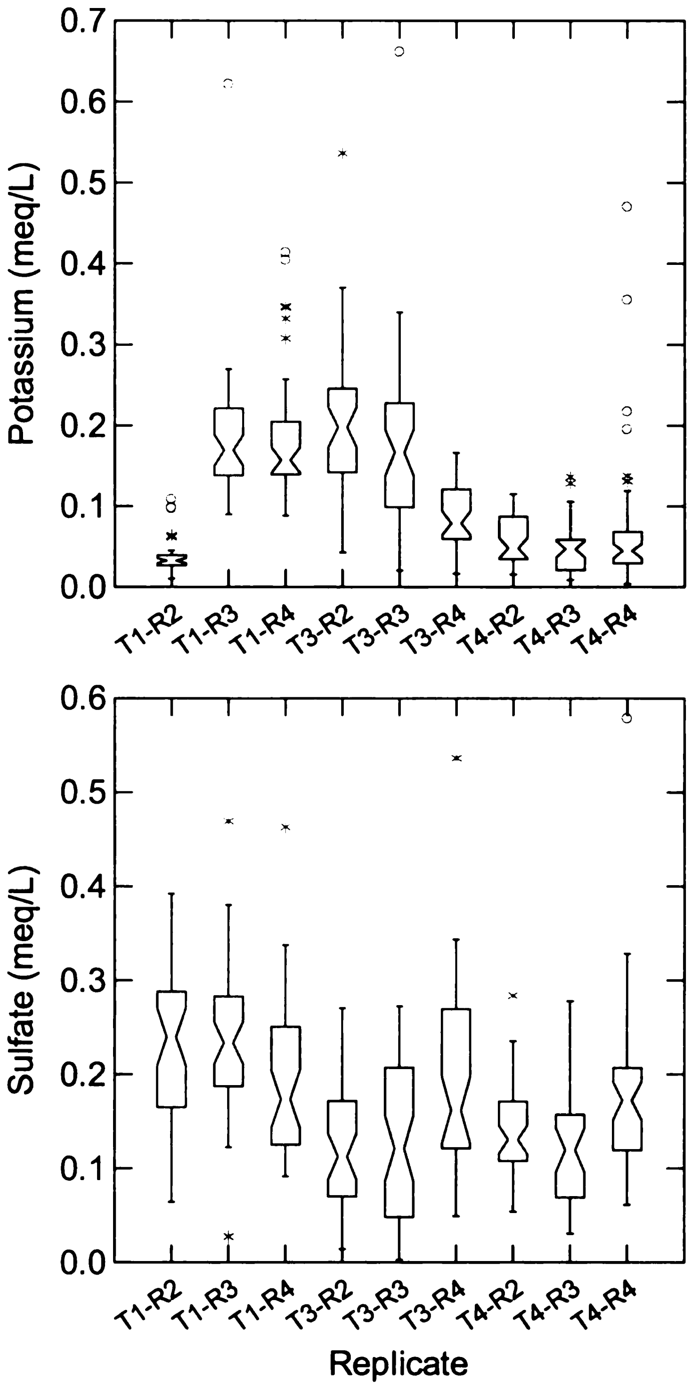


Figure 49: Notched box plots for potassium and sulfate by replicate for Treatments T1, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median.

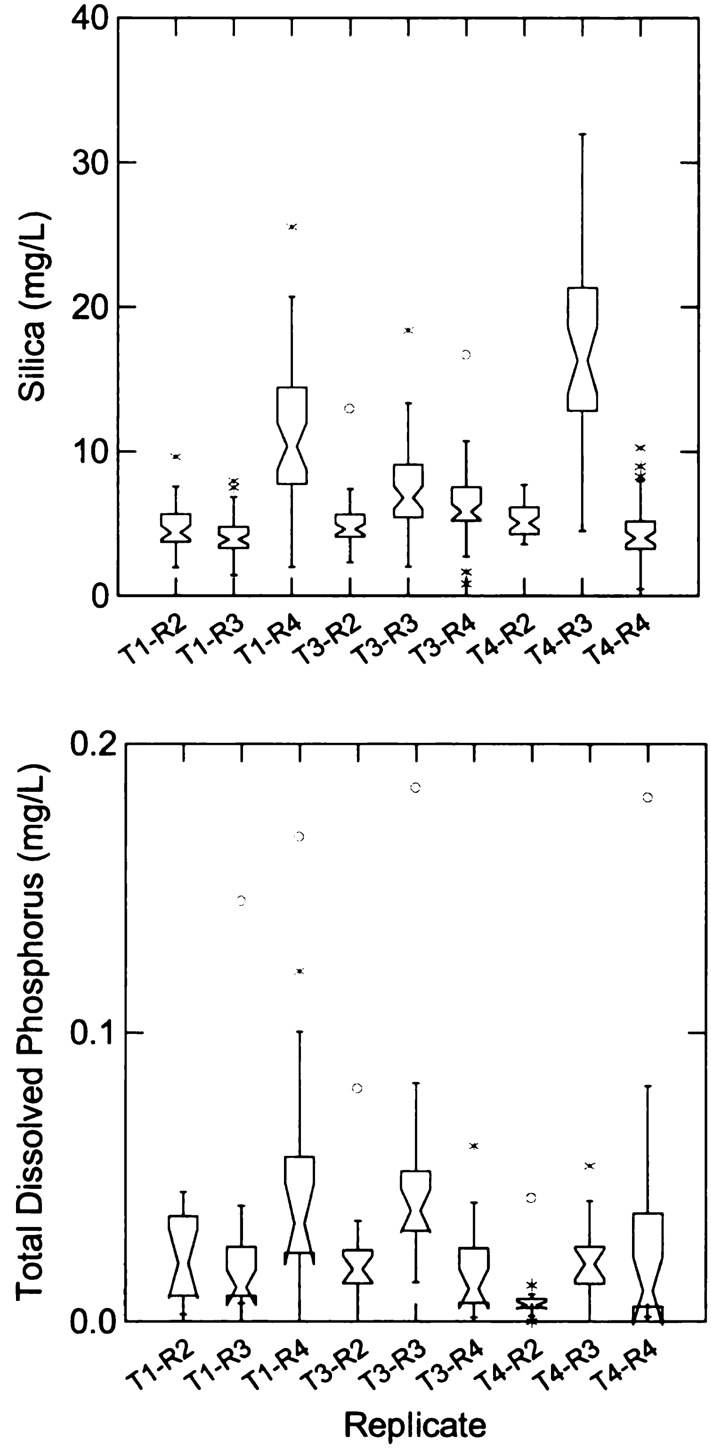


Figure 50: Notched box plots for silica and total dissolved phosphorus by replicate for Treatments T1, T3, and T4. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases, 4 were excluded by making the TDP graph range less than data range.

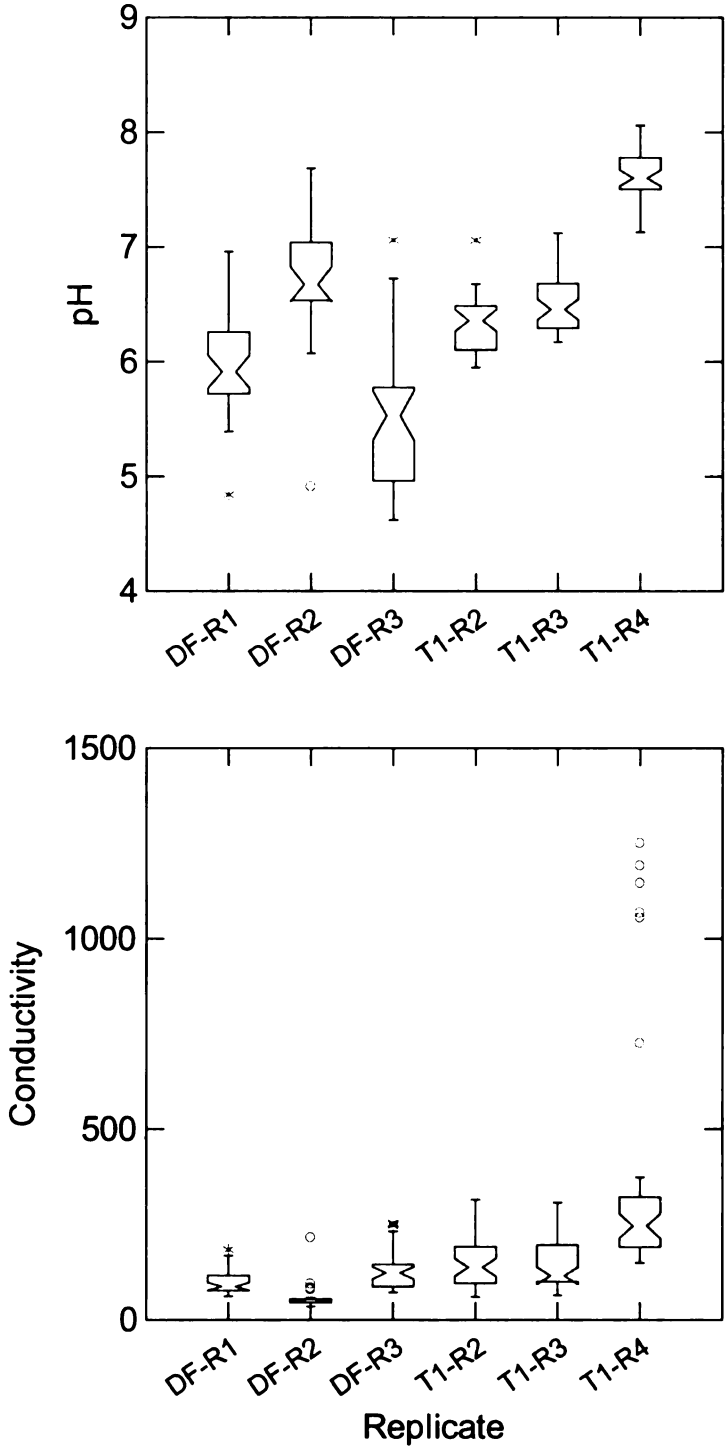


Figure 51: Notched box plots for pH (air-equilibrated) and conductance (µS/cm@25°C) by replicate for Treatments DF and T1. The notches indicate the approximate 95% confidence intervals around the median.

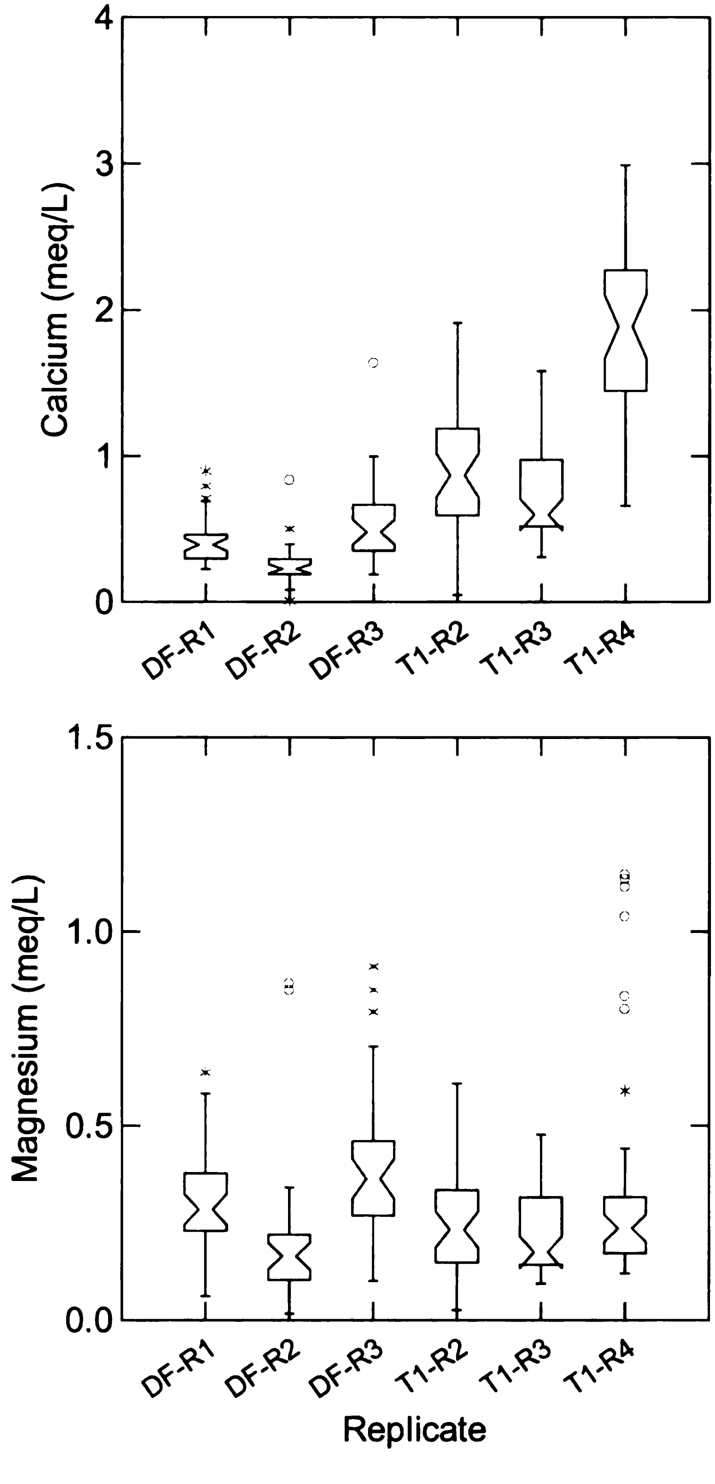


Figure 52: Notched box plots for calcium and magnesium by replicate for Treatments DF and T1. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 226 cases, 6 were excluded by making the calcium graph range less than data range.

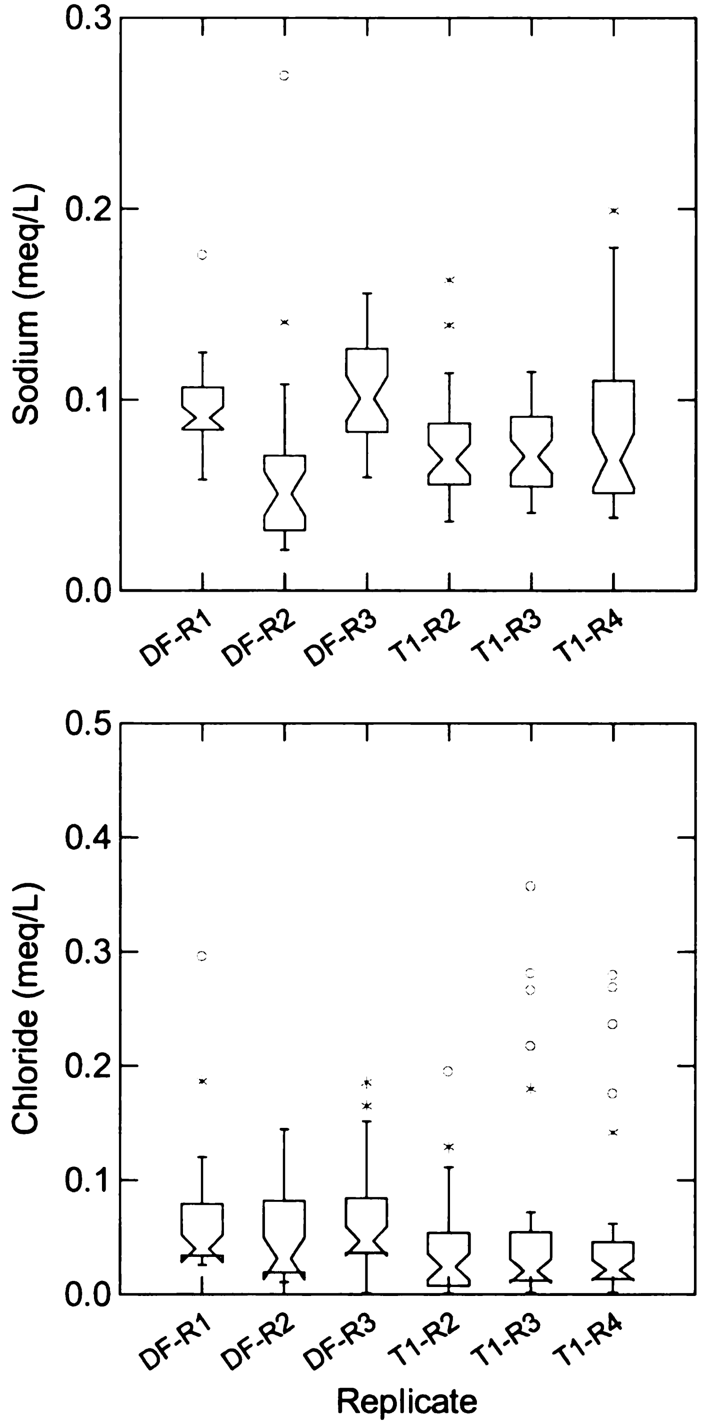


Figure 53: Notched box plots for sodium and chloride by replicate for Treatments DF and T1. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 226 cases, 10 were excluded by making the chloride graph range less than data range.

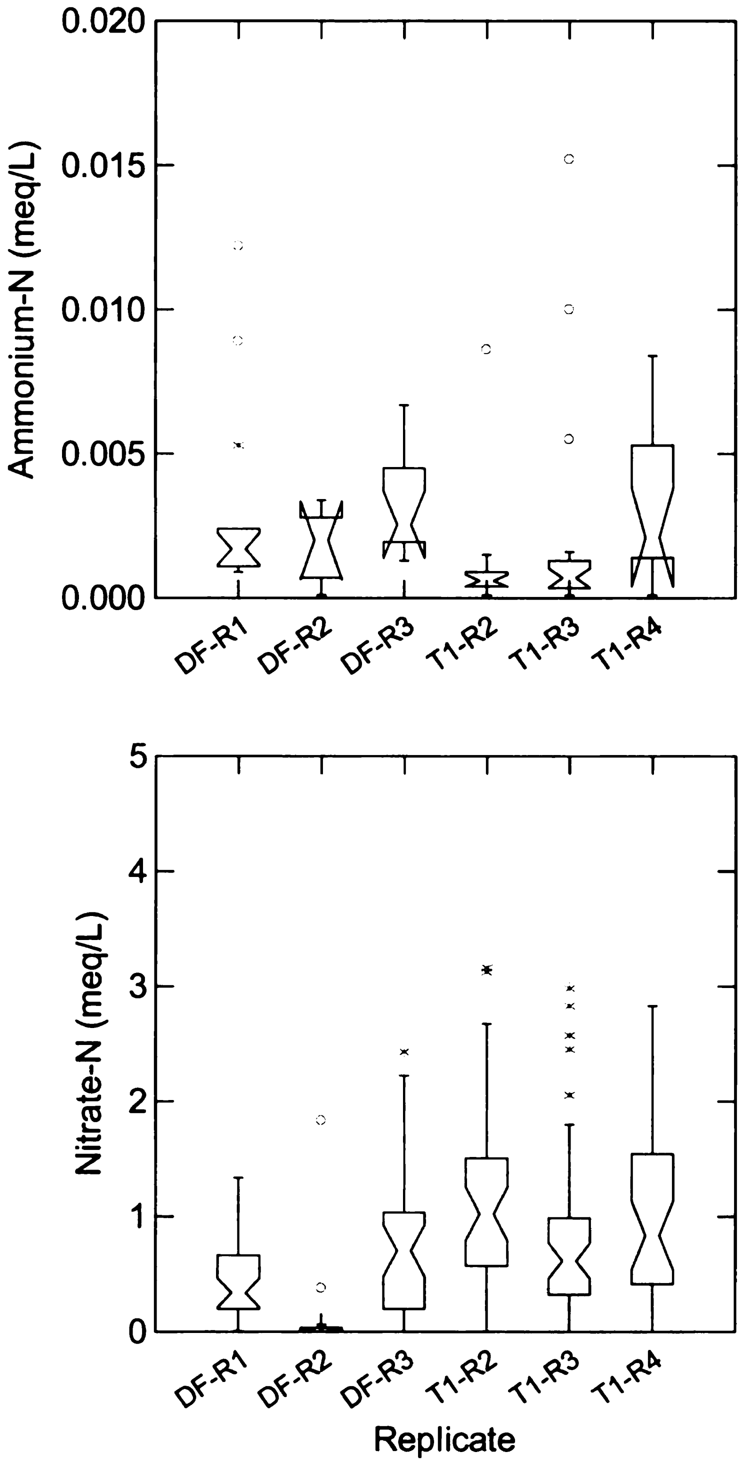


Figure 54: Notched box plots for ammonium-N and nitrate-N by replicate for Treatments DF and T1. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 226 cases, 4 and 6, respectively, were excluded by making the ammonium-N and nitrate-N graph ranges less than data ranges.

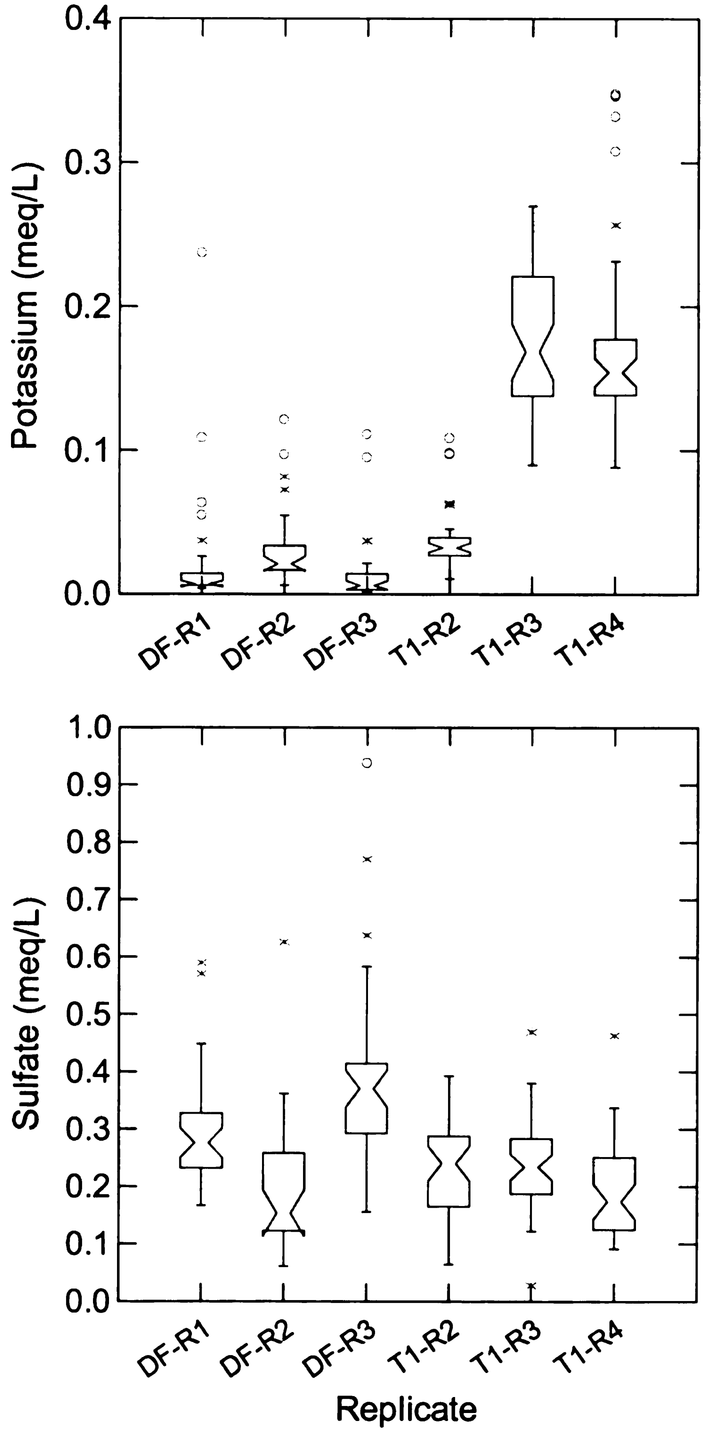


Figure 55: Notched box plots for potassium and sulfate by replicate for Treatments DF and T1. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 226 cases, 3 were excluded by making the sulfate graph range less than data range.

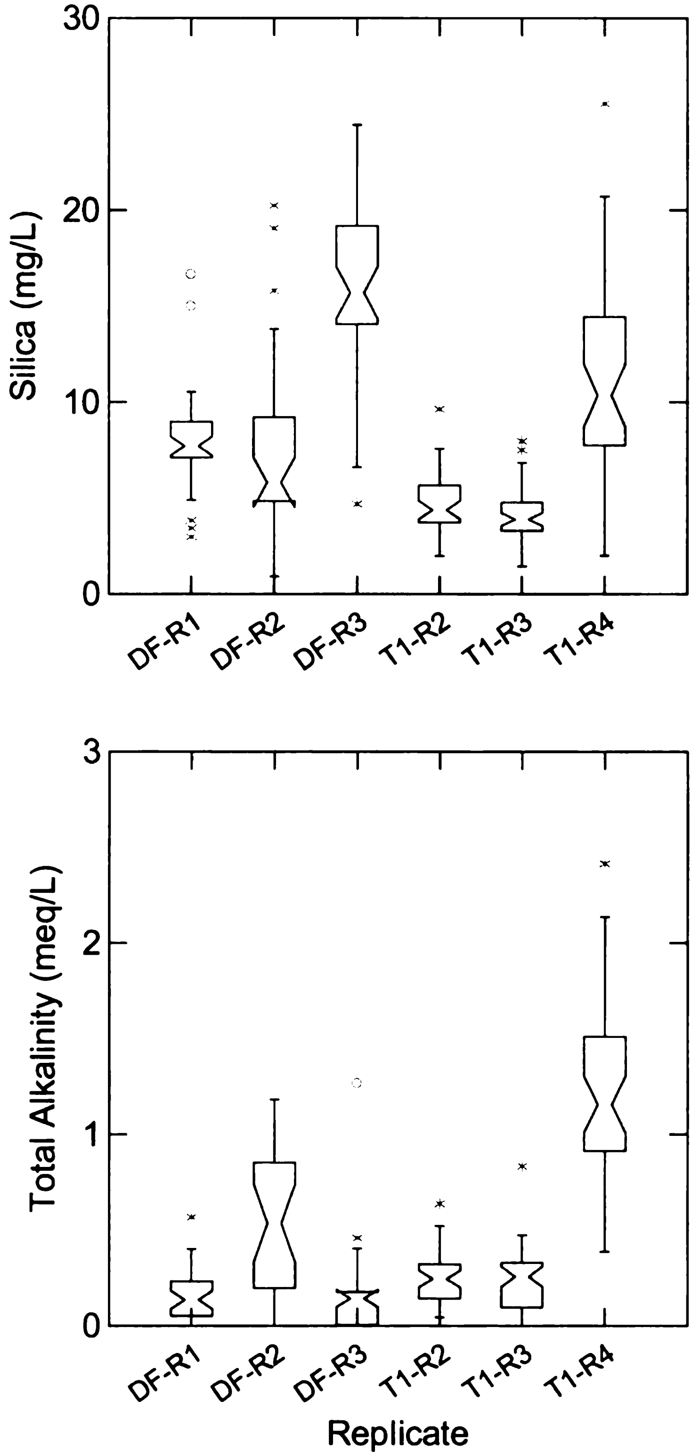


Figure 56: Notched box plots for silica and total alkalinity by replicate for Treatments DF and T1. The notches indicate the approximate 95% confidence intervals around the median.

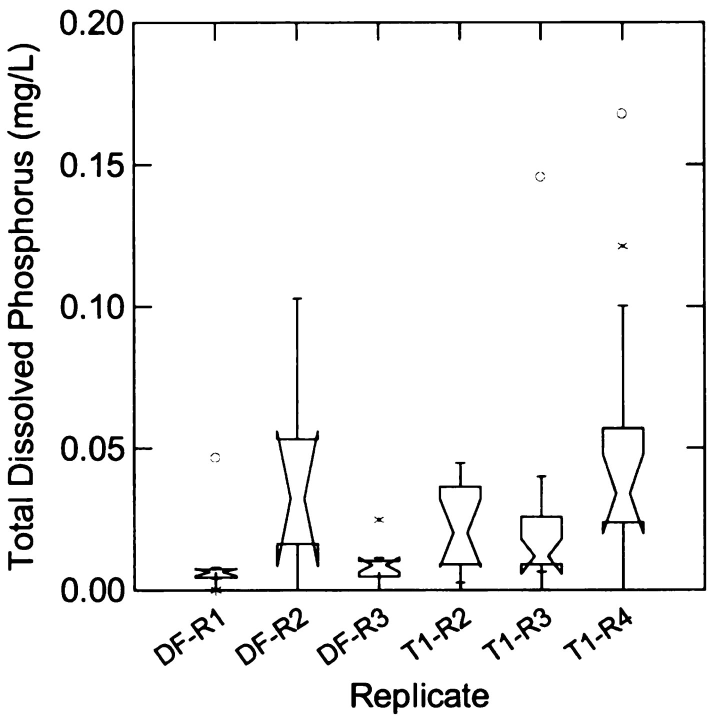


Figure 57: Notched box plot for total dissolved phosphorus by replicate for Treatments DF and T1. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 226 cases, 5 were excluded by making the TDP graph range less than data range.

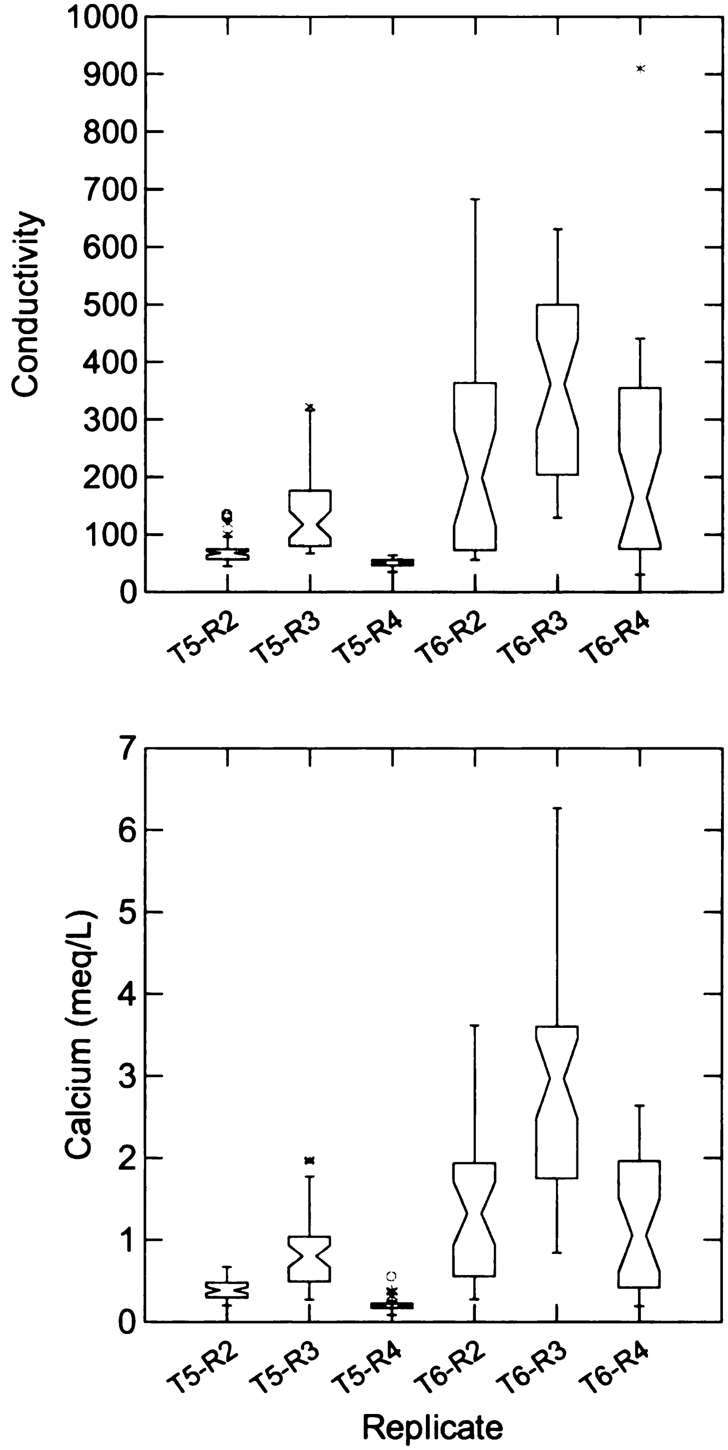


Figure 58: Notched box plots for conductance and calcium by replicate for Treatments T5 and T6. The notches indicate the approximate 95% confidence intervals around the median.

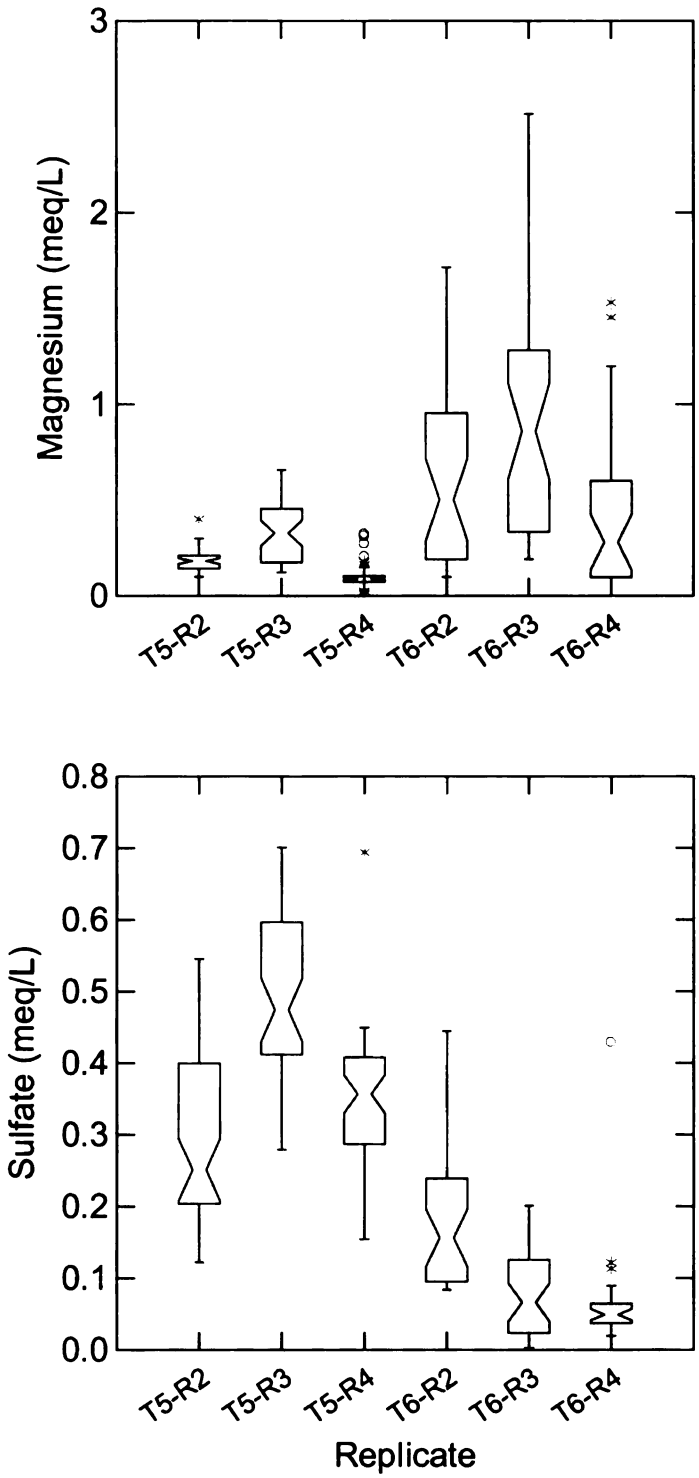


Figure 59: Notched box plots for magnesium and sulfate by replicate for Treatments T5 and T6. The notches indicate the approximate 95% confidence intervals around the median.

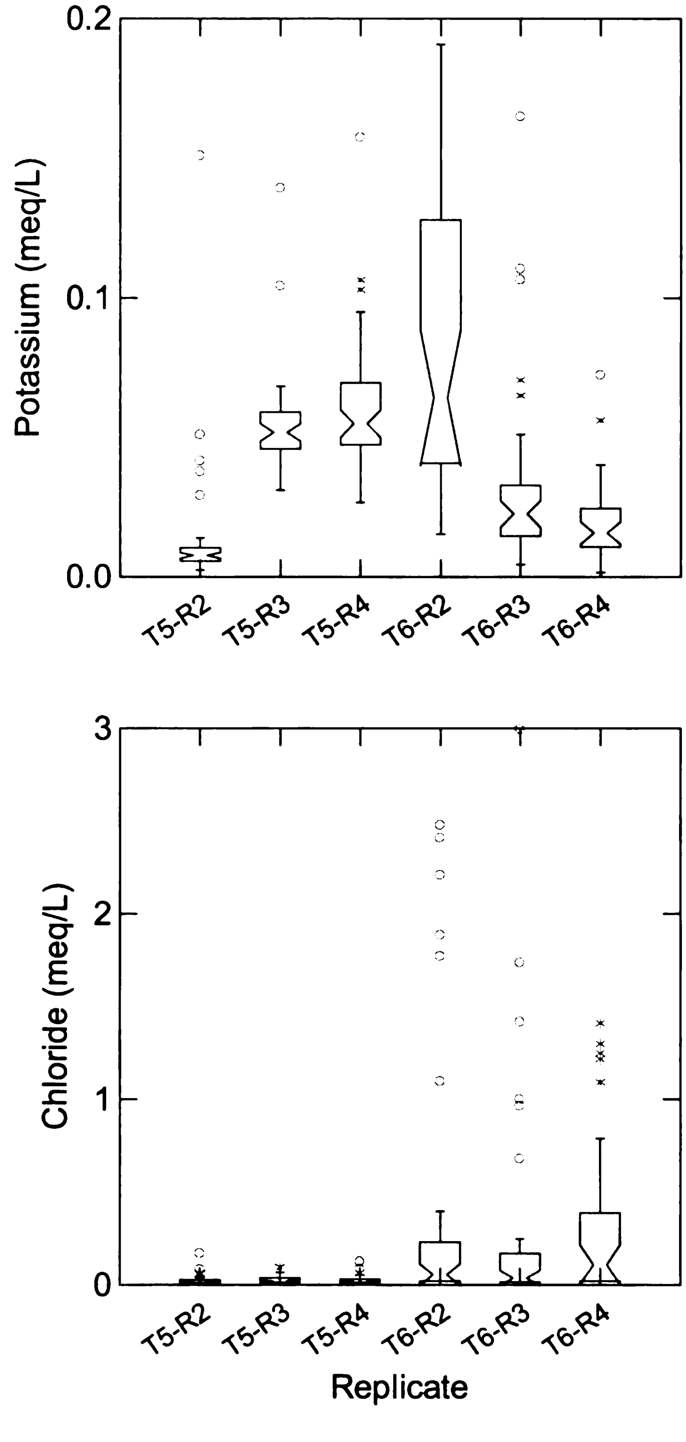


Figure 60: Notched box plots for potassium and chloride by replicate for Treatments T5 and T6. The notches indicate the approximate 95% confidence intervals around the median. Of 243 cases, 1 was excluded by making the potassium graph range less than data range.

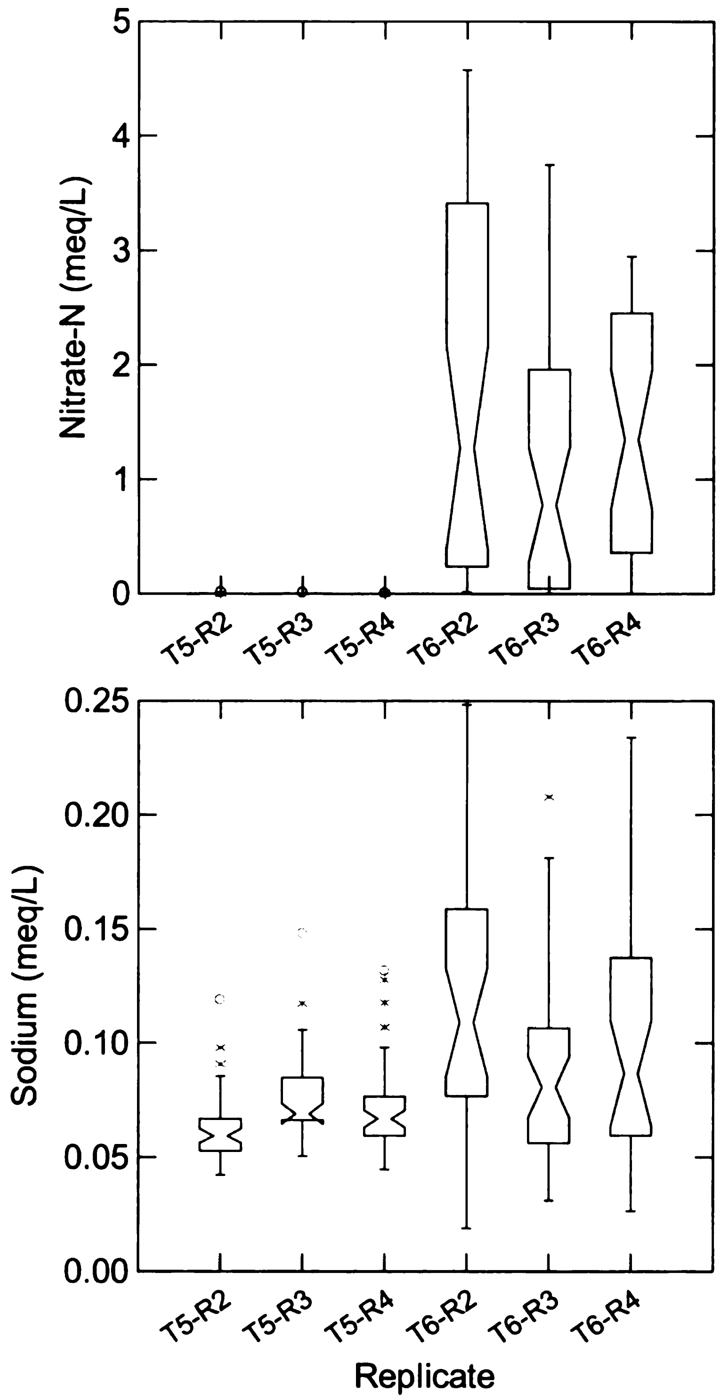


Figure 61: Notched box plots for nitrate and sodium by replicate for Treatments T5 and T6. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 243 cases, 4 were excluded by making the sodium graph range less than data range.

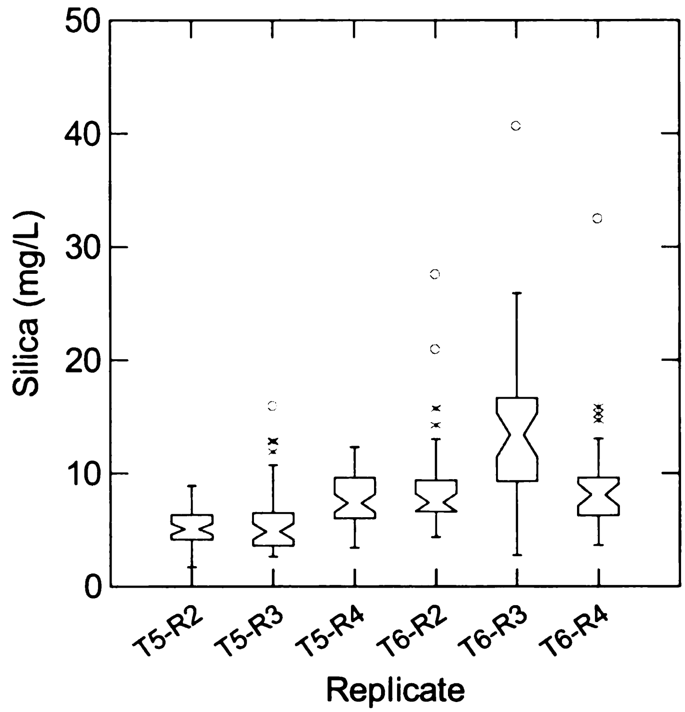


Figure 62: Notched box plot for silica by replicate for Treatments T5 and T6. The notches indicate the approximate 95% confidence intervals around the median.

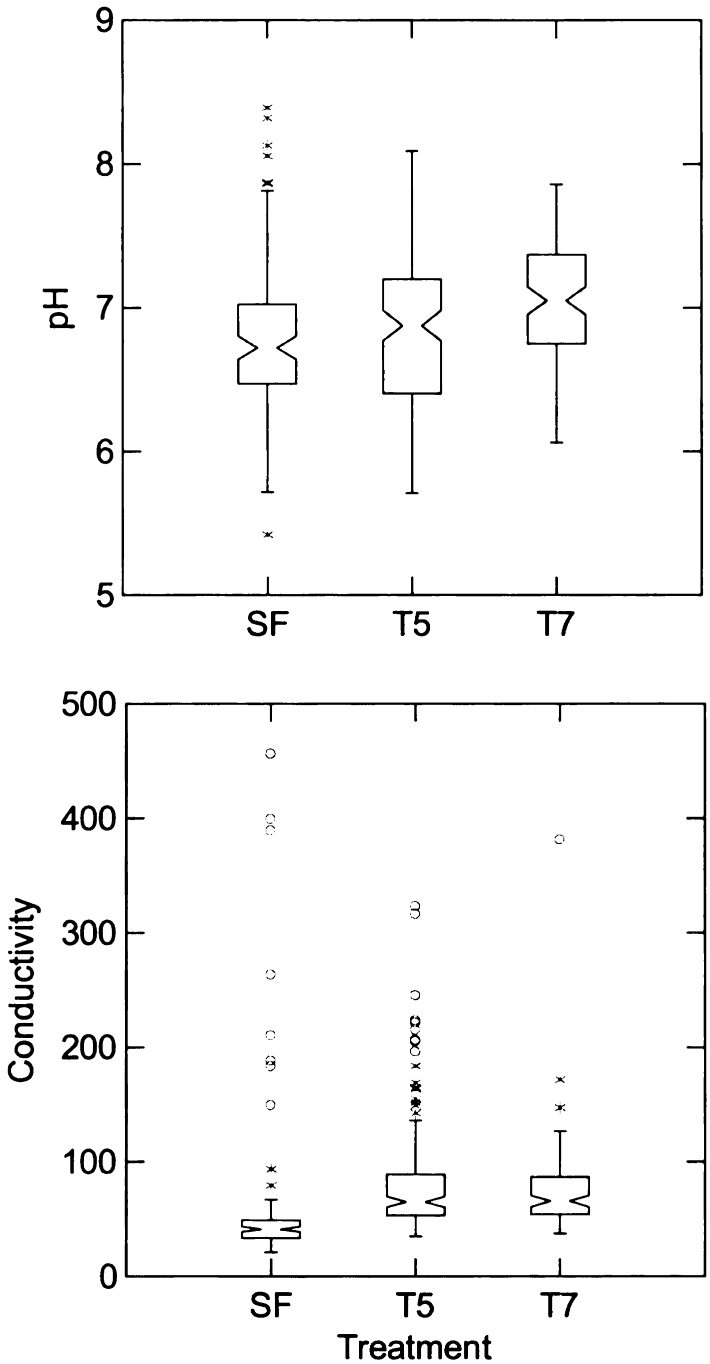


Figure 63: Notched box plots for pH (air-equilibrated) and conductance, Treatments SF, T5, and T6. The notches indicate the approximate 95% confidence intervals around the median.

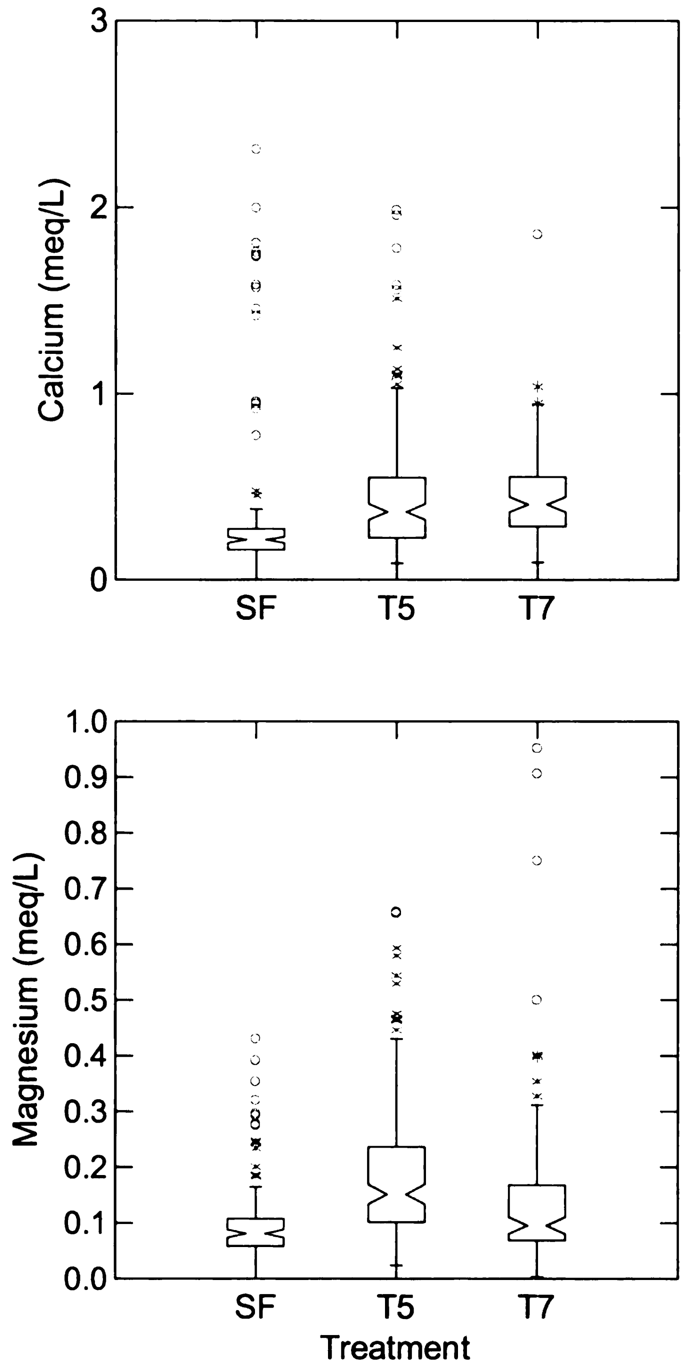


Figure 64: Notched box plots for calcium and magnesium, Treatments SF, T5, and T6. The notches indicate the approximate 95% confidence intervals around the median.

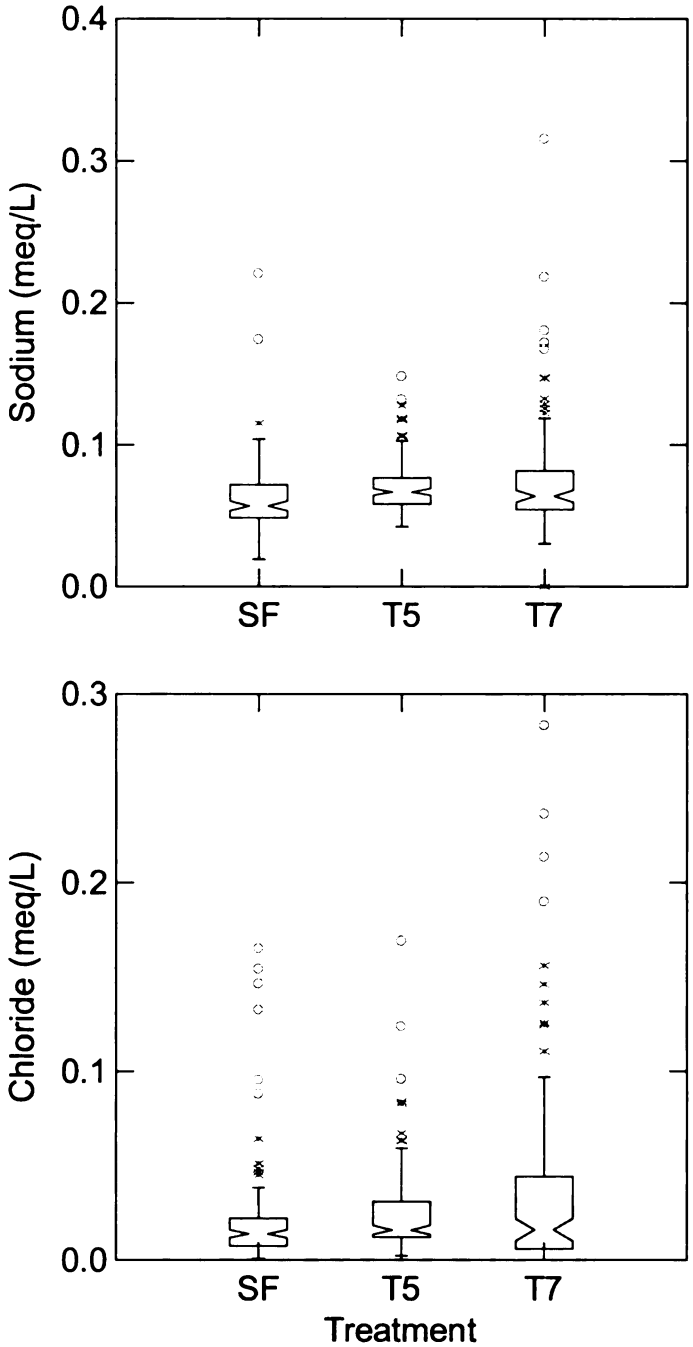


Figure 65: Notched box plots for sodium and chloride, Treatments SF, T5, and T6. The notches indicate the approximate 95% confidence intervals around the median.

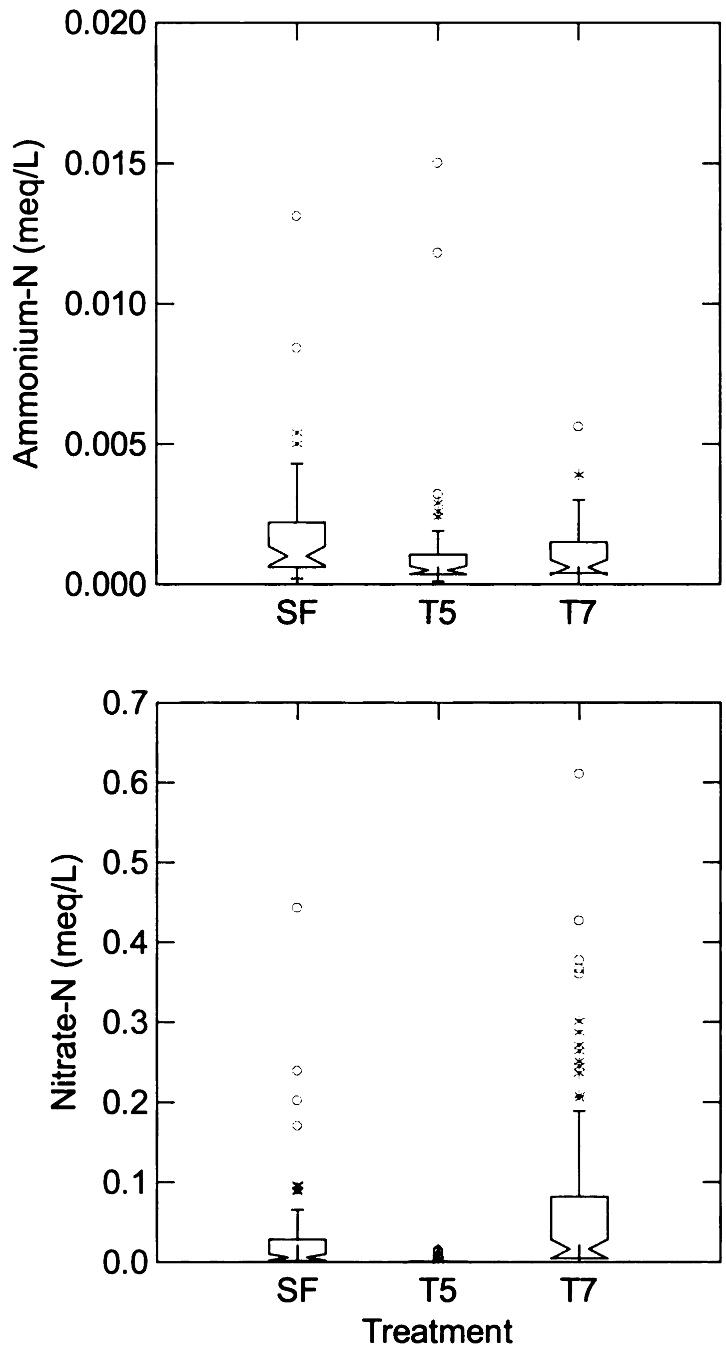


Figure 66: Notched box plots for ammonium and nitrate, Treatments SF, T5, and T6. The notches indicate the approximate 95% confidence intervals around the median.

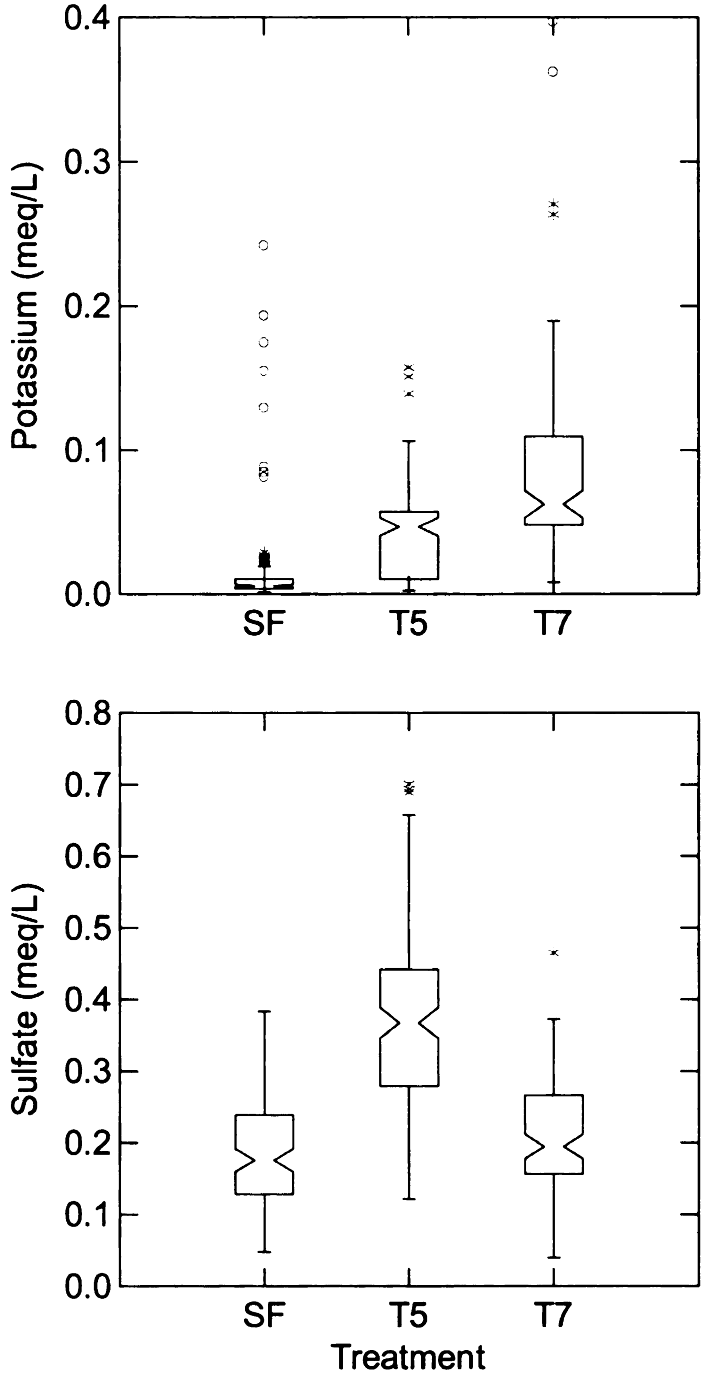


Figure 67: Notched box plots for potassium and sulfate, Treatments SF, T5, and T6. The notches indicate the approximate 95% confidence intervals around the median.

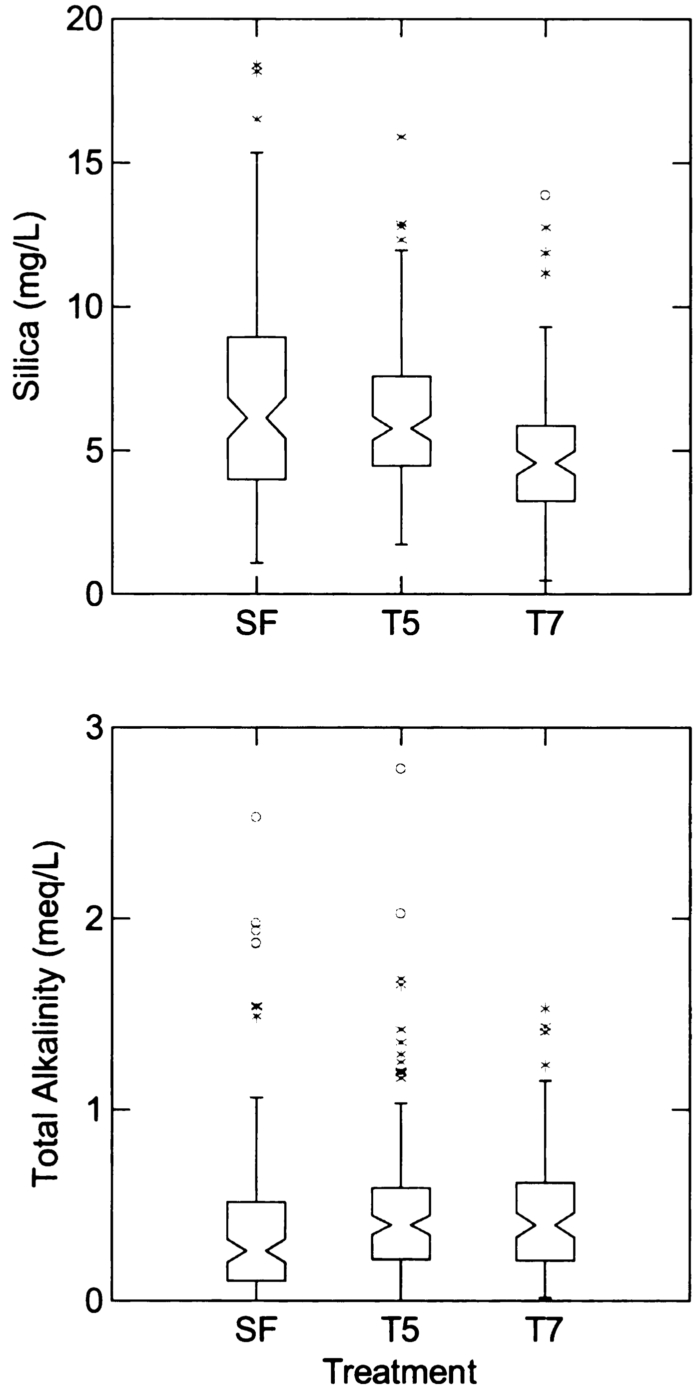


Figure 68: Notched box plots for silica and alkalinity, Treatments SF, T5, and T6. The notches indicate the approximate 95% confidence intervals around the median.

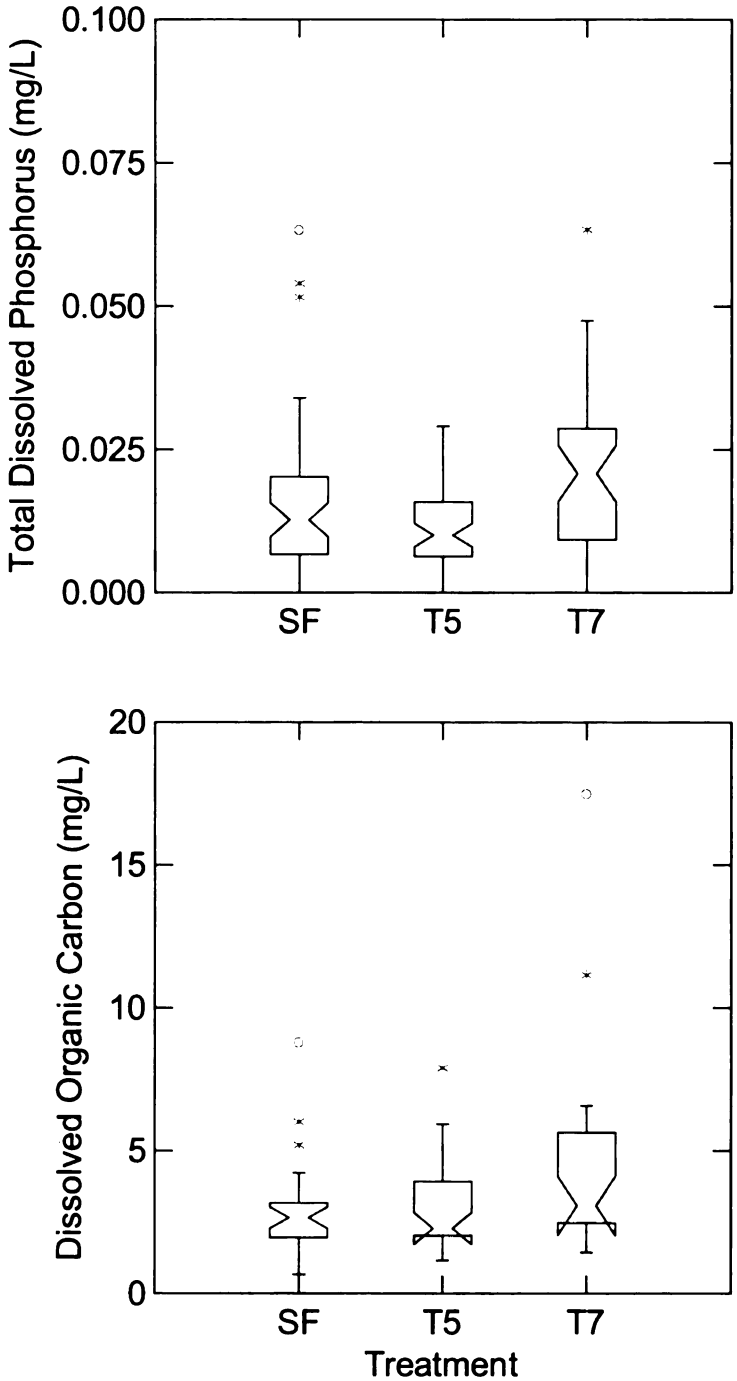


Figure 69: Notched box plots for total dissolved phosphorus and dissolved organic carbon, Treatments SF, T5, and T6. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases, 5 were excluded by making the TDP graph range less than data range.

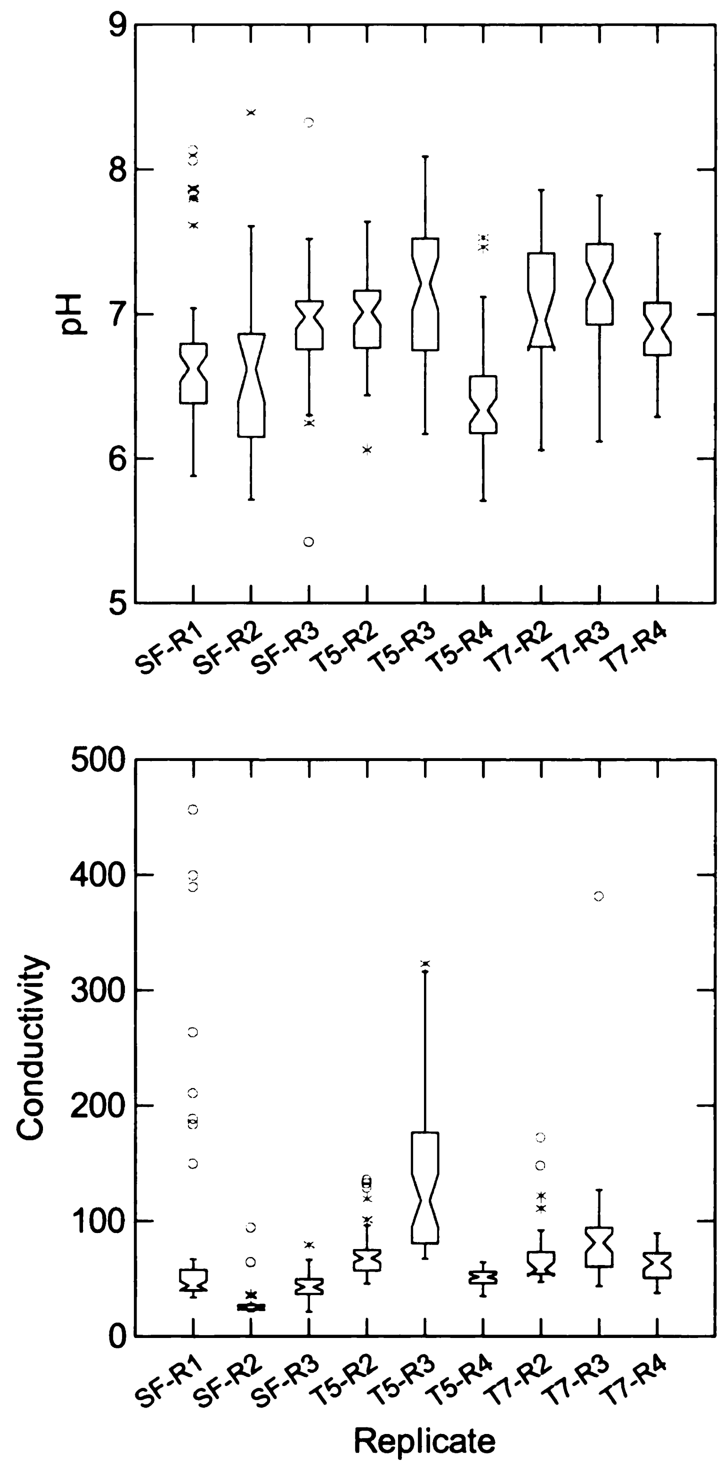


Figure 70: Notched box plots for pH (air-equilibrated) and conductance (μS/cm@25°C) by replicate for Treatments SF, T5, and T7. The notches indicate the approximate 95% confidence intervals around the median.

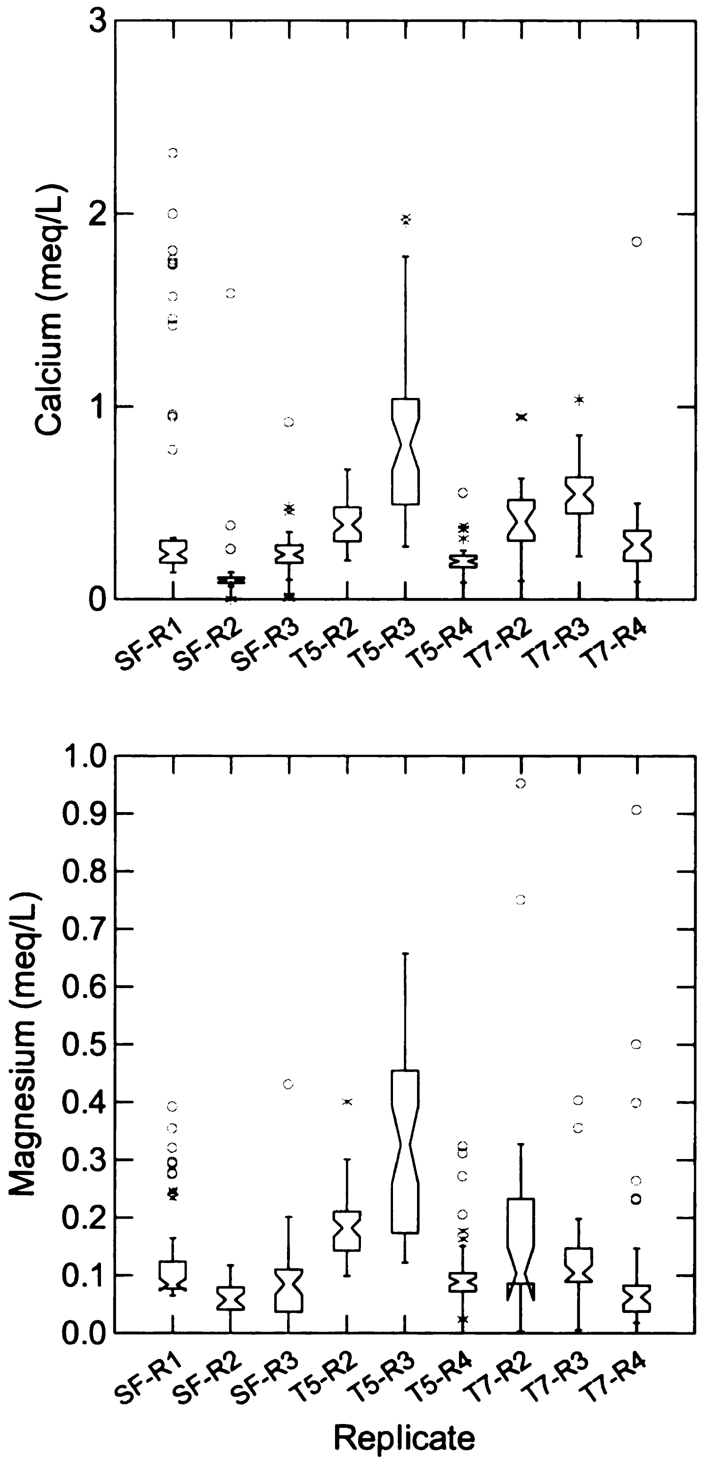


Figure 71: Notched box plots for calcium and magnesium by replicate for Treatments SF, T5, and T7. The notches indicate the approximate 95% confidence intervals around the median.

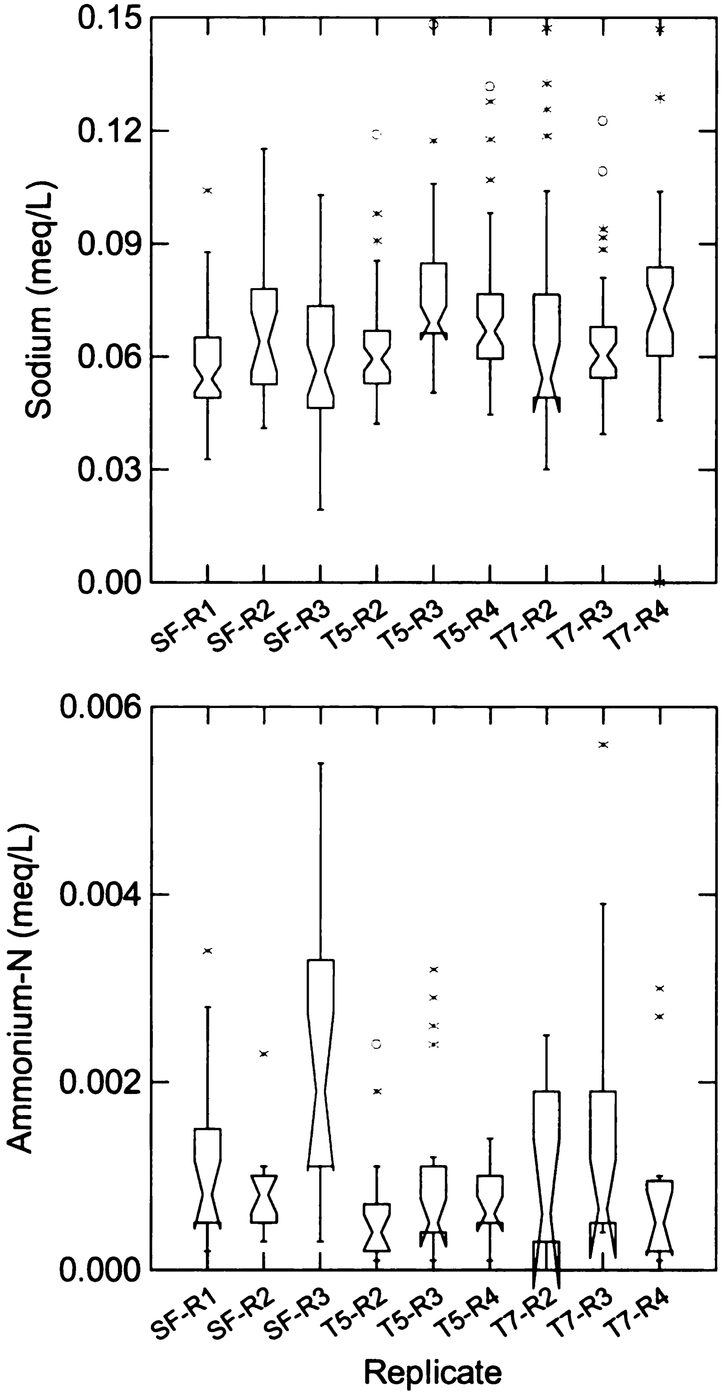


Figure 72: Notched box plots for sodium and ammonium by replicate for Treatments SF, T5, and T7. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases, 7 were excluded by making the sodium graph range less than data range

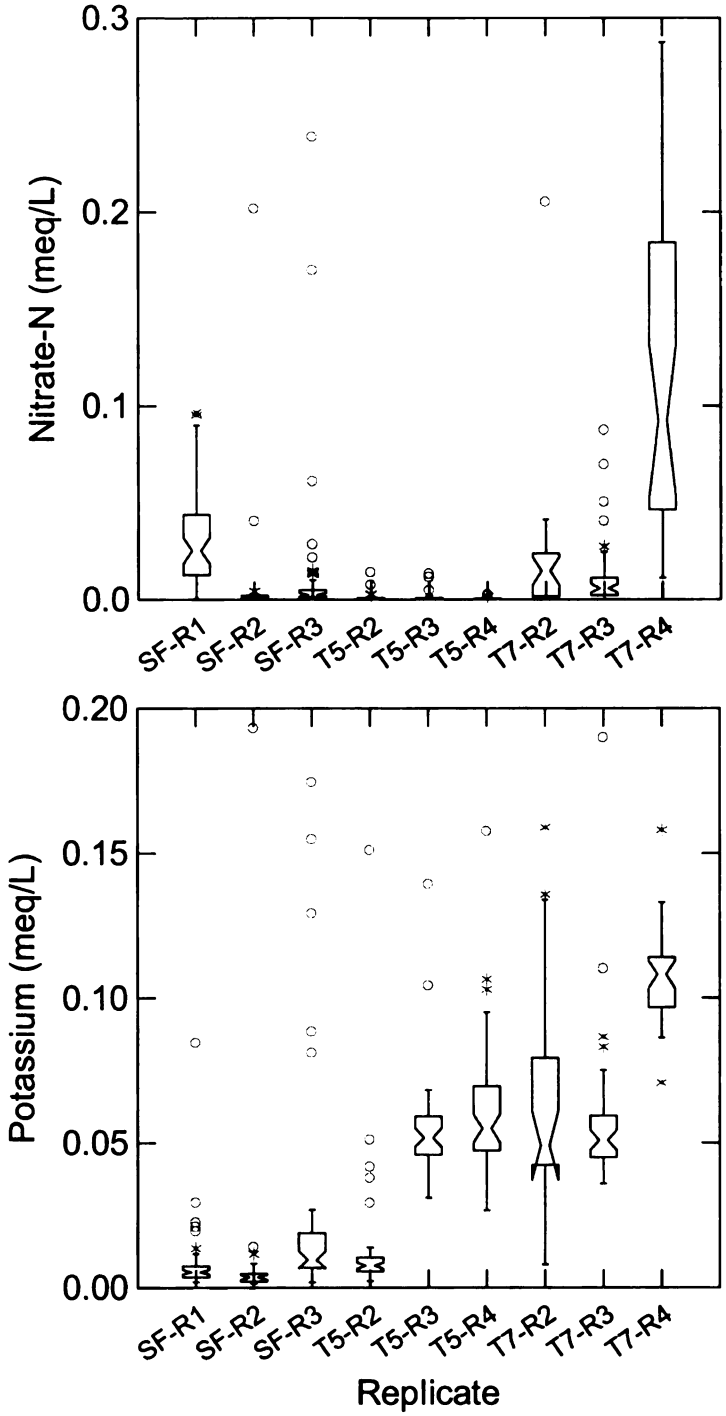


Figure 73: Notched box plots for nitrate and potassium by replicate for Treatments SF, T5, and T7. The notches indicate the approximate 95% confidence intervals around the median. Note: Of 393 cases, 7 and 5, respectively, were excluded by making the nitrate and potassium graph ranges less than data ranges.

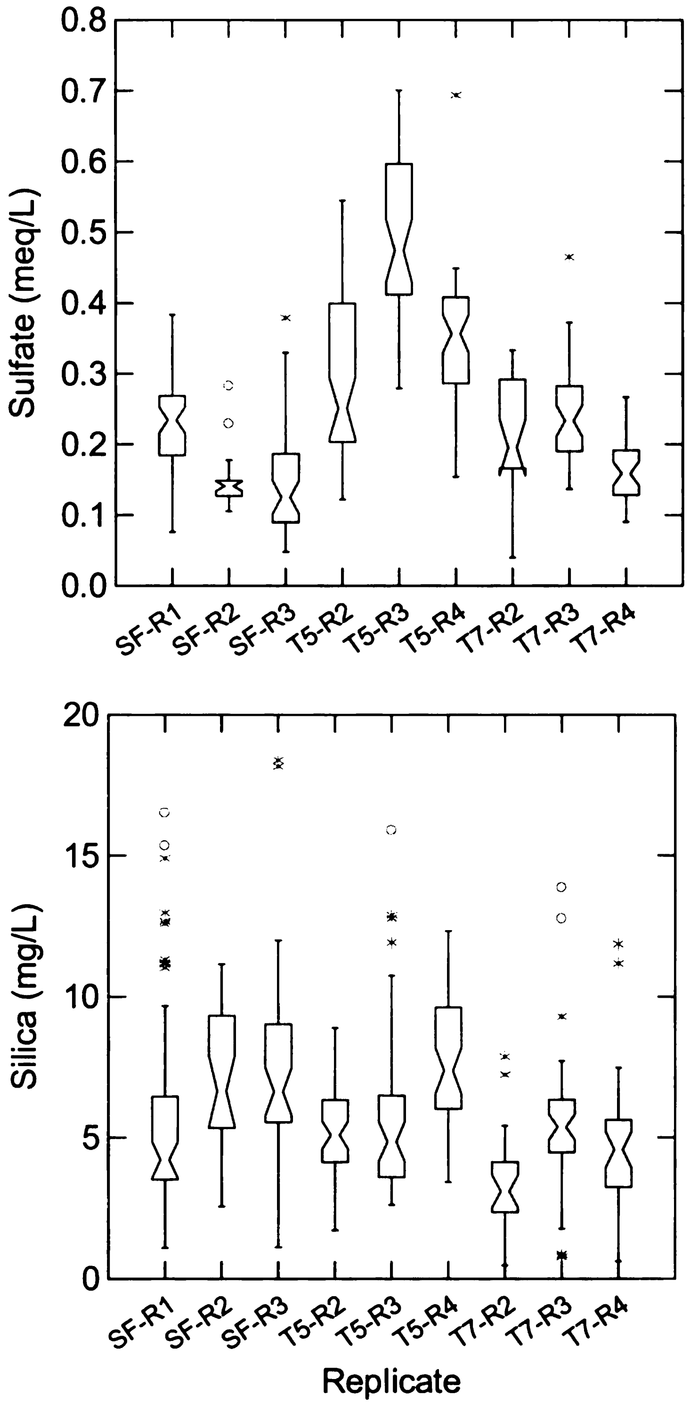


Figure 74: Notched box plots for sulfate and silica by replicate for Treatments SF, T5, and T7. The notches indicate the approximate 95% confidence intervals around the median.

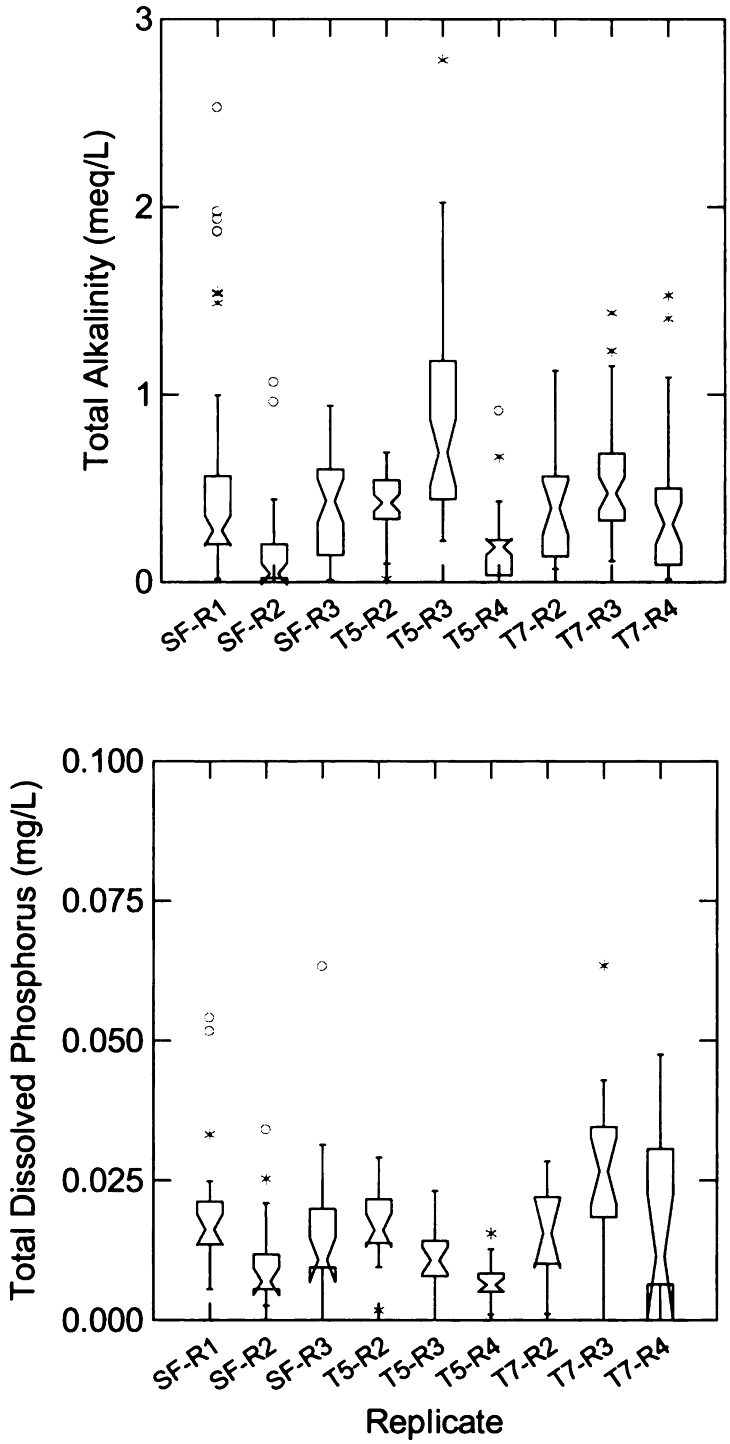


Figure 75: Notched box plots for total alkalinity and total dissolved phosphorus by replicate for Treatments SF, T5, and T7. The notches indicate the approximate 95% confidence intervals around the median. Of 393 cases, 5 were excluded by making the TDP graph range less than data range.

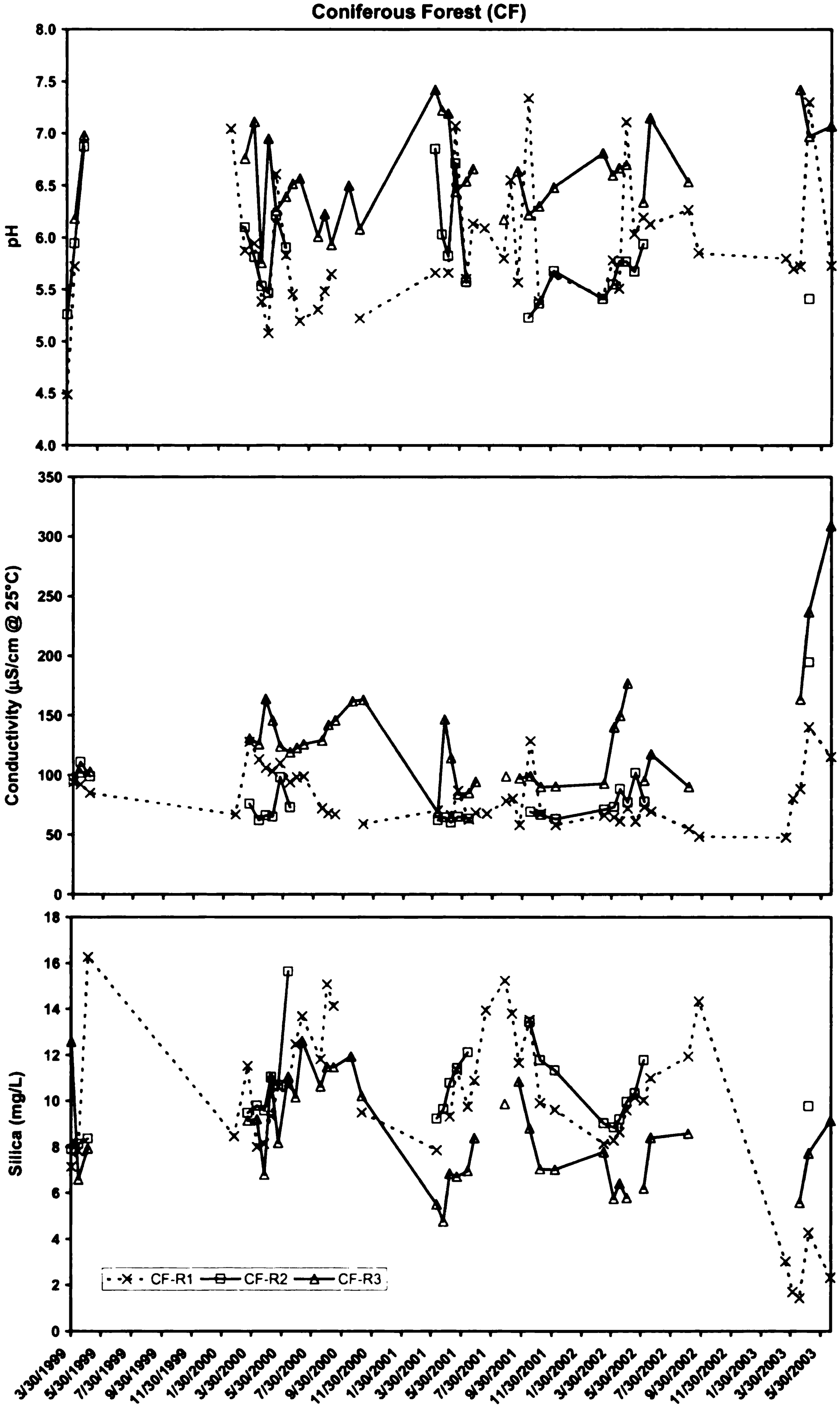


Figure 76: Coniferous Forest Time Series

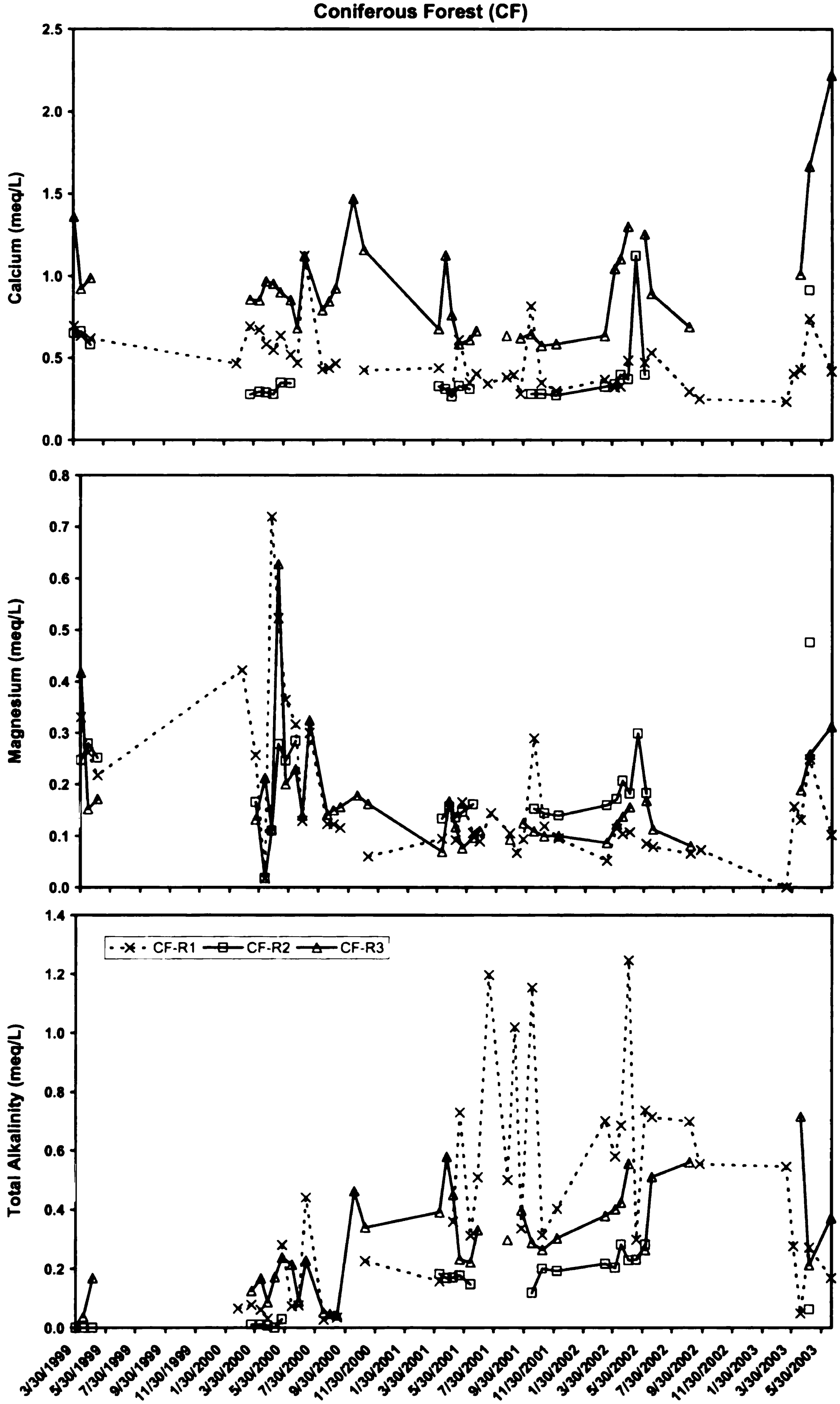


Figure 77: Coniferous Forest Time Series

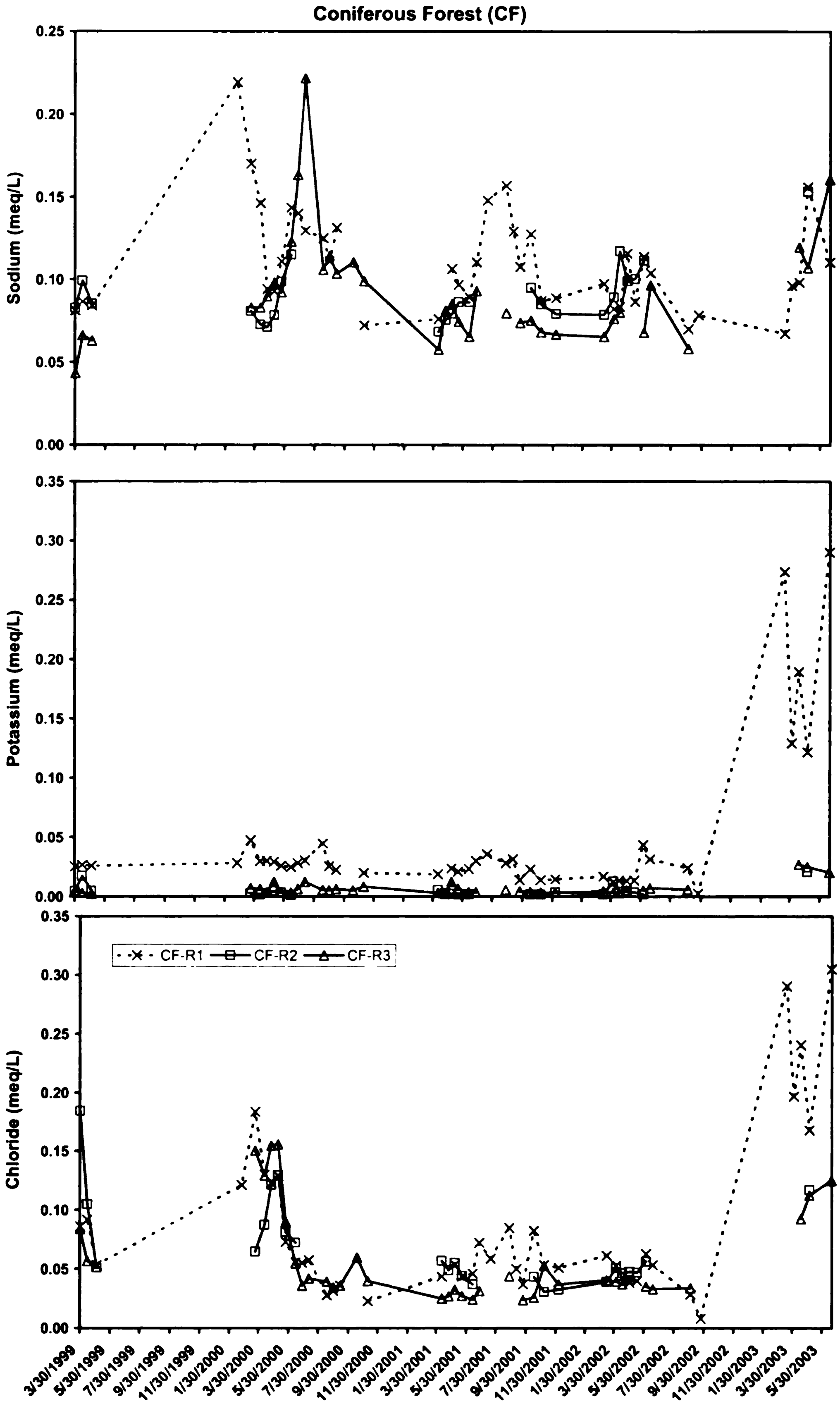


Figure 78: Coniferous Forest Time Series

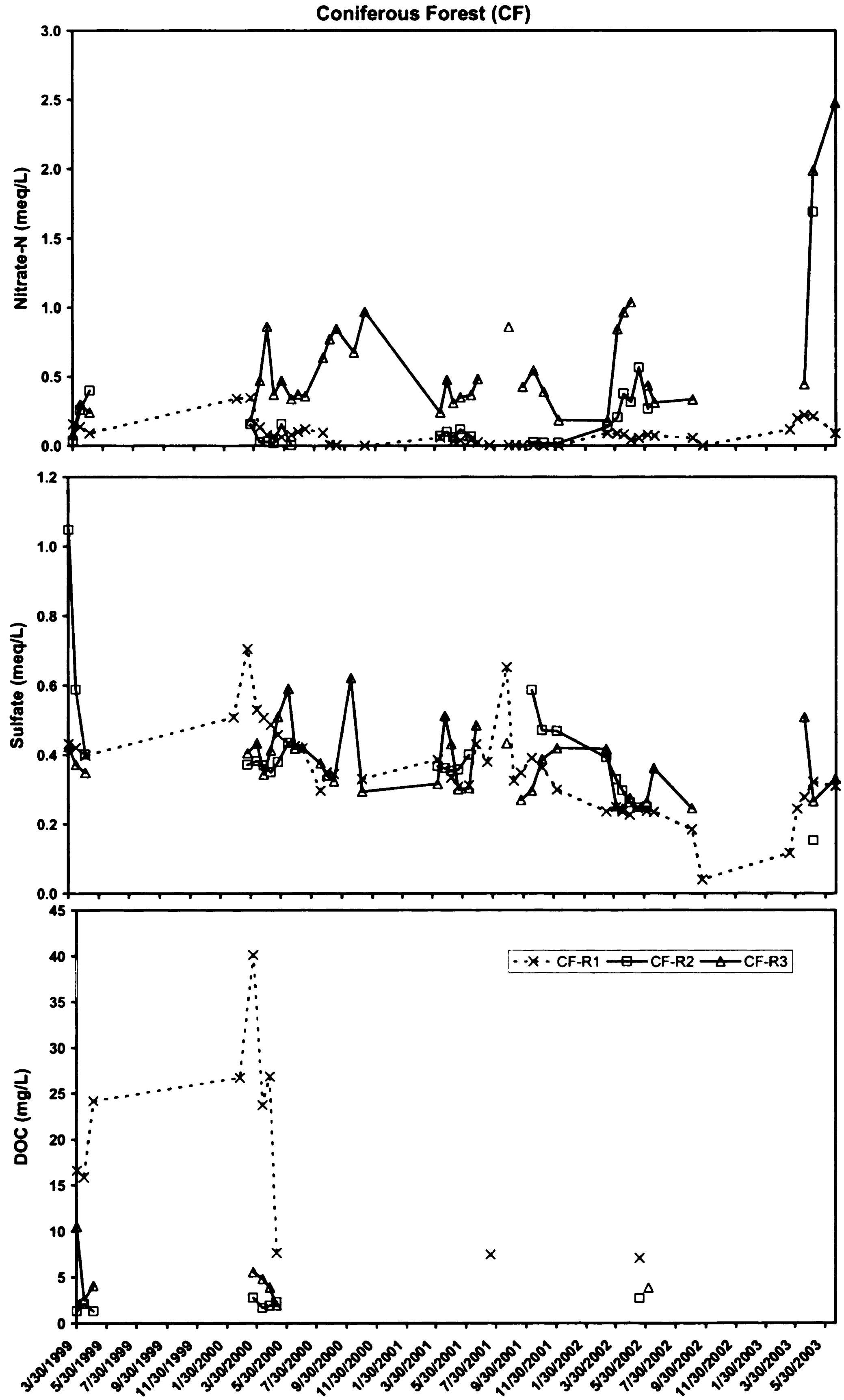


Figure 79: Coniferous Forest Time Series

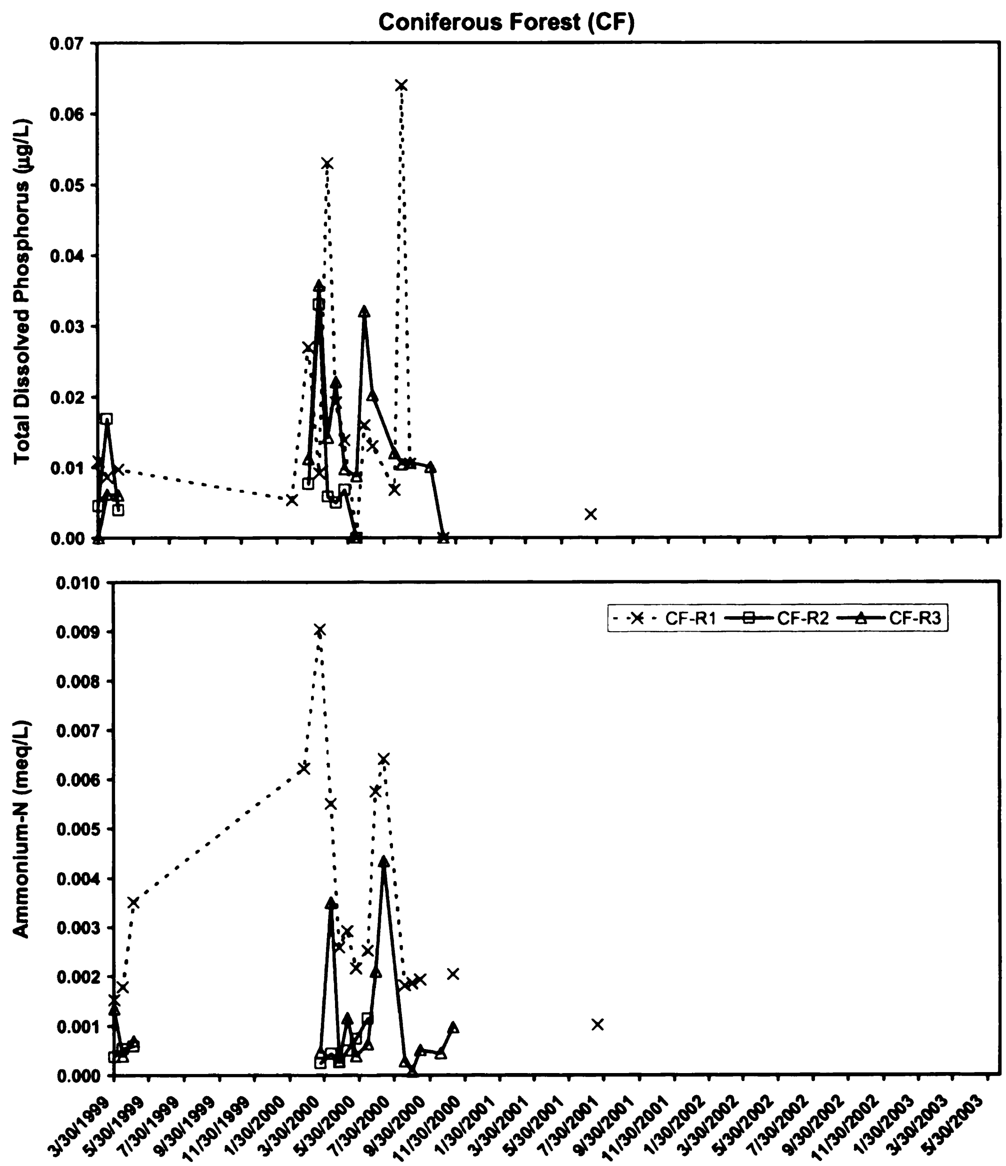


Figure 80: Coniferous Forest Time Series

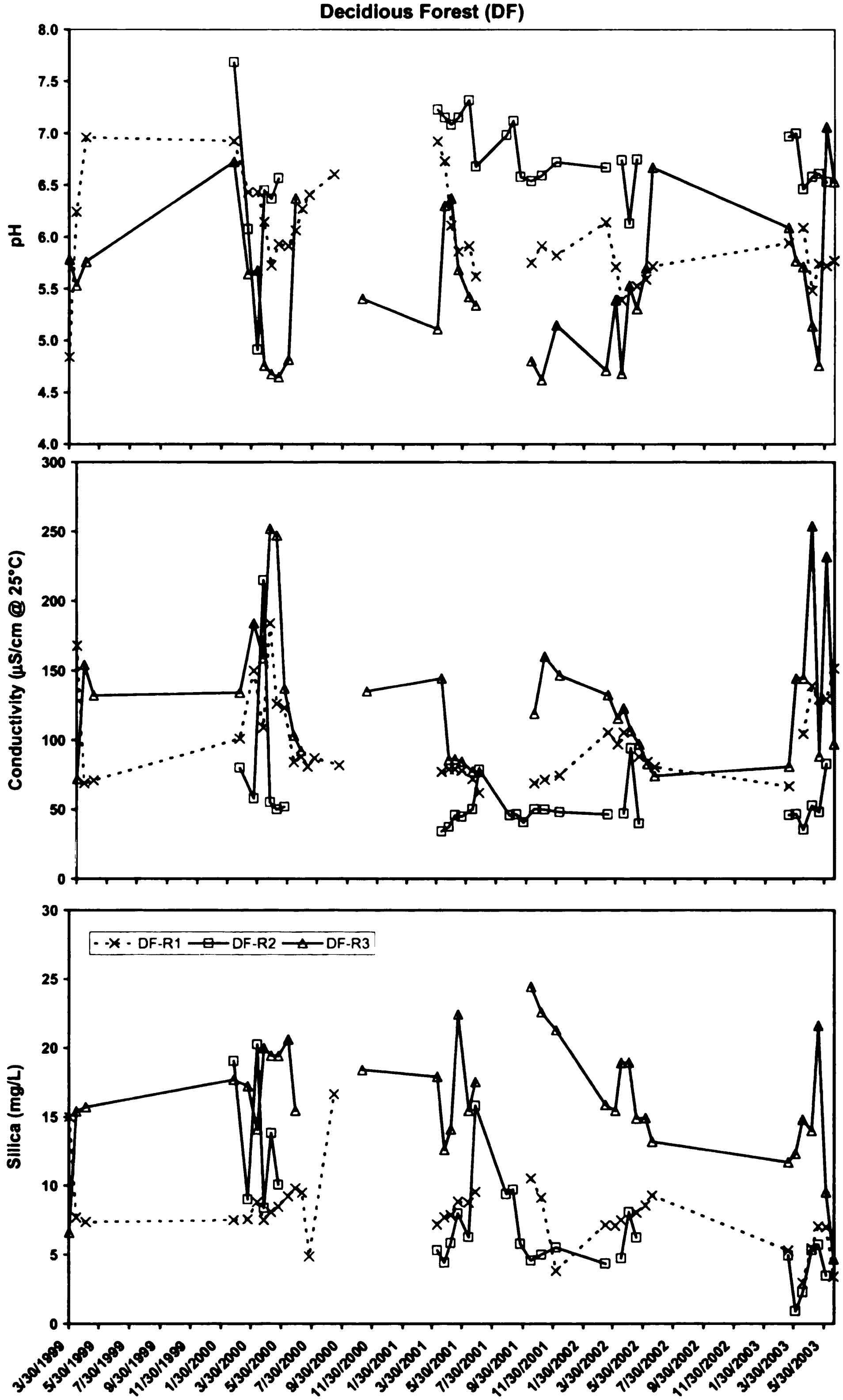


Figure 81: Deciduous Forest Time Series

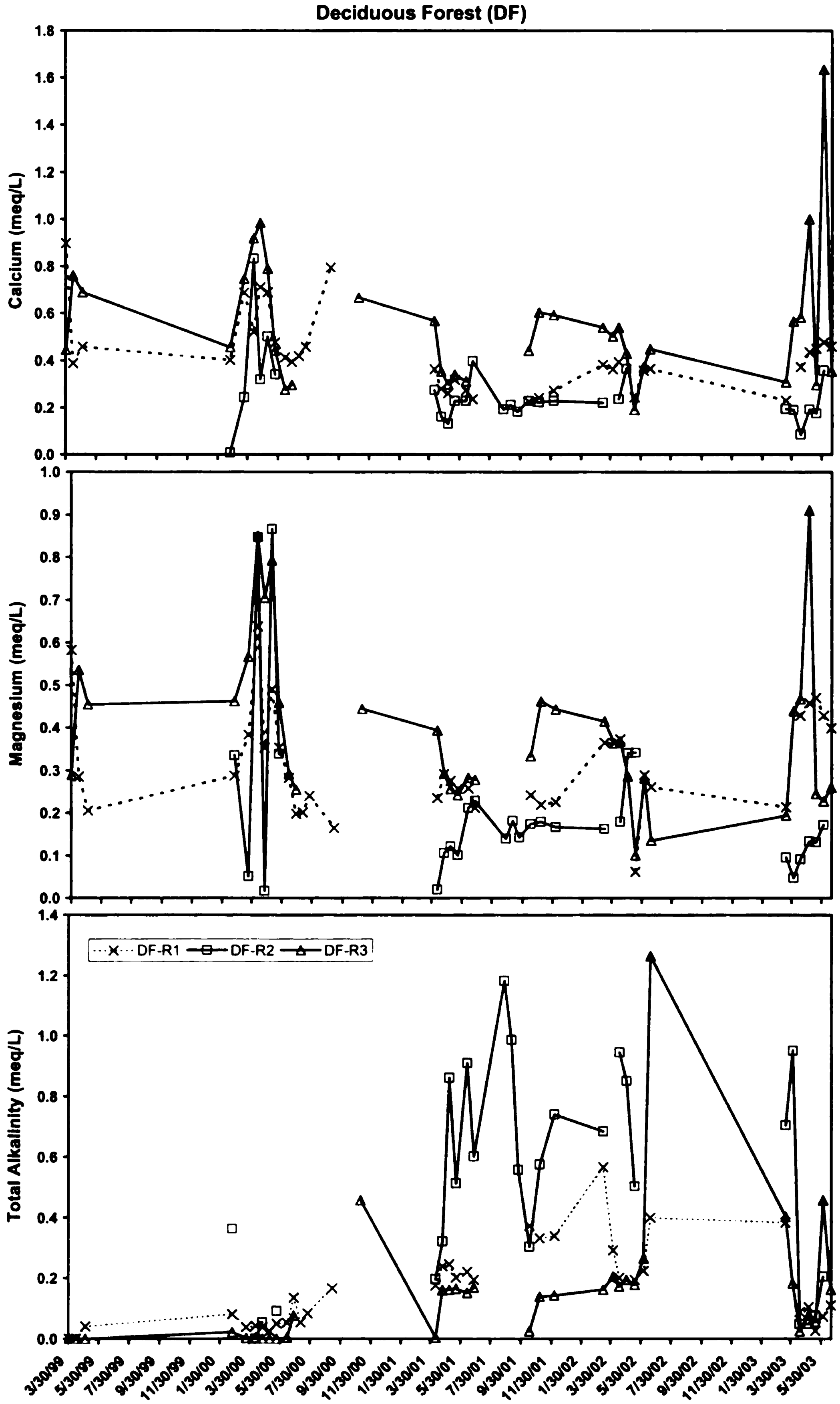


Figure 82: Deciduous Forest Time Series

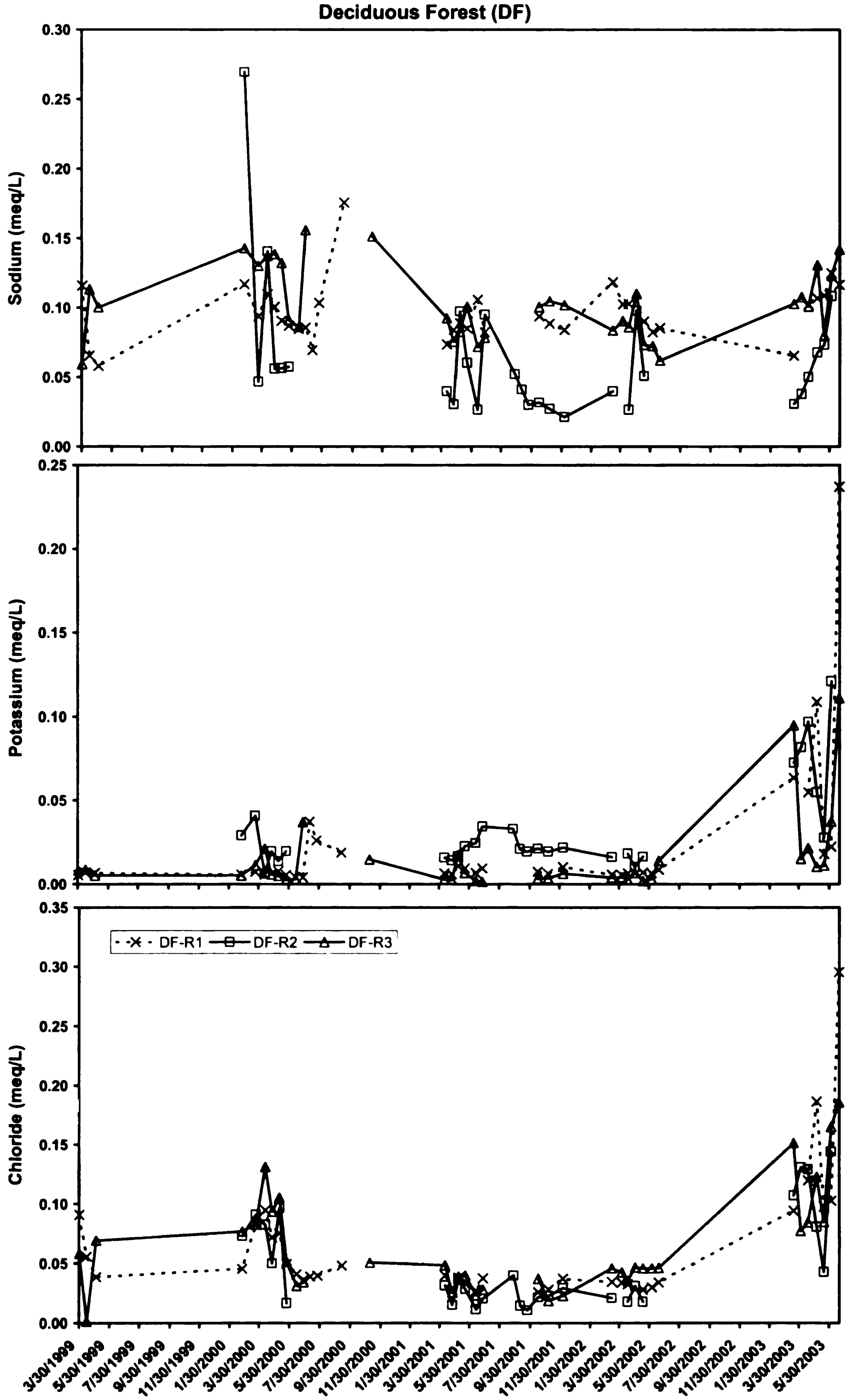


Figure 83: Deciduous Forest Time Series

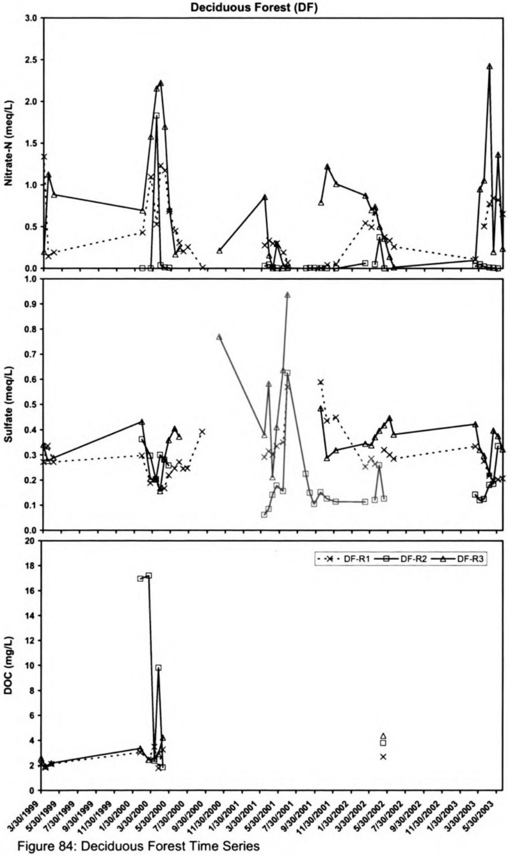


Figure 84: Deciduous Forest Time Series

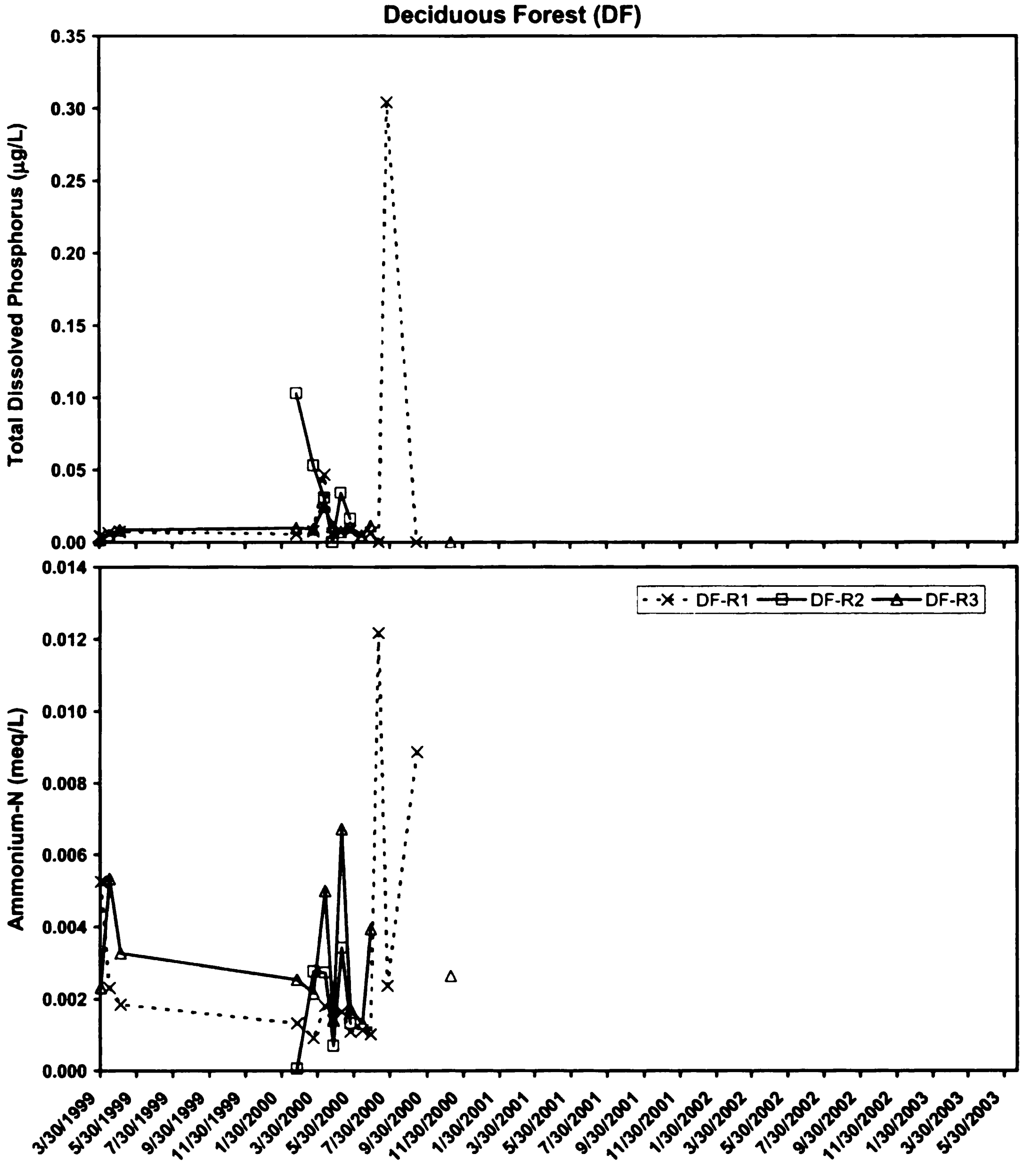


Figure 85: Deciduous Forest Time Series

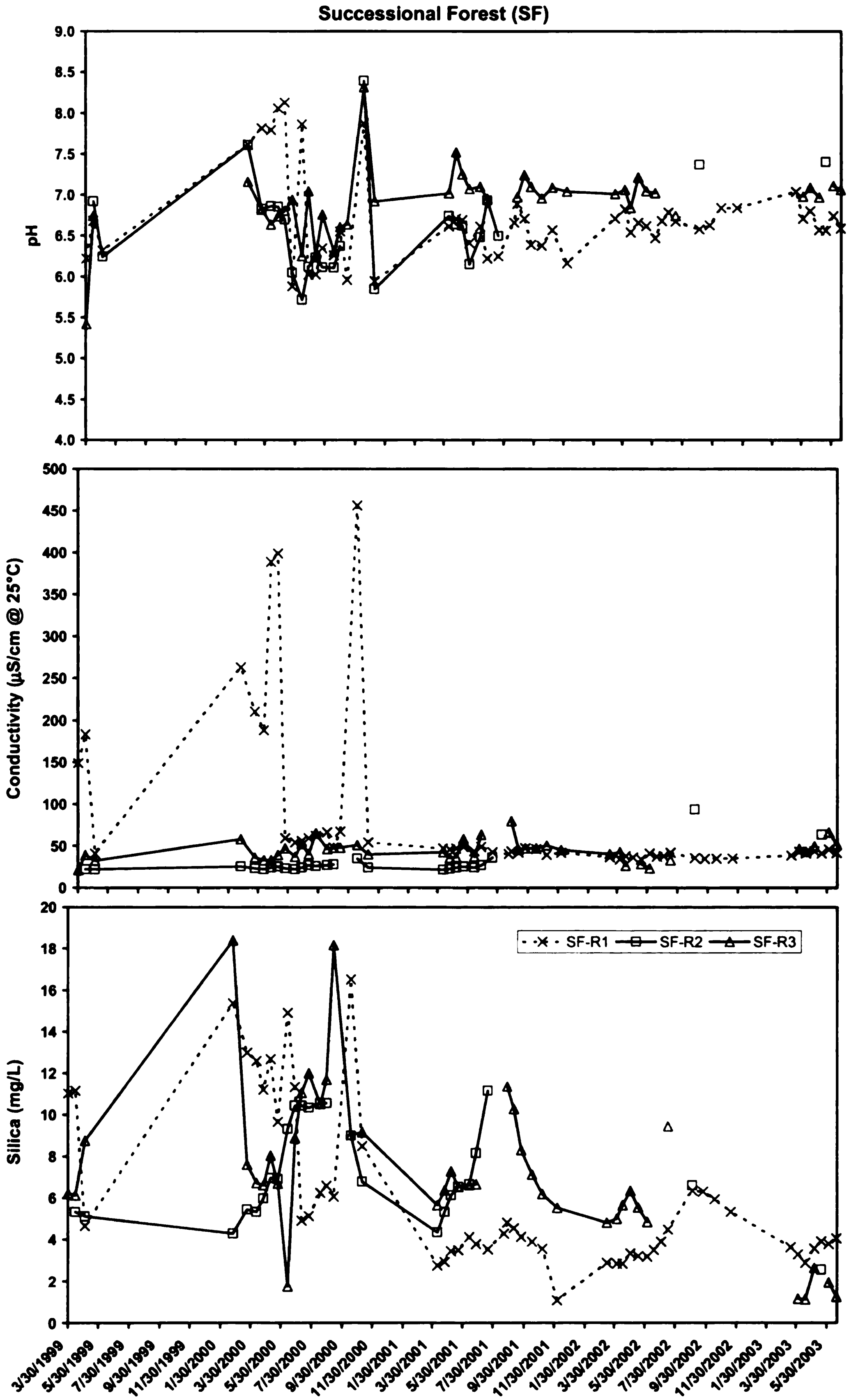


Figure 86: Successional Forest Time Series

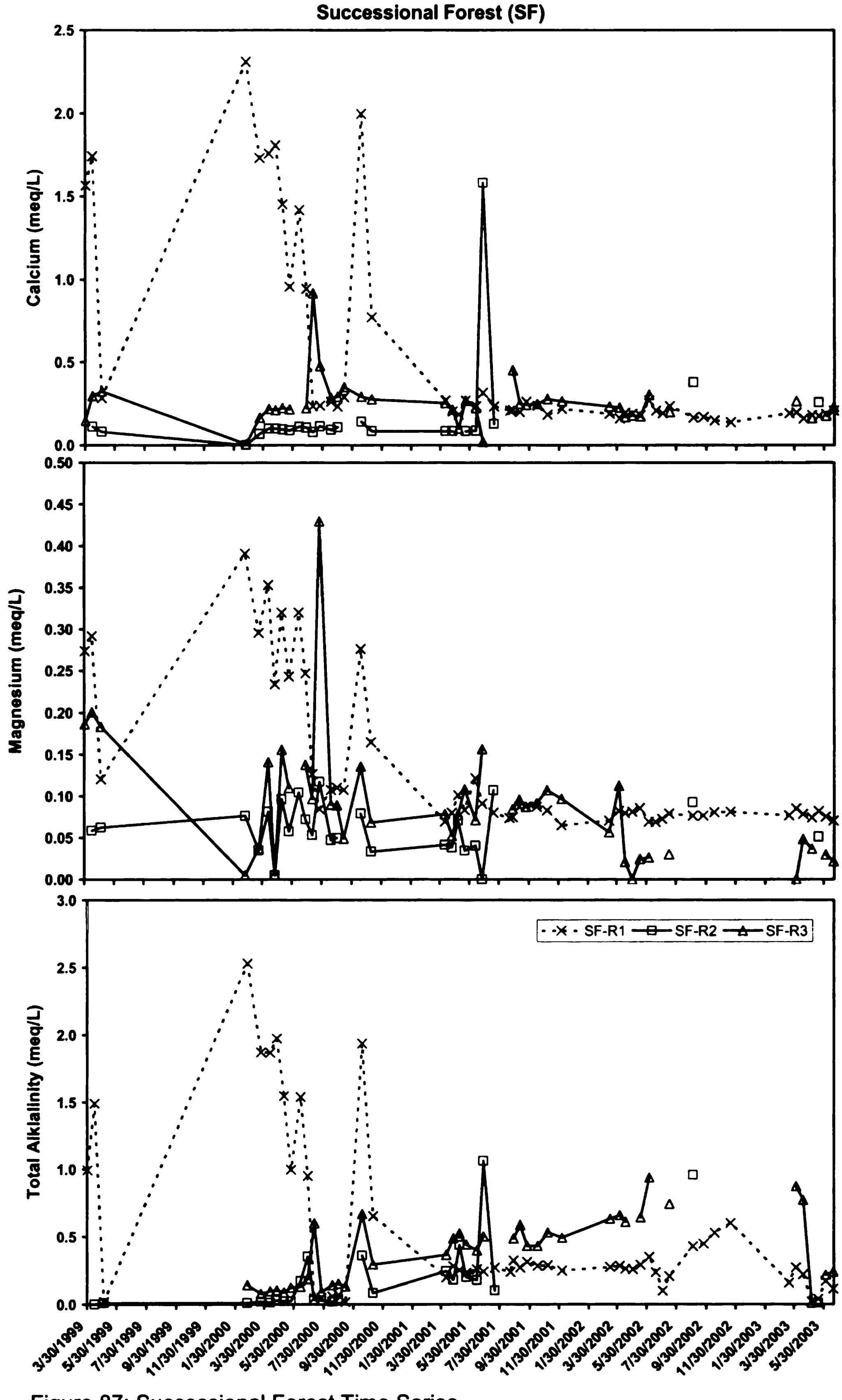


Figure 87: Successional Forest Time Series

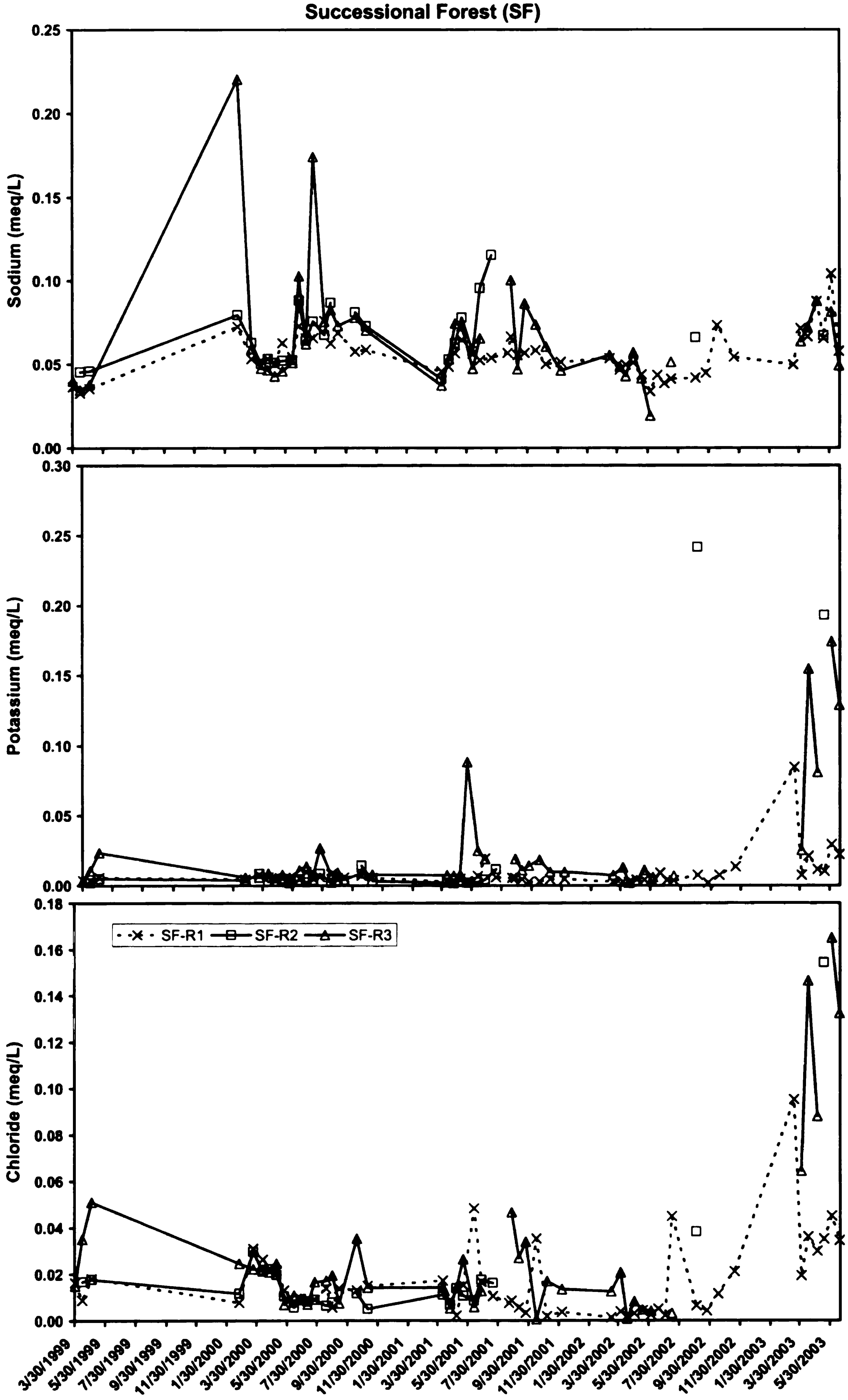


Figure 88: Successional Forest Time Series

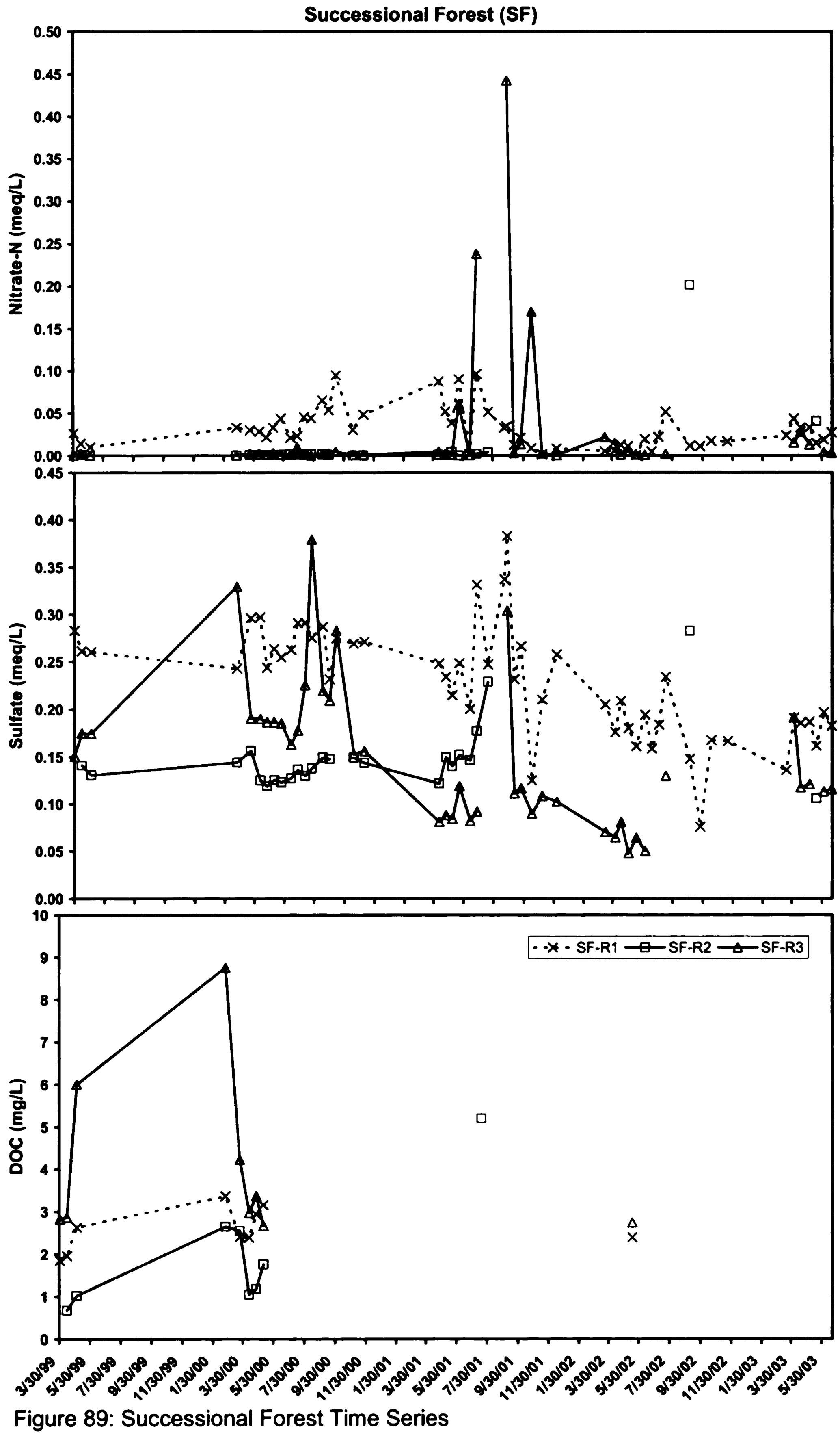


Figure 89: Successional Forest Time Series

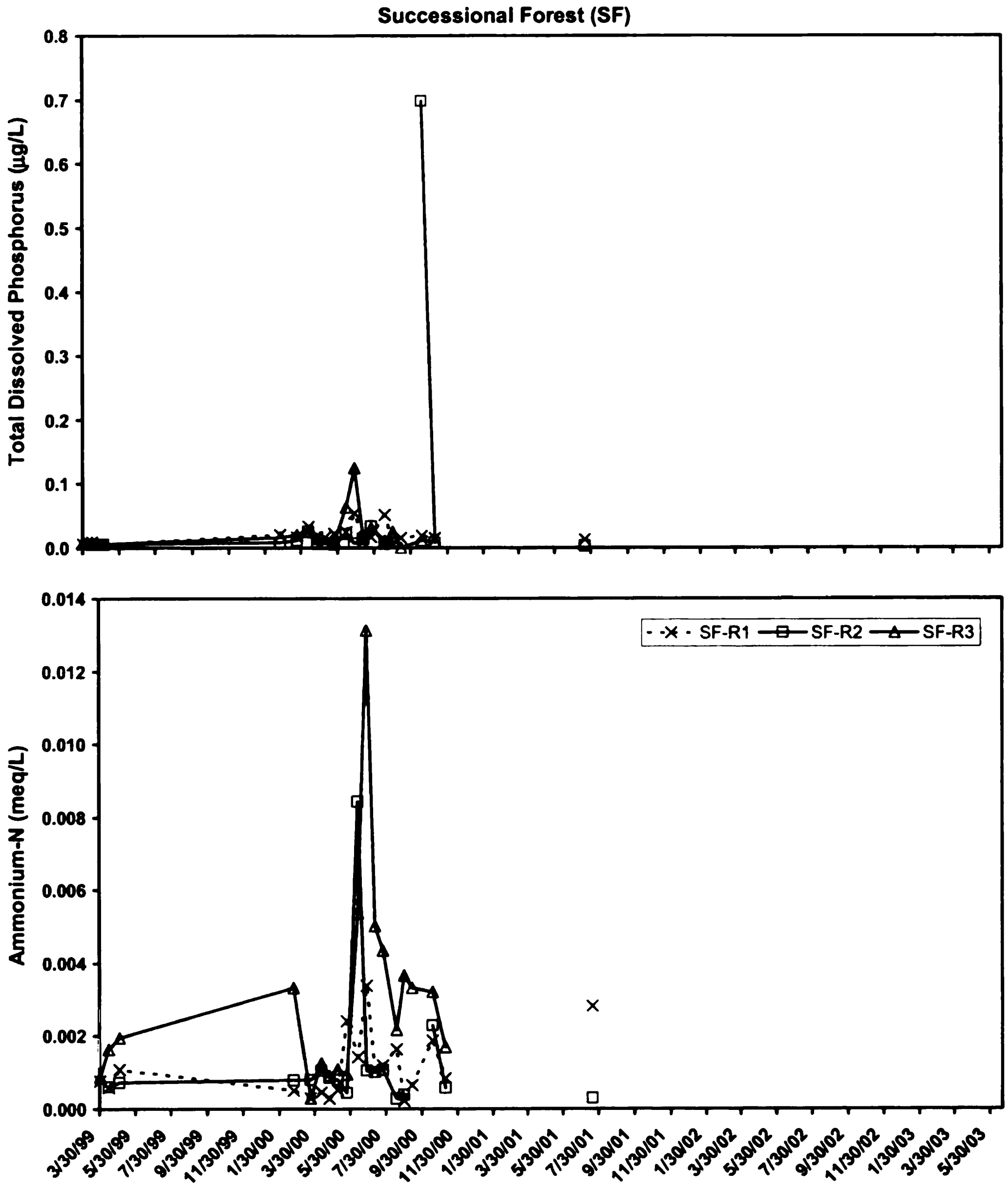


Figure 90: Successional Forest Time Series

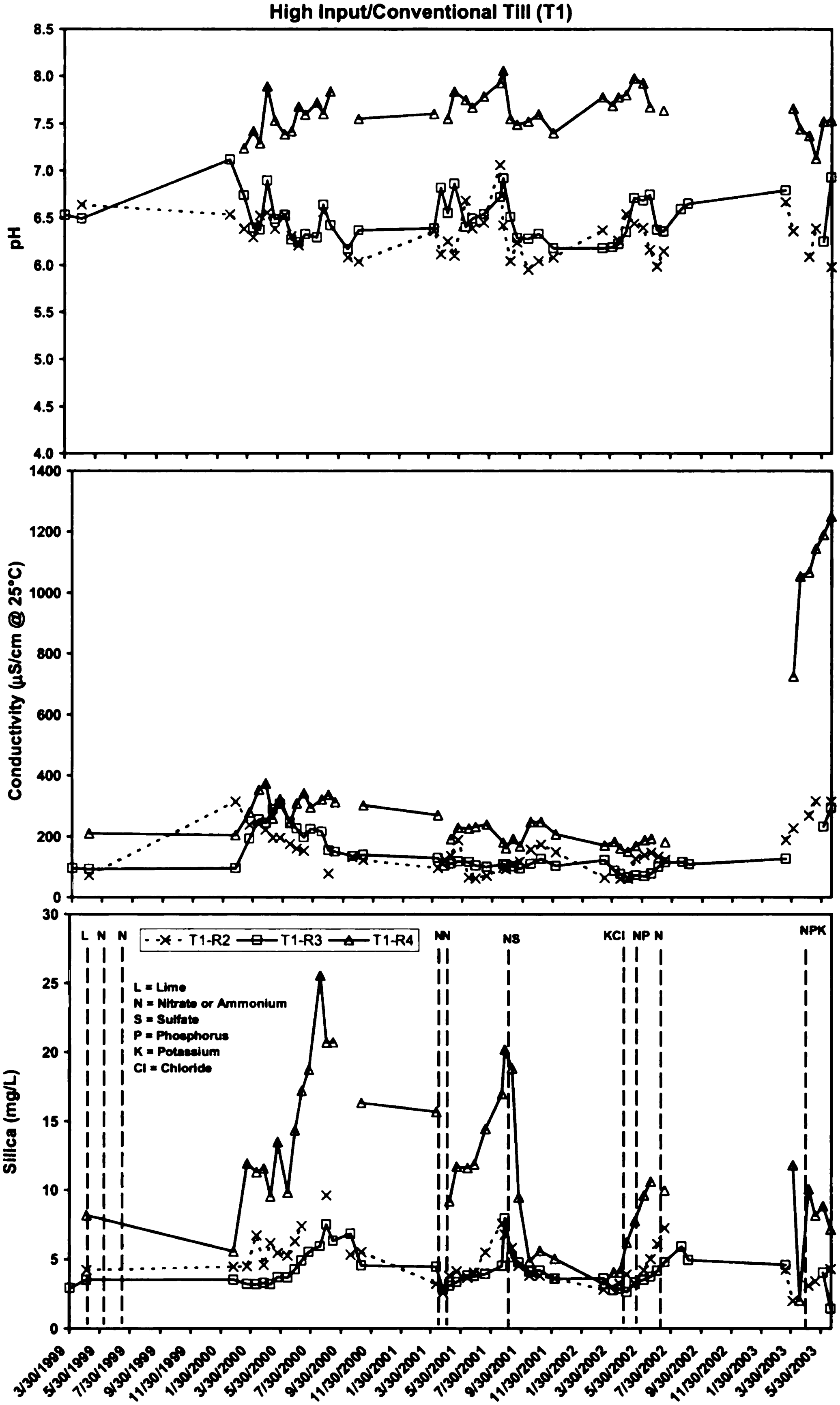


Figure 91: High Input//Conventional Till (T1) Time Series

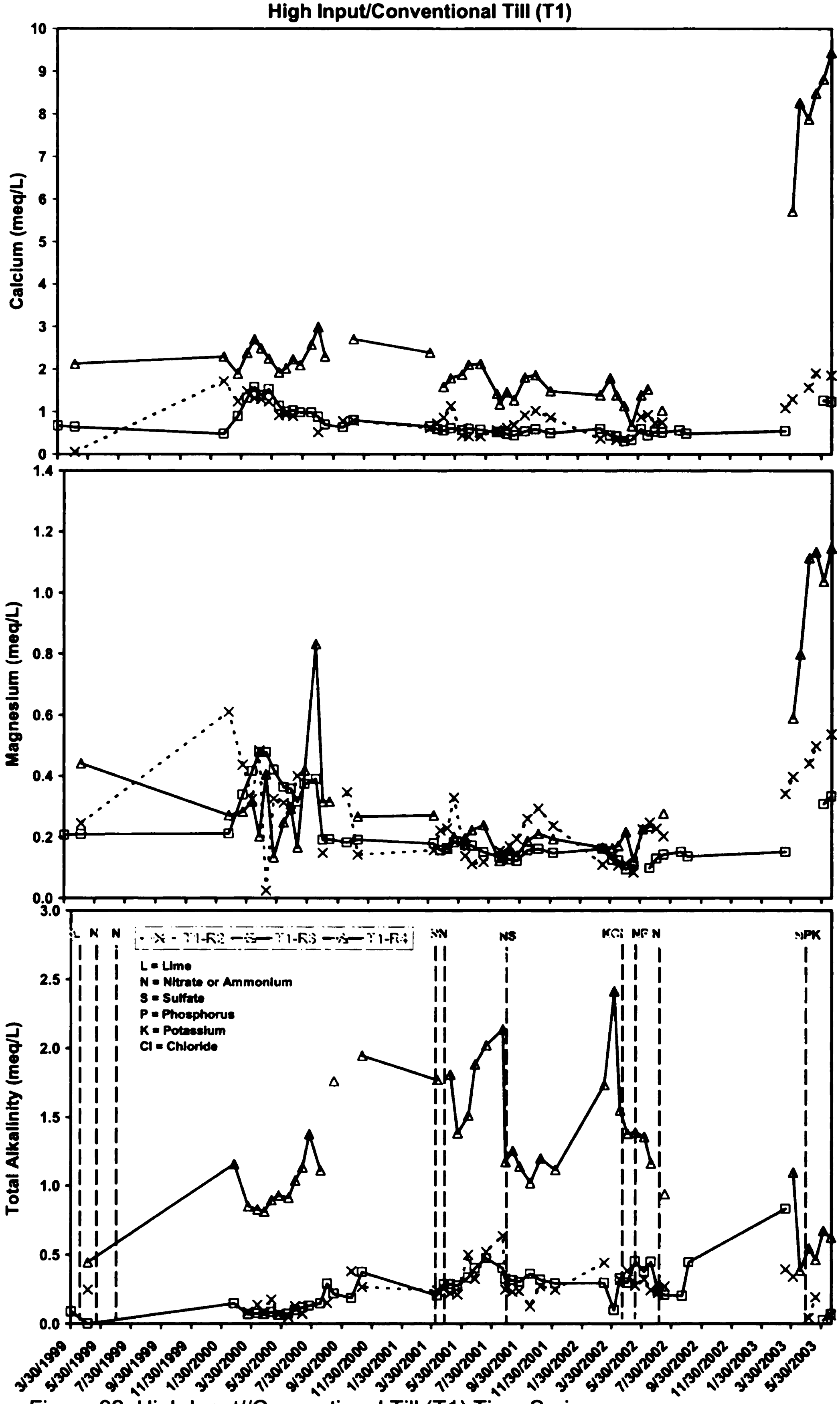


Figure 92: High Input//Conventional Till (T1) Time Series

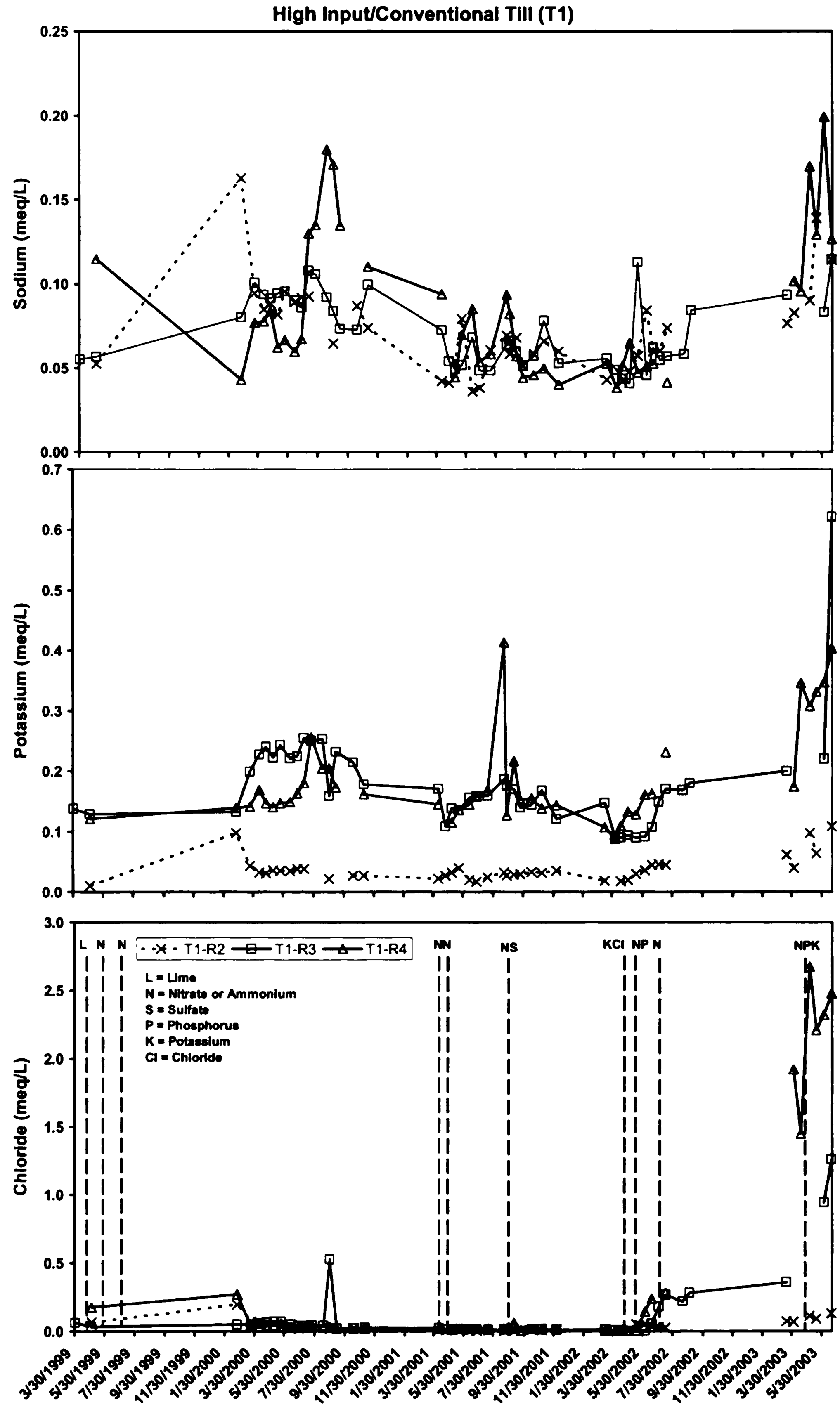


Figure 93: High Input//Conventional Till (T1) Time Series

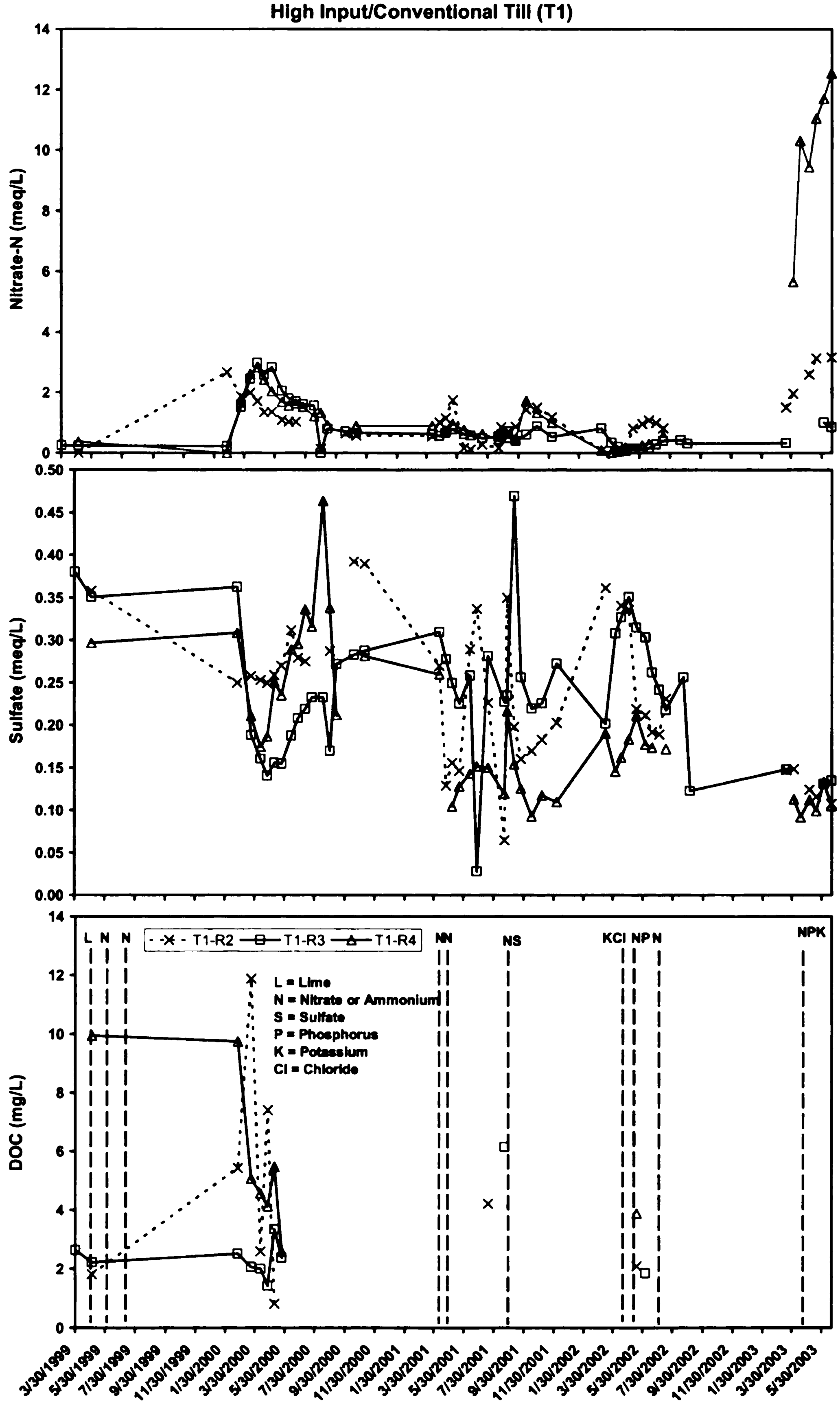


Figure 94: High Input//Conventional Till (T1) Time Series

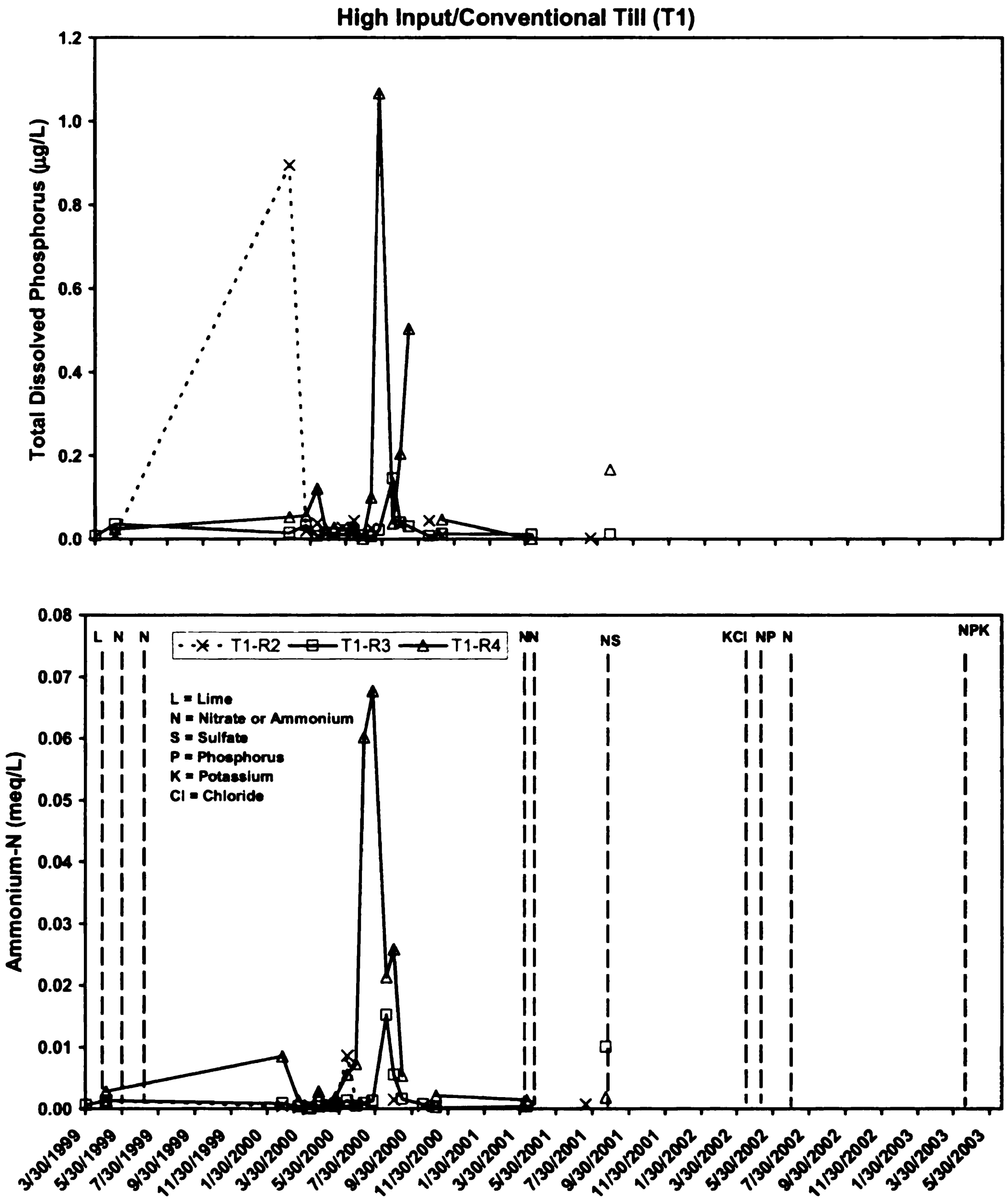


Figure 95: High Input//Conventional Till (T1) Time Series

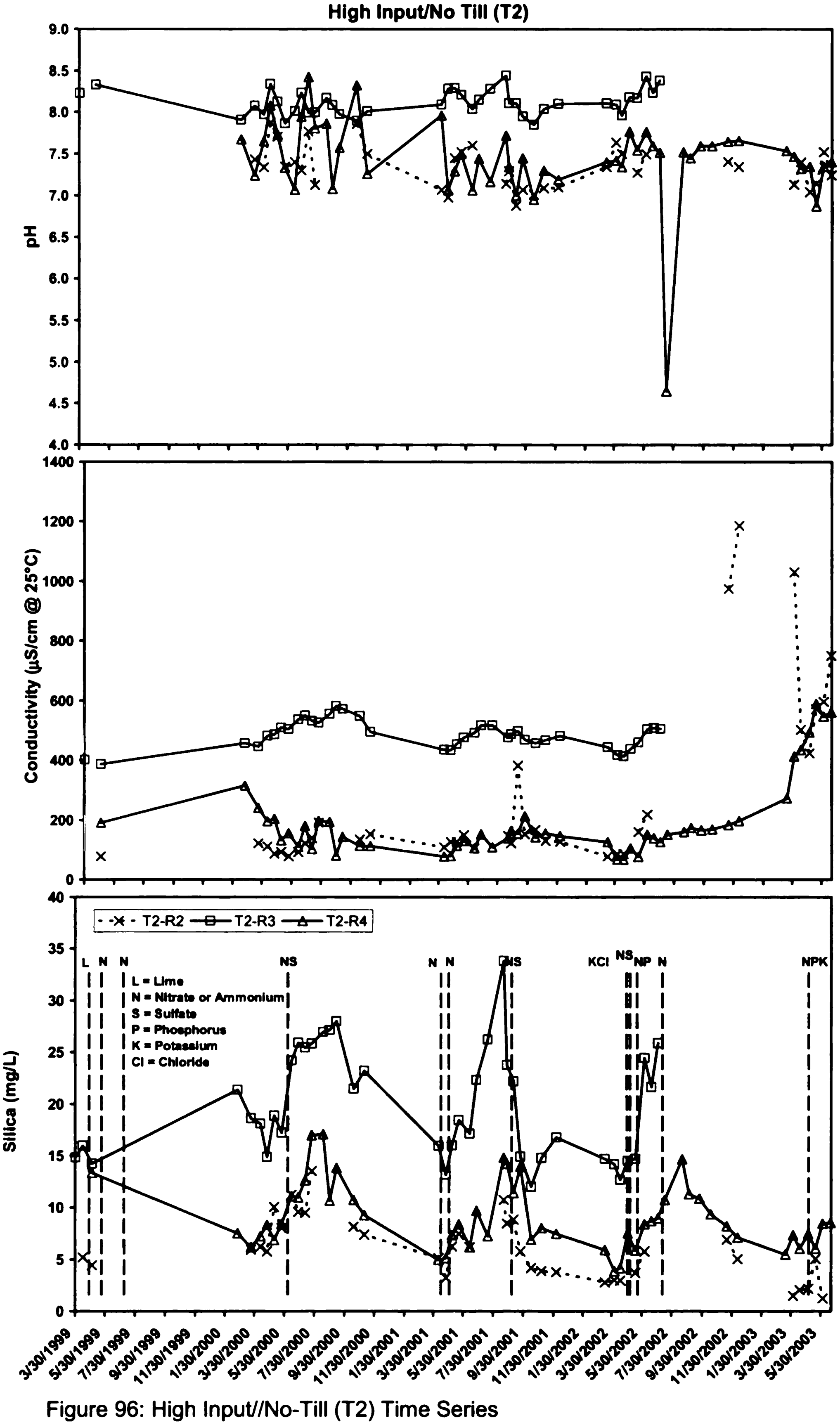


Figure 96: High Input//No-Till (T2) Time Series

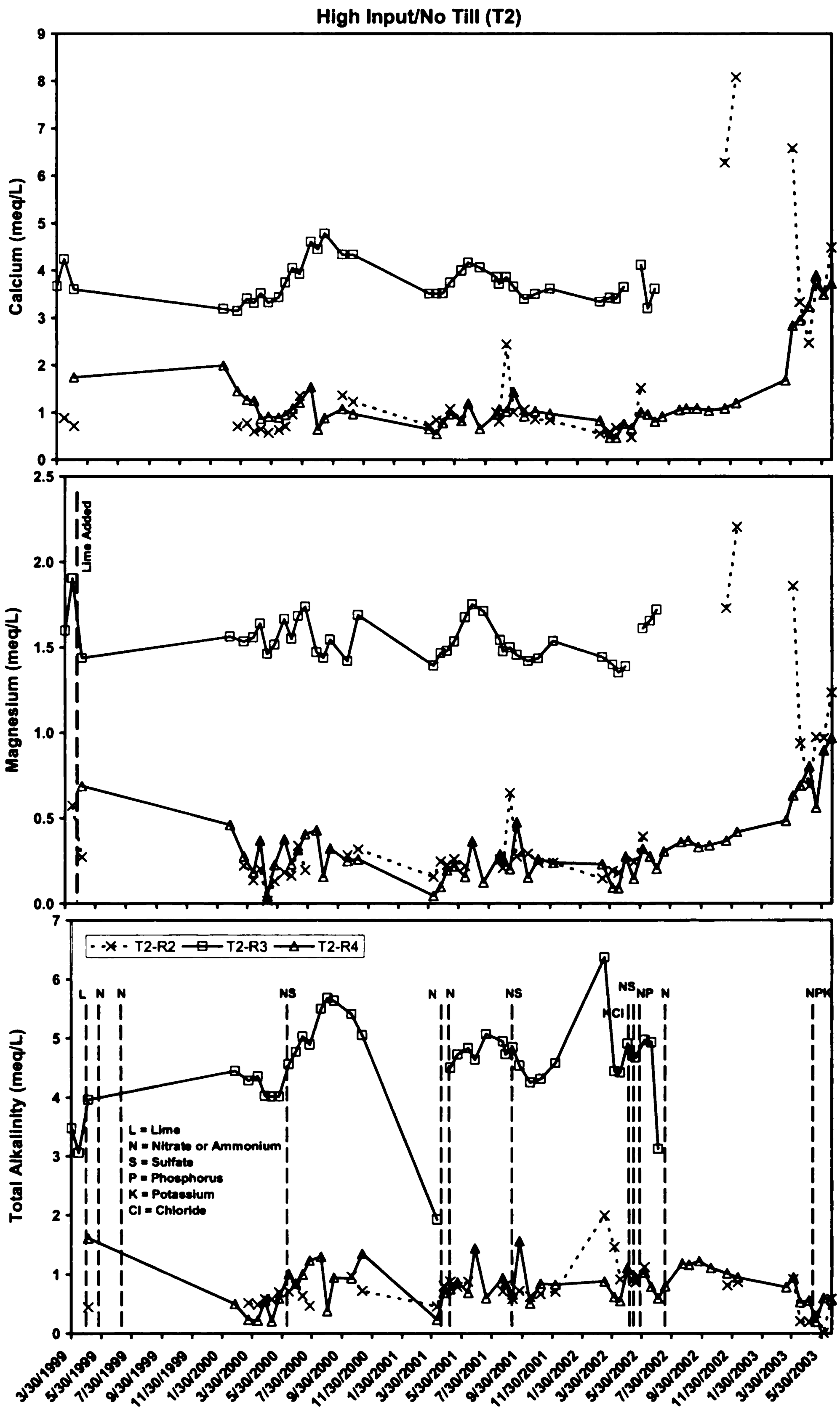


Figure 97: High Input//No-Till (T2) Time Series

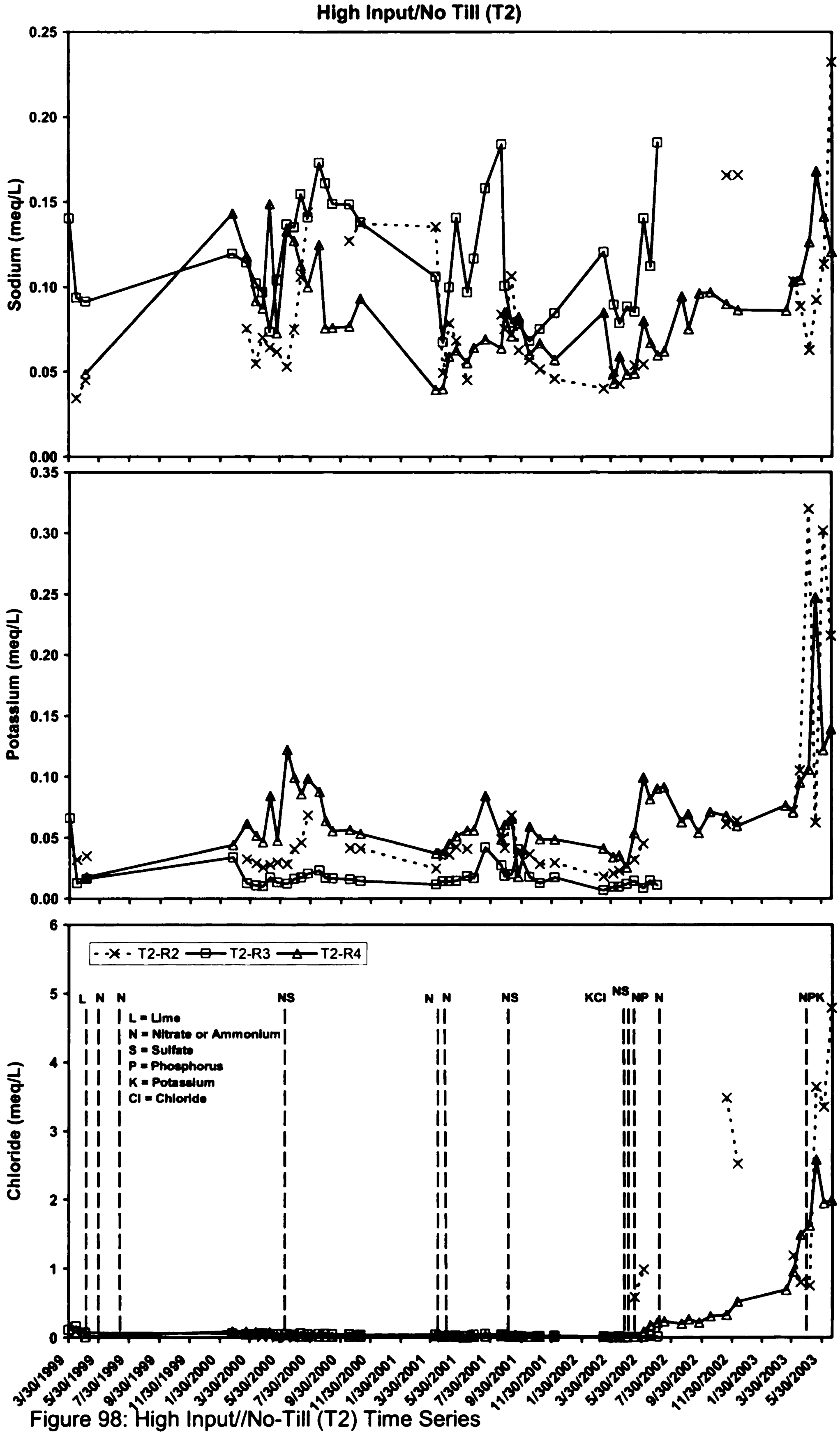


Figure 98: High Input//No-Till (T2) Time Series

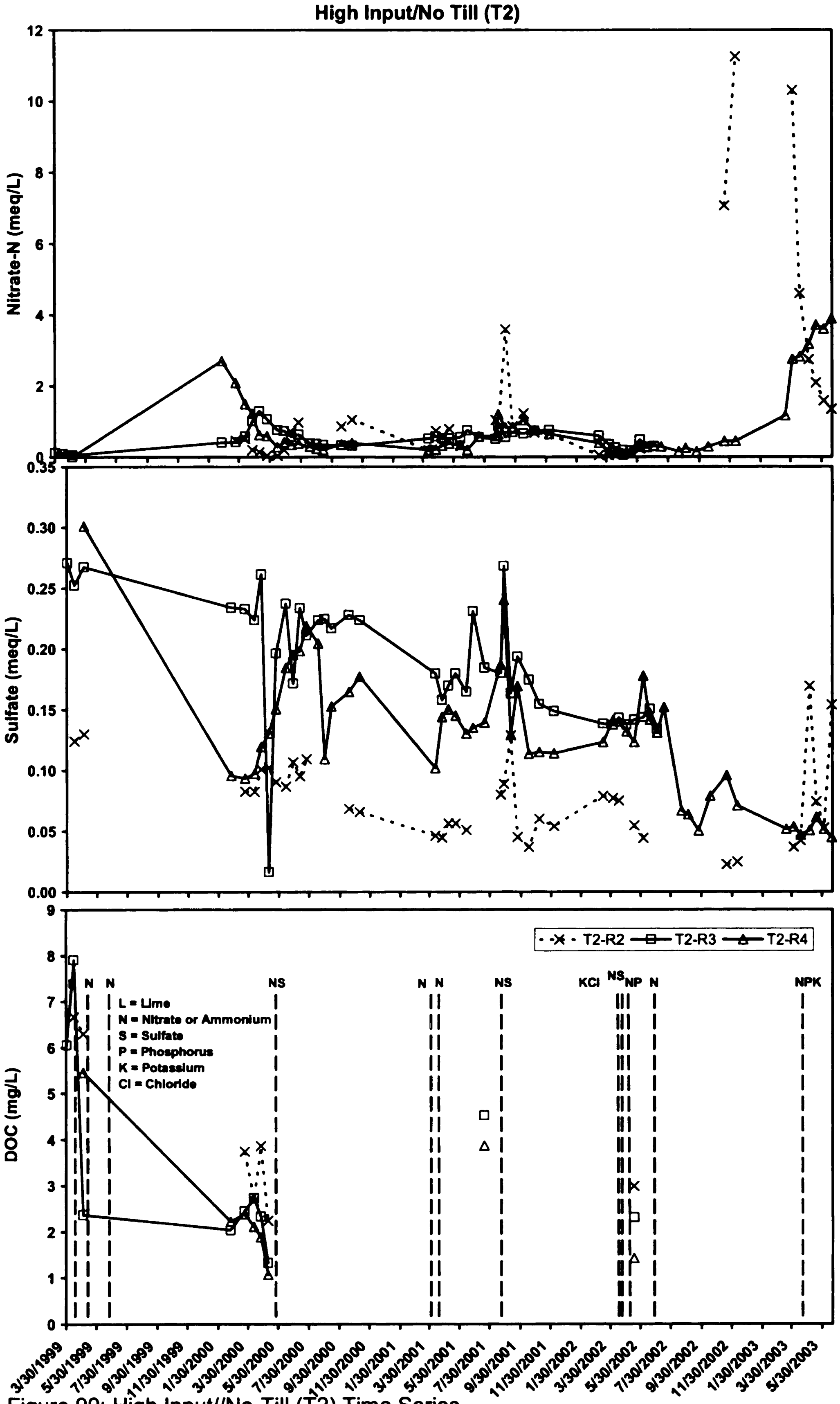


Figure 99: High Input//No-Till (T2) Time Series

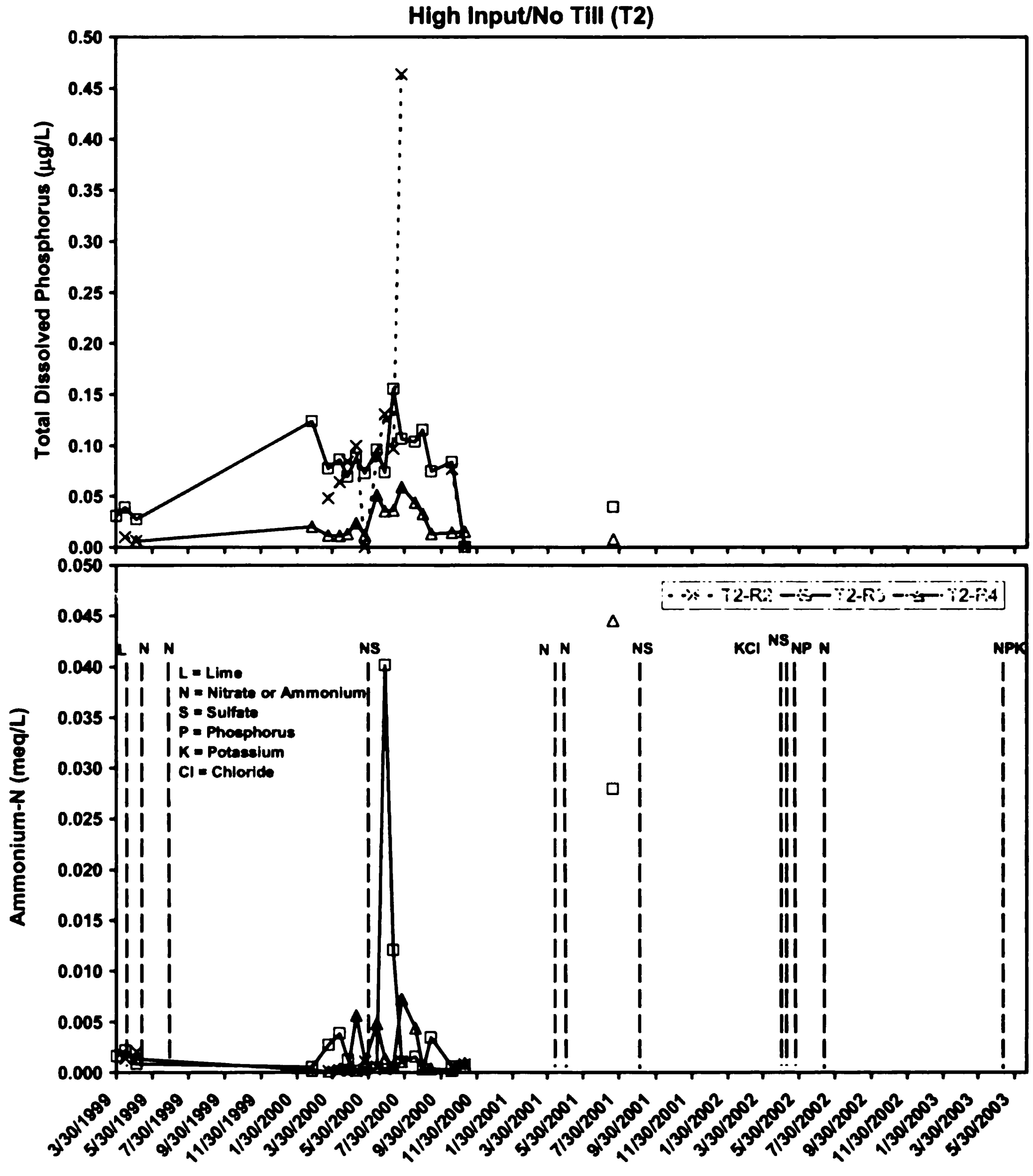


Figure 100: High Input//No-Till (T2) Time Series

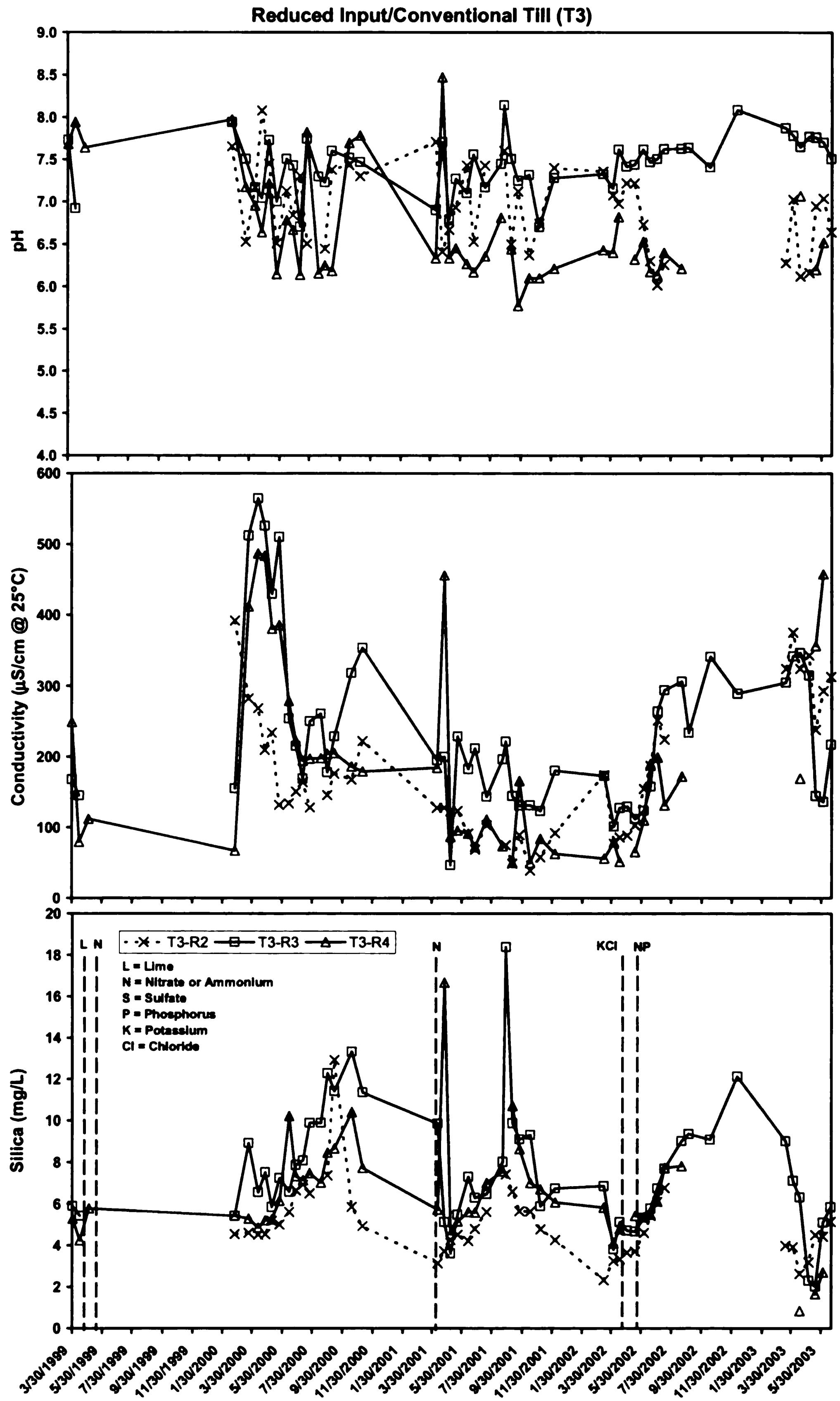


Figure 101: Reduced Input//Conventional Till (T3) Time Series

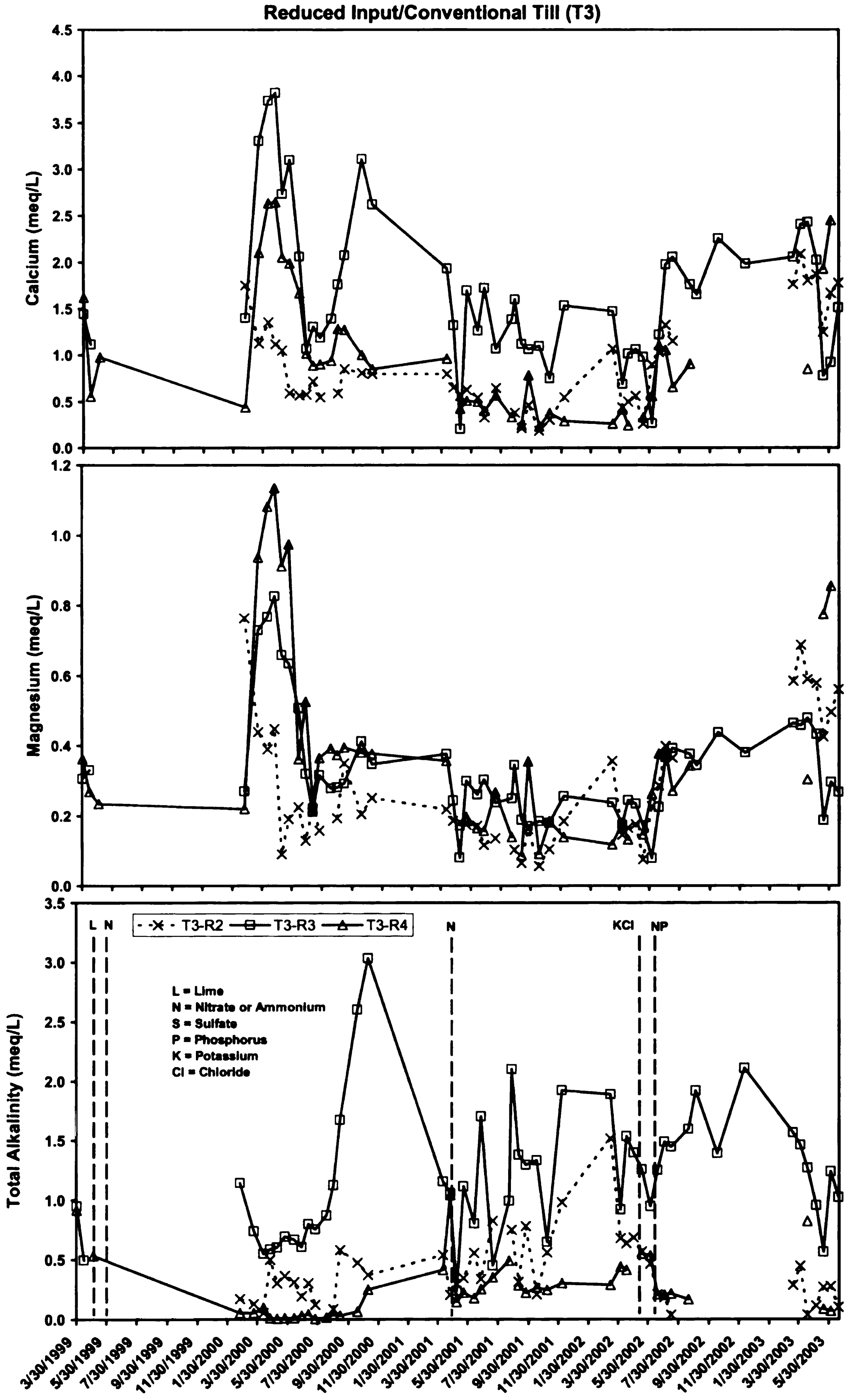


Figure 102: Reduced Input//Conventional Till (T3) Time Series

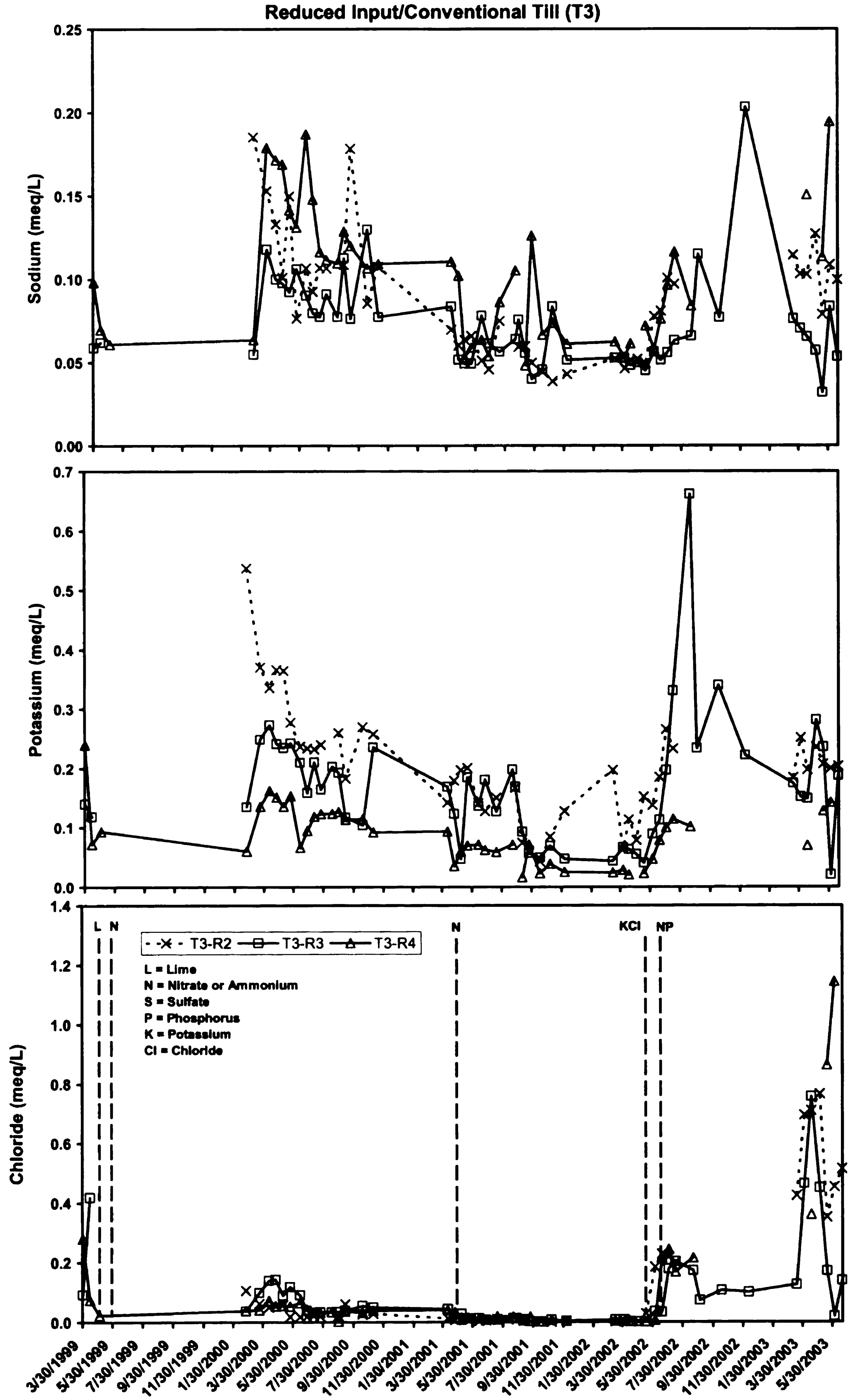


Figure 103: Reduced Input//Conventional Till (T3) Time Series

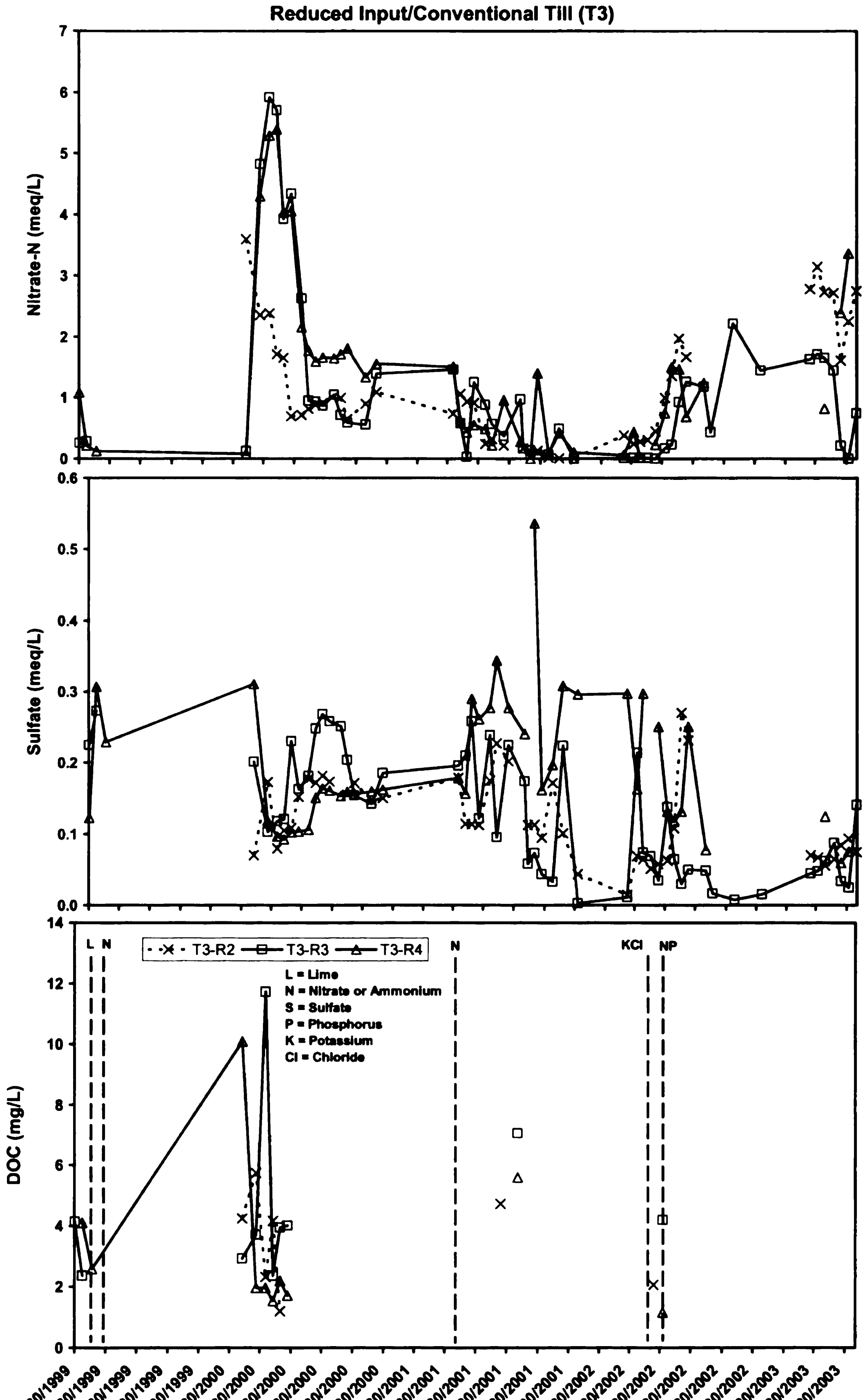


Figure 104: Reduced Input//Conventional Till (T3) Time Series

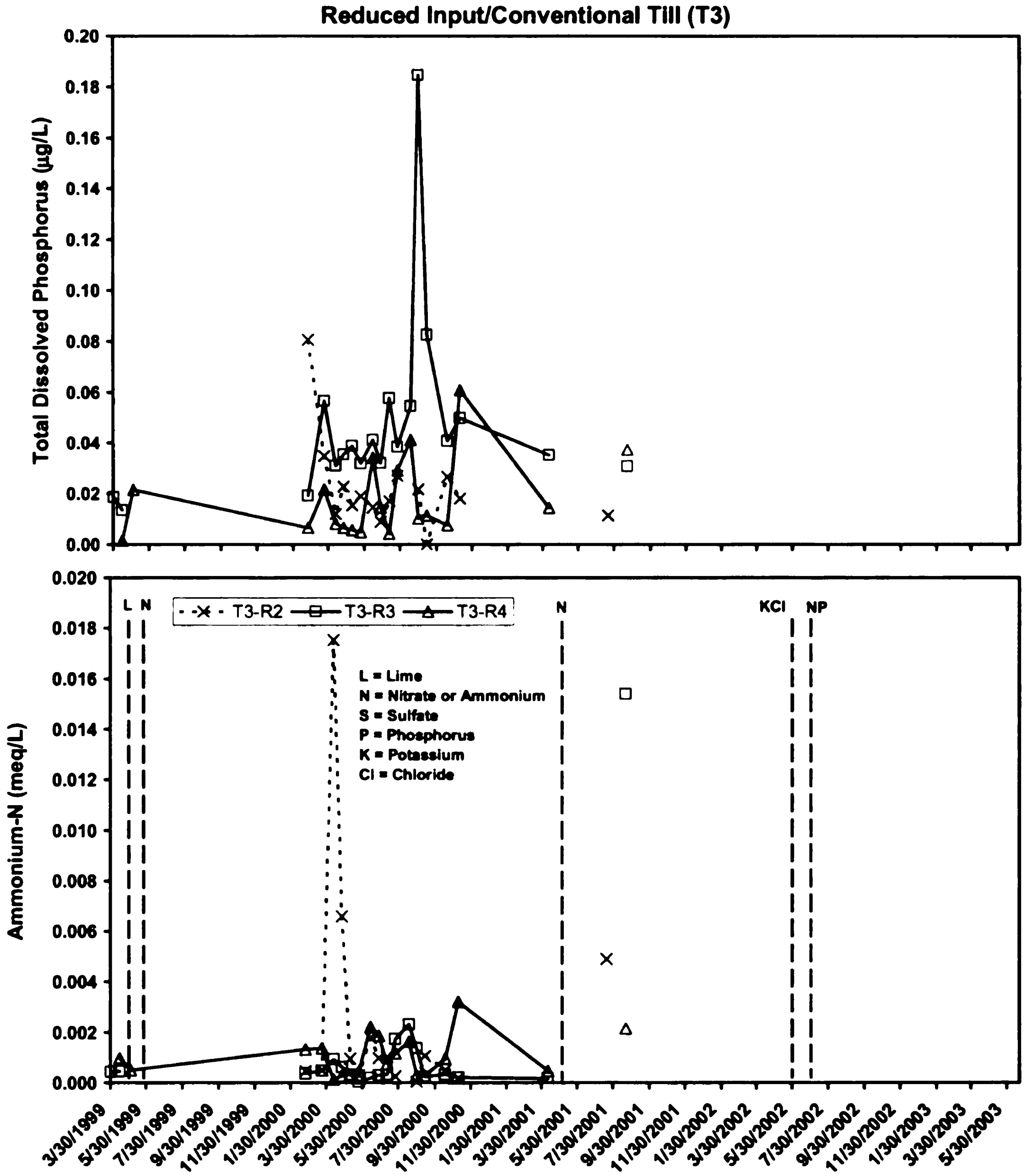


Figure 105: Reduced Input//Conventional Till (T3) Time Series

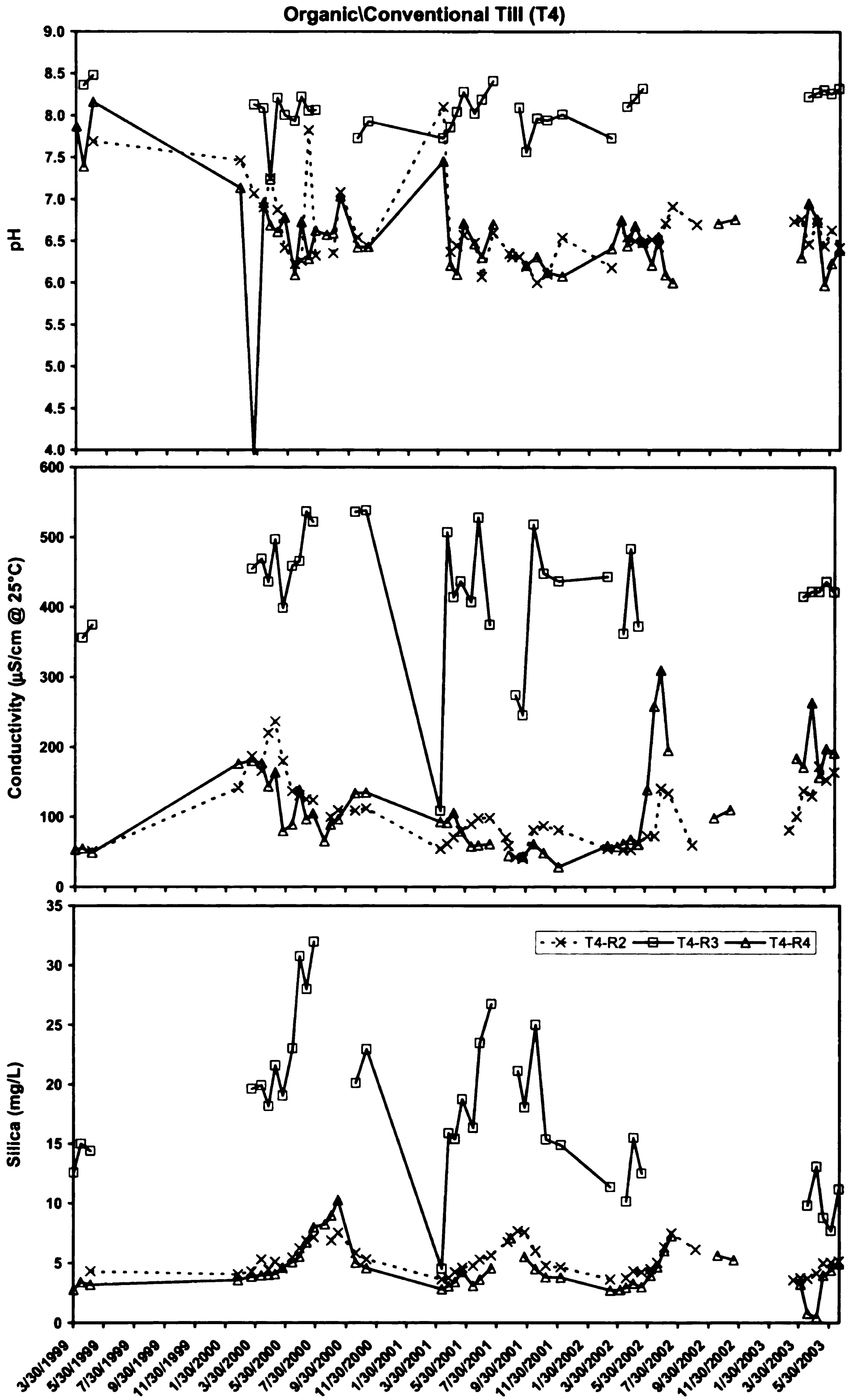


Figure 106: Organic (Zero Input)//Conventional Till (T4) Time Series

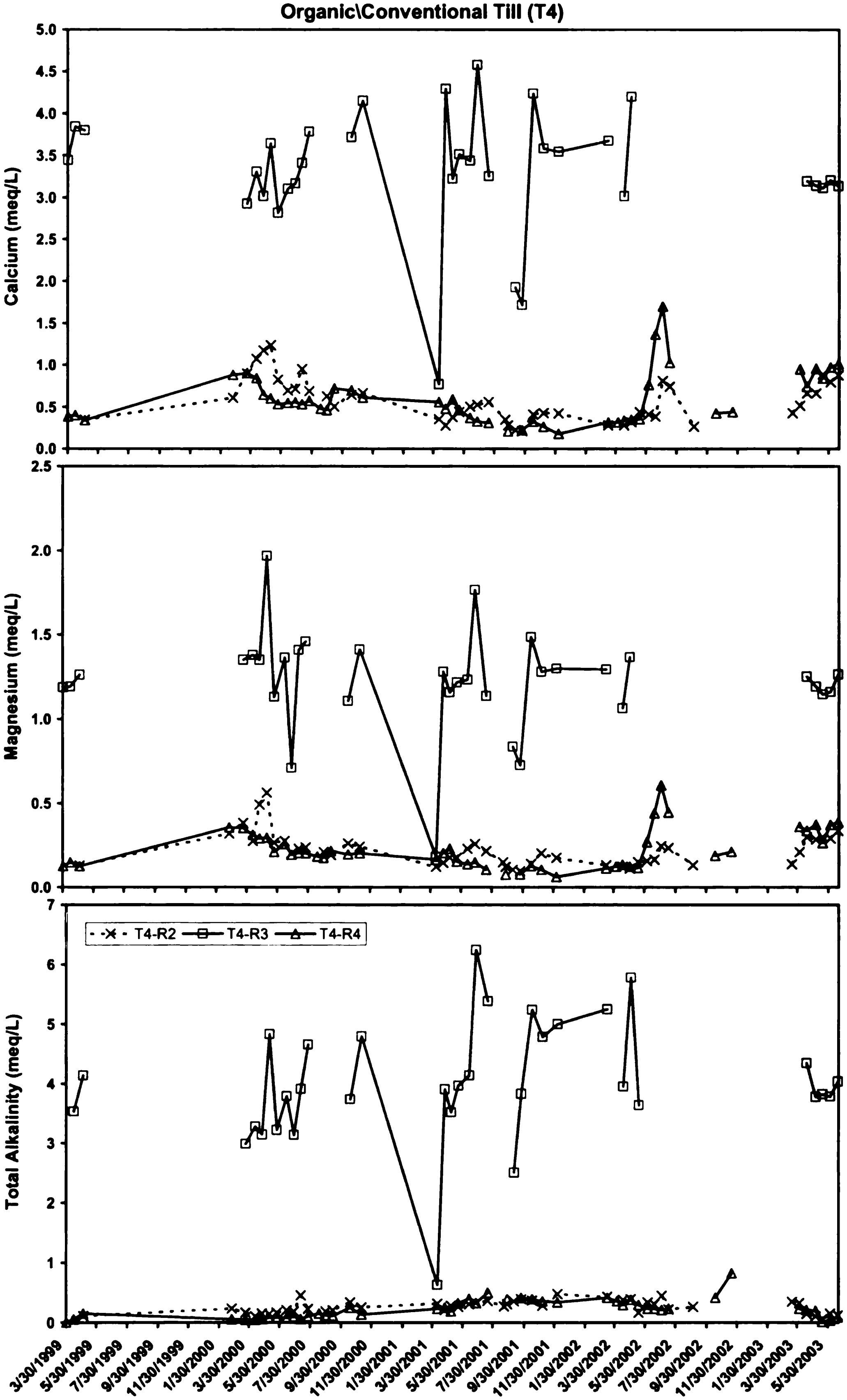


Figure 107: Organic (Zero Input)//Conventional Till (T4) Time Series

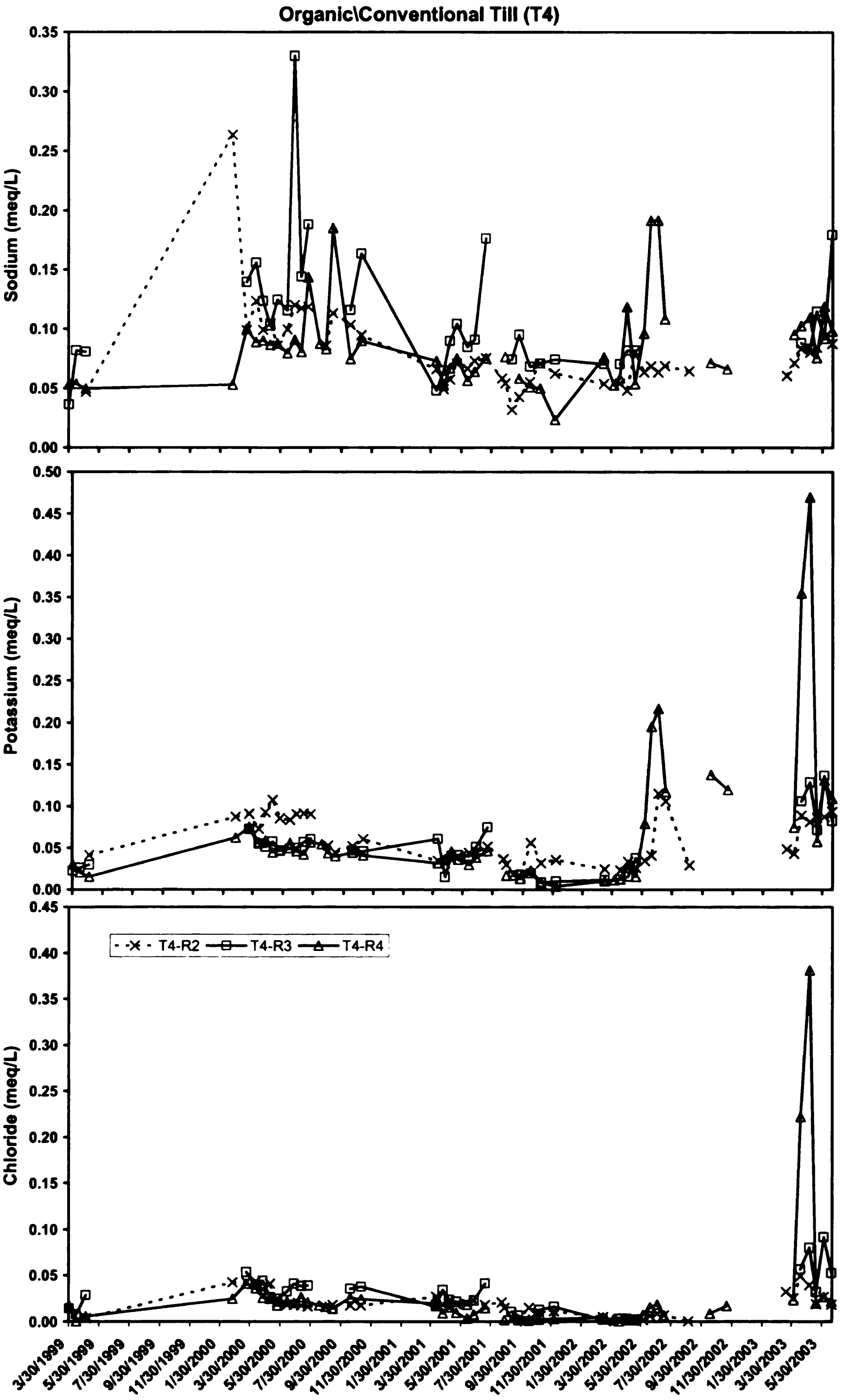


Figure 108: Organic (Zero Input)//Conventional Till (T4) Time Series

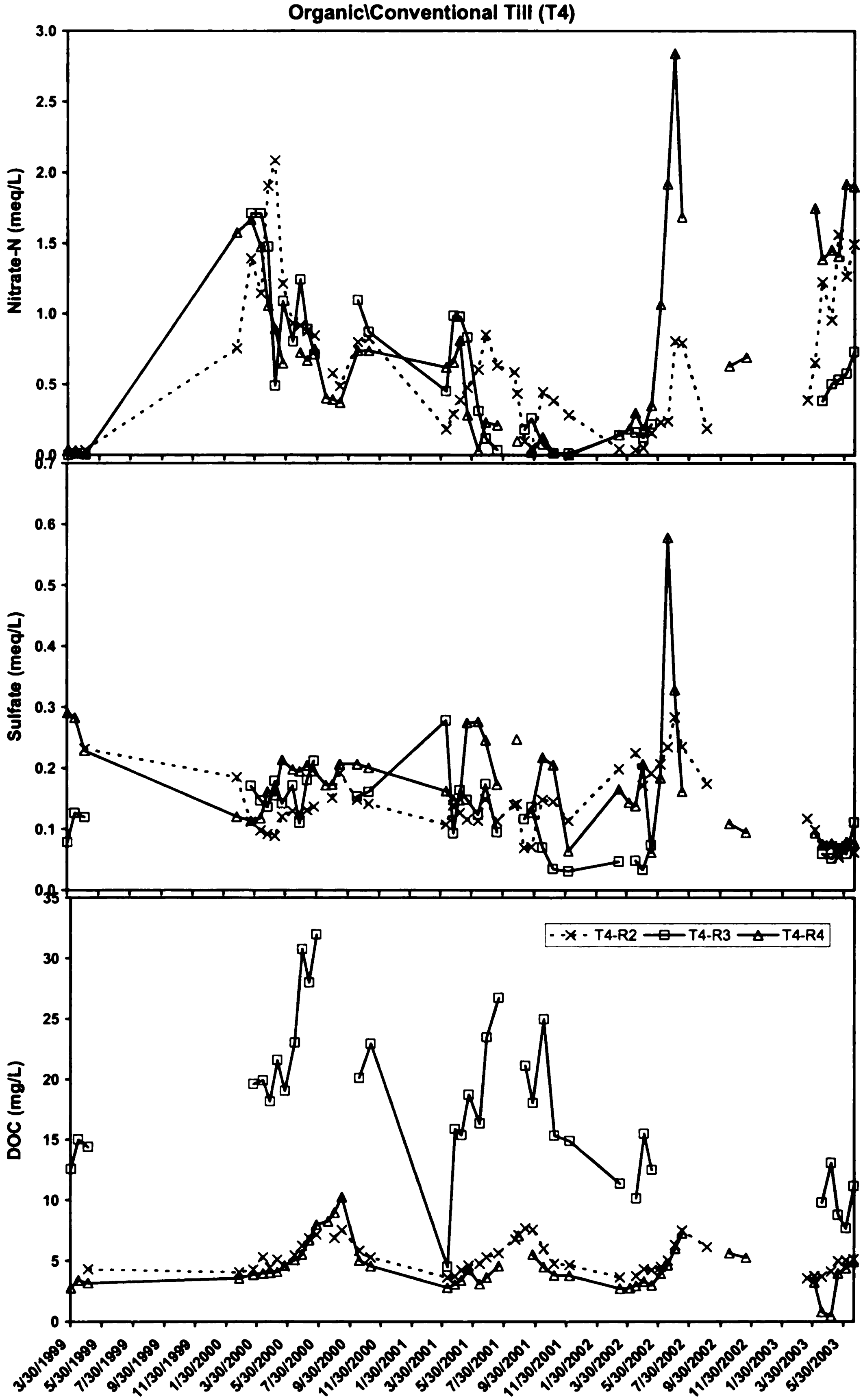


Figure 109: Organic (Zero Input)//Conventional Till (T4) Time Series

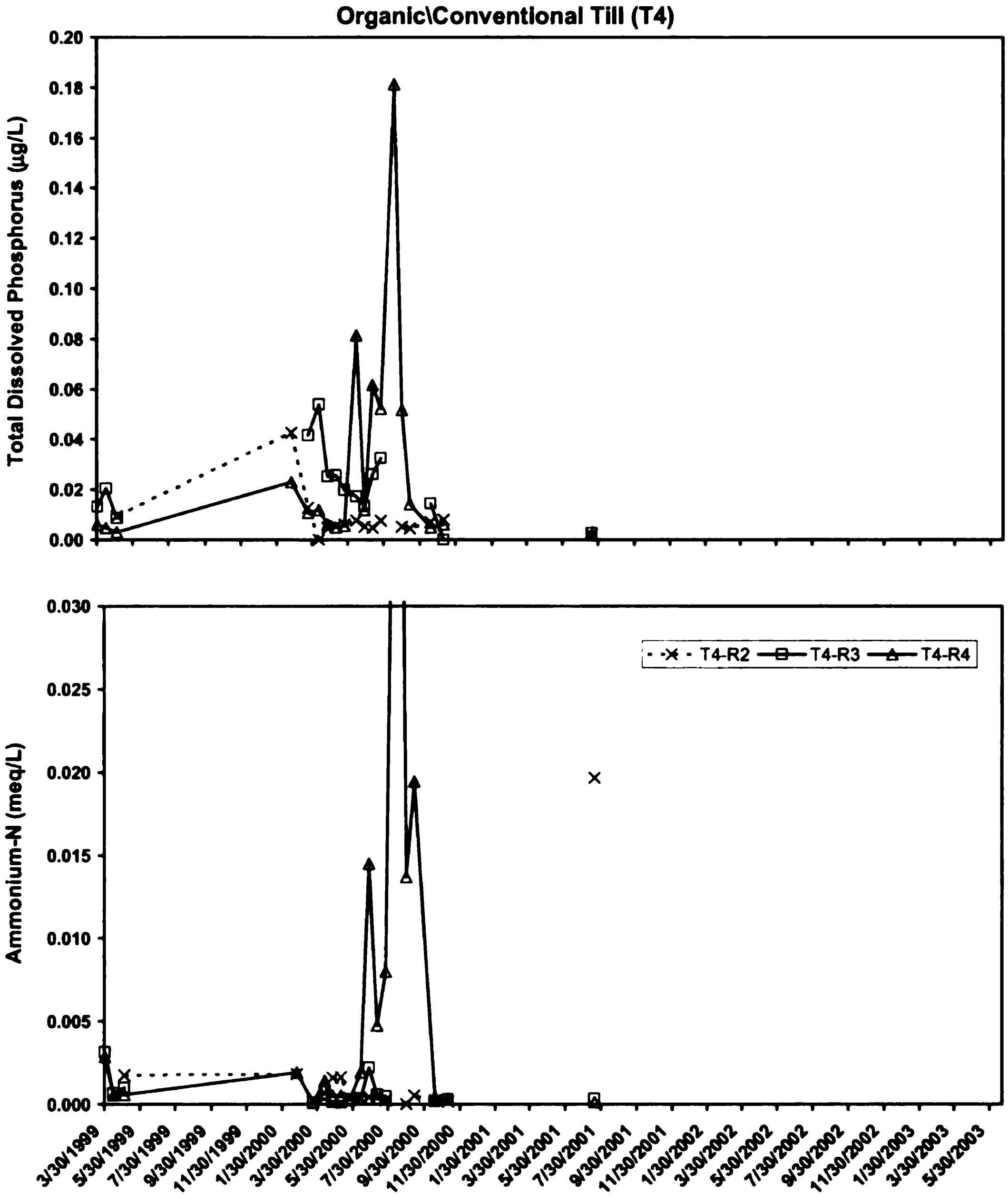


Figure 110: Organic (Zero Input)//Conventional Till (T4) Time Series

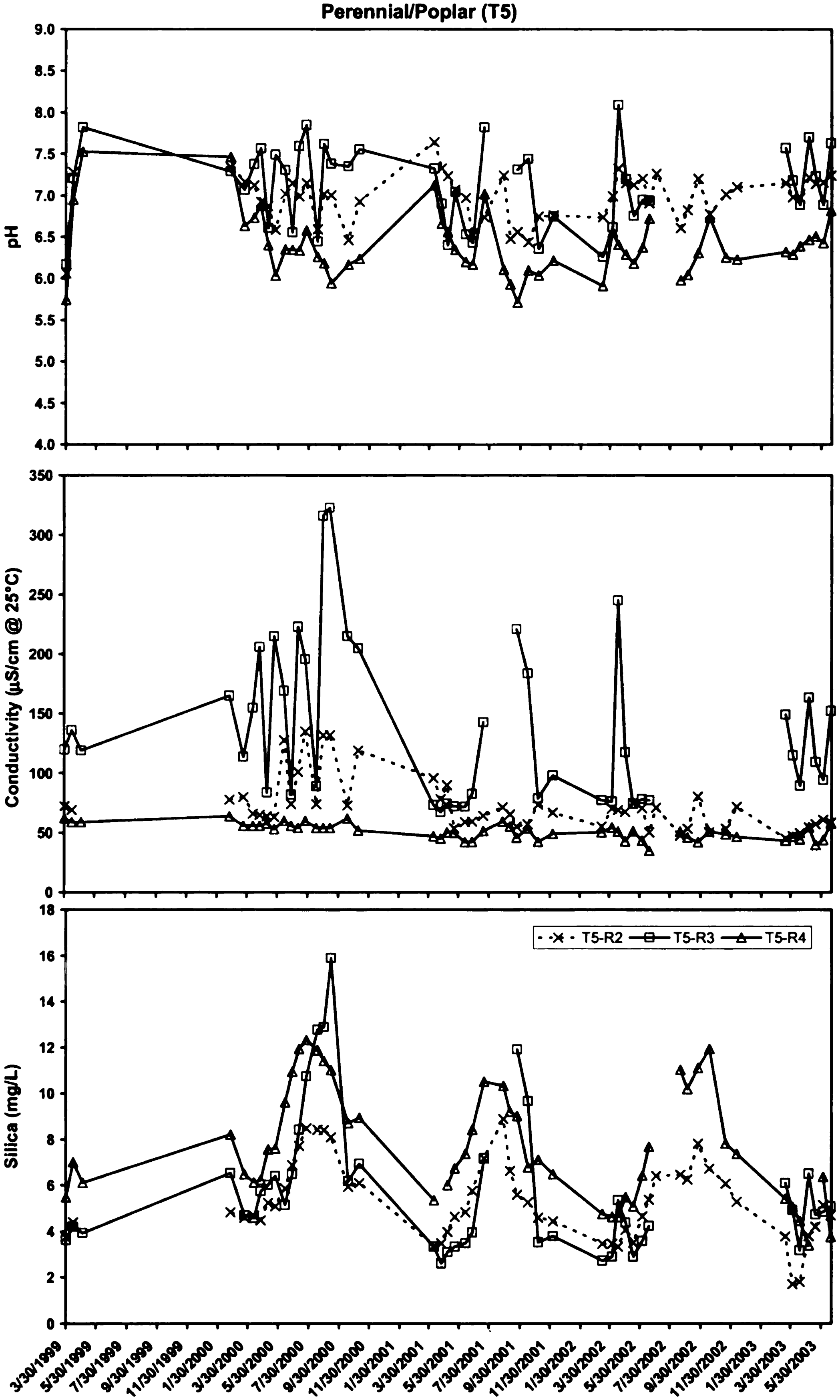


Figure 111: Perennial/Poplar (T5) Time Series

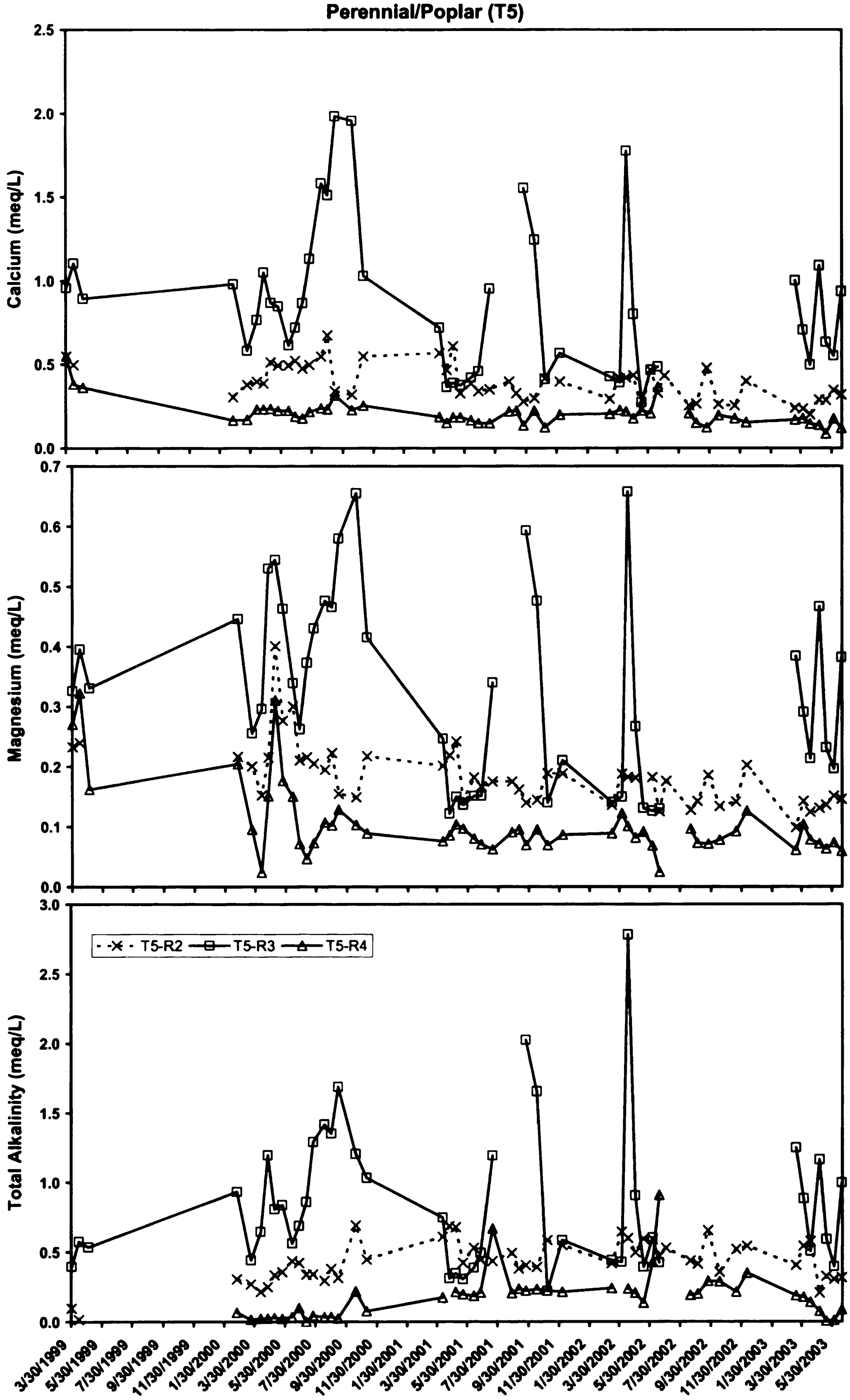


Figure 112: Perennial/Poplar (T5) Time Series

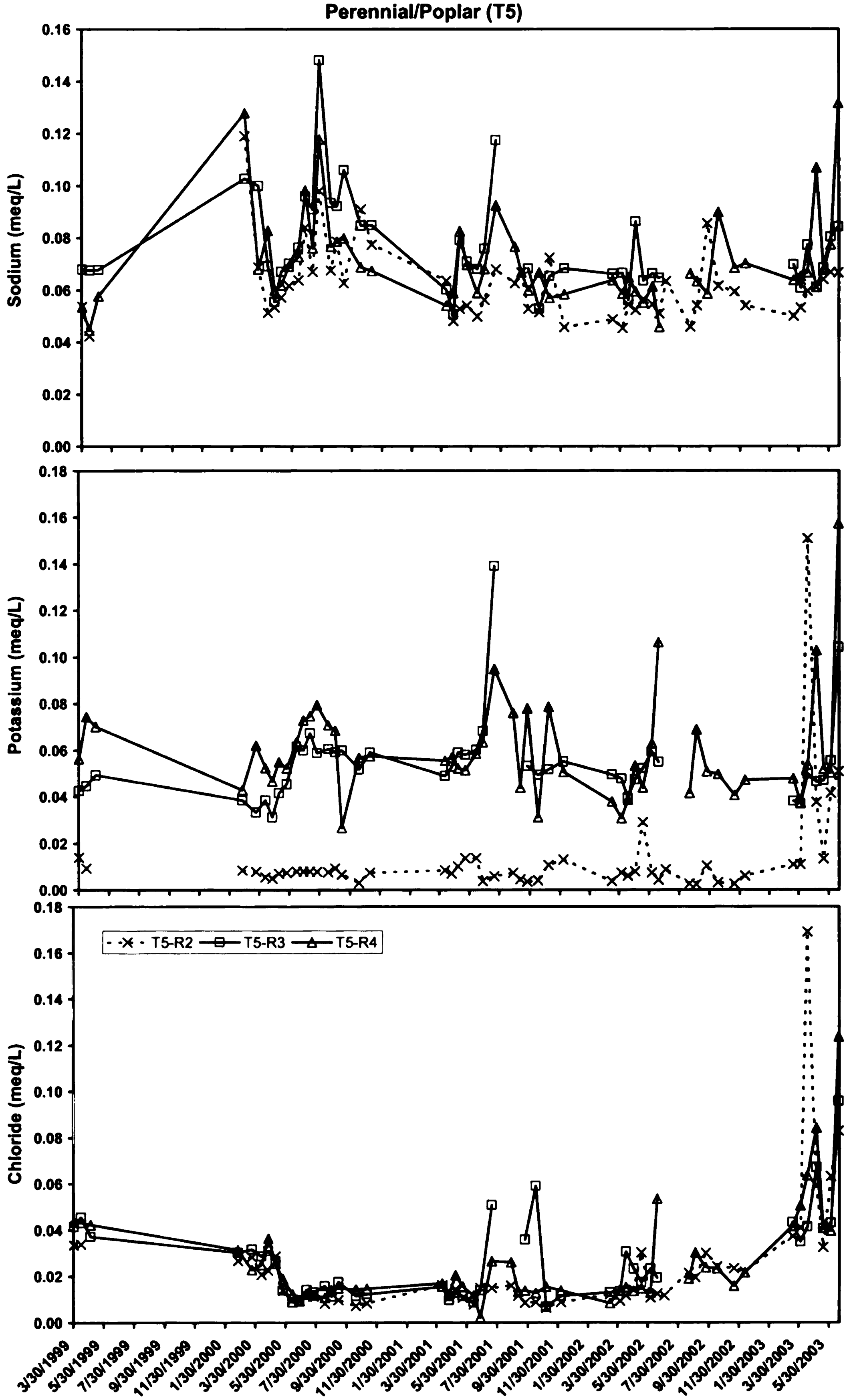


Figure 113: Perennial/Poplar (T5) Time Series

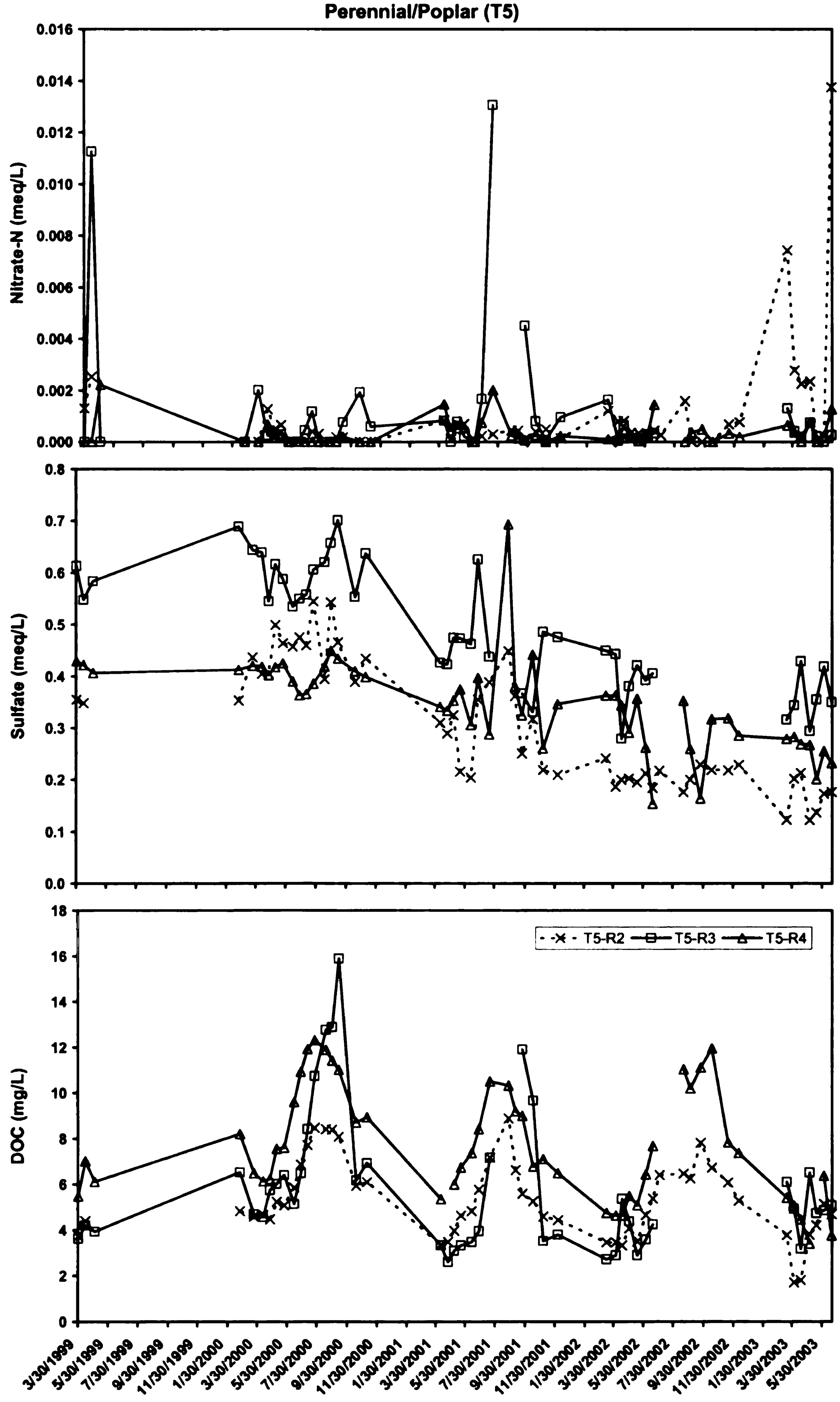


Figure 114: Perennial/Poplar (T5) Time Series

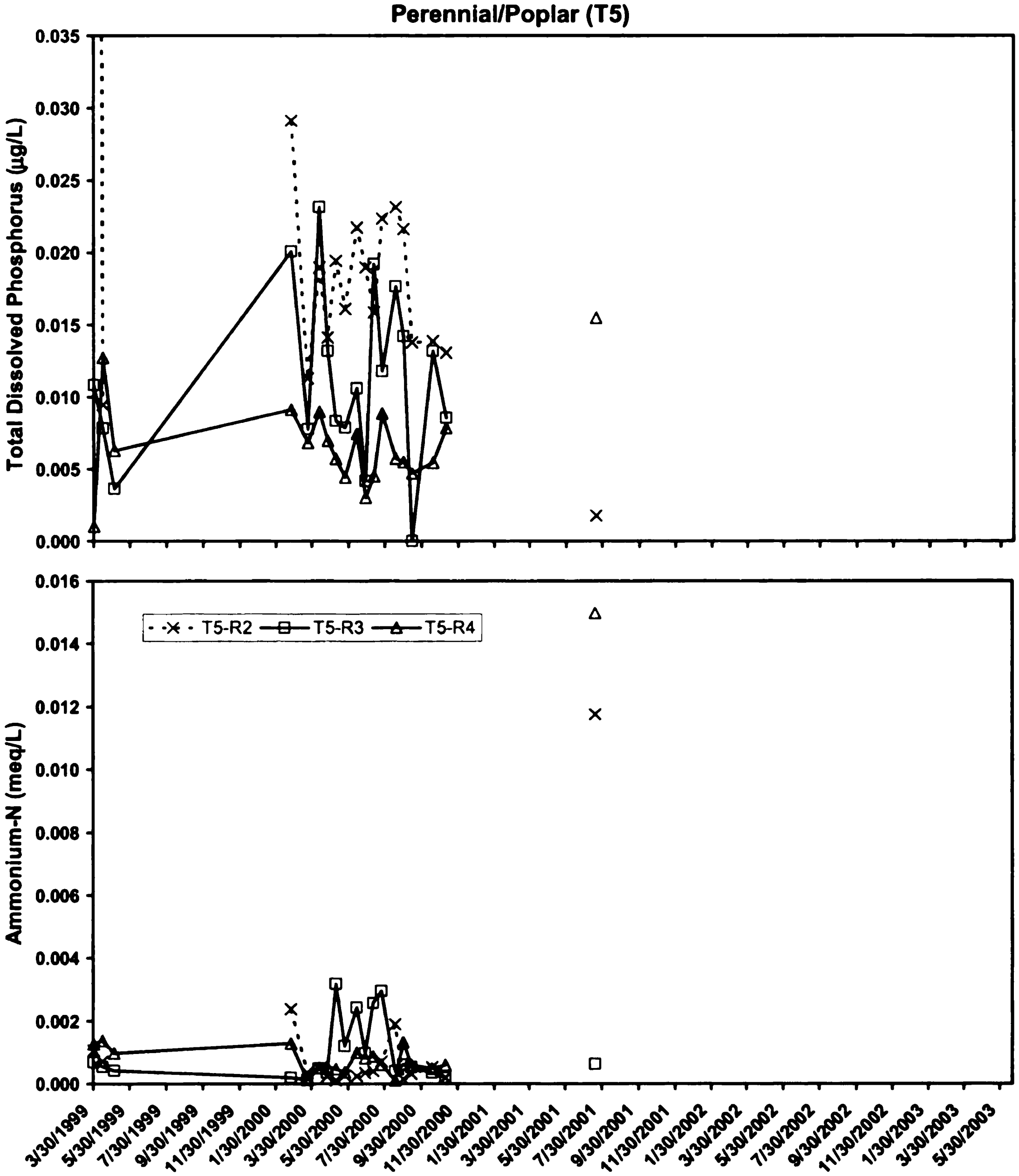


Figure 115: Perennial/Poplar (T5) Time Series

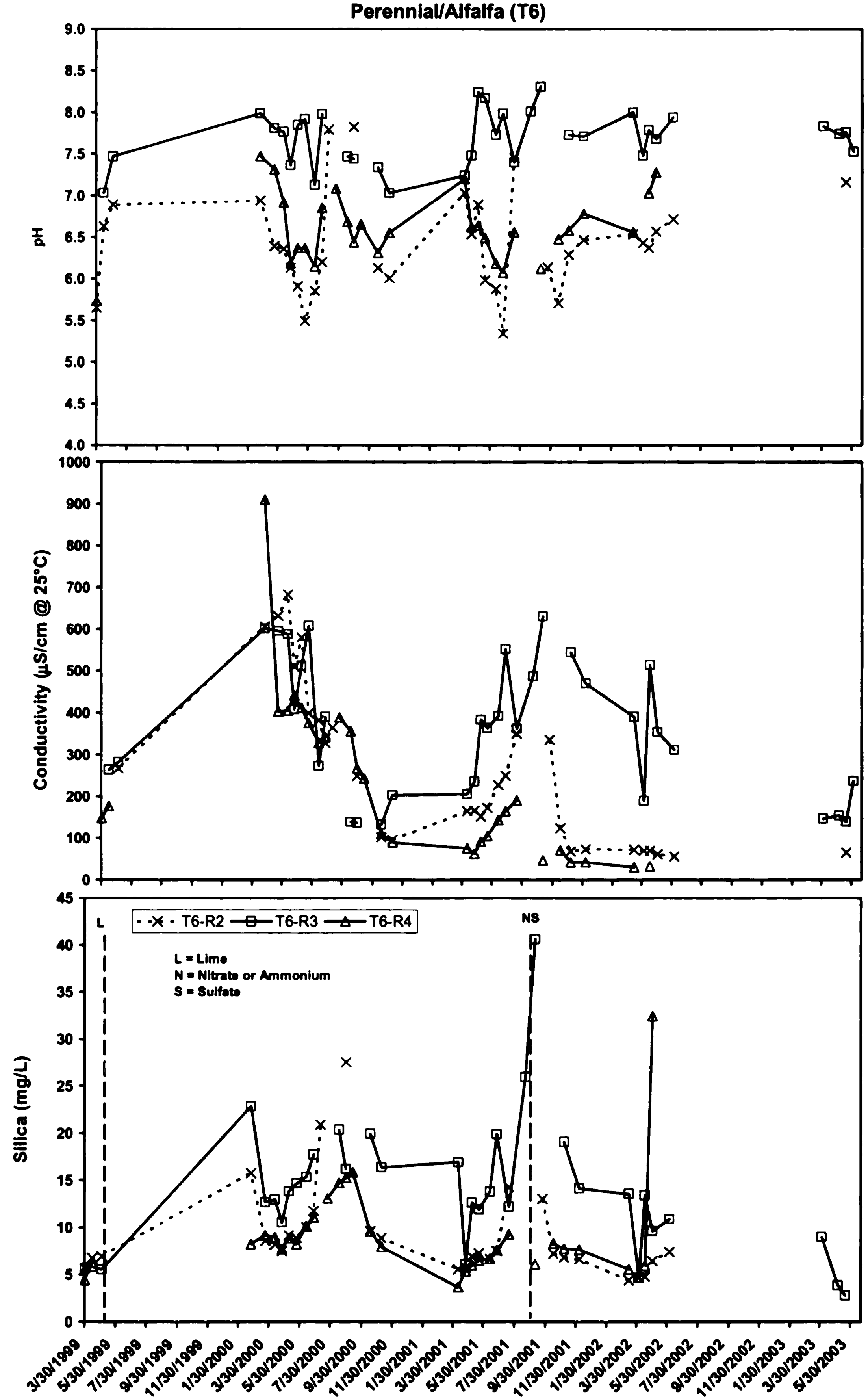


Figure 116: Perennial/Alfalfa (T6) Time Series

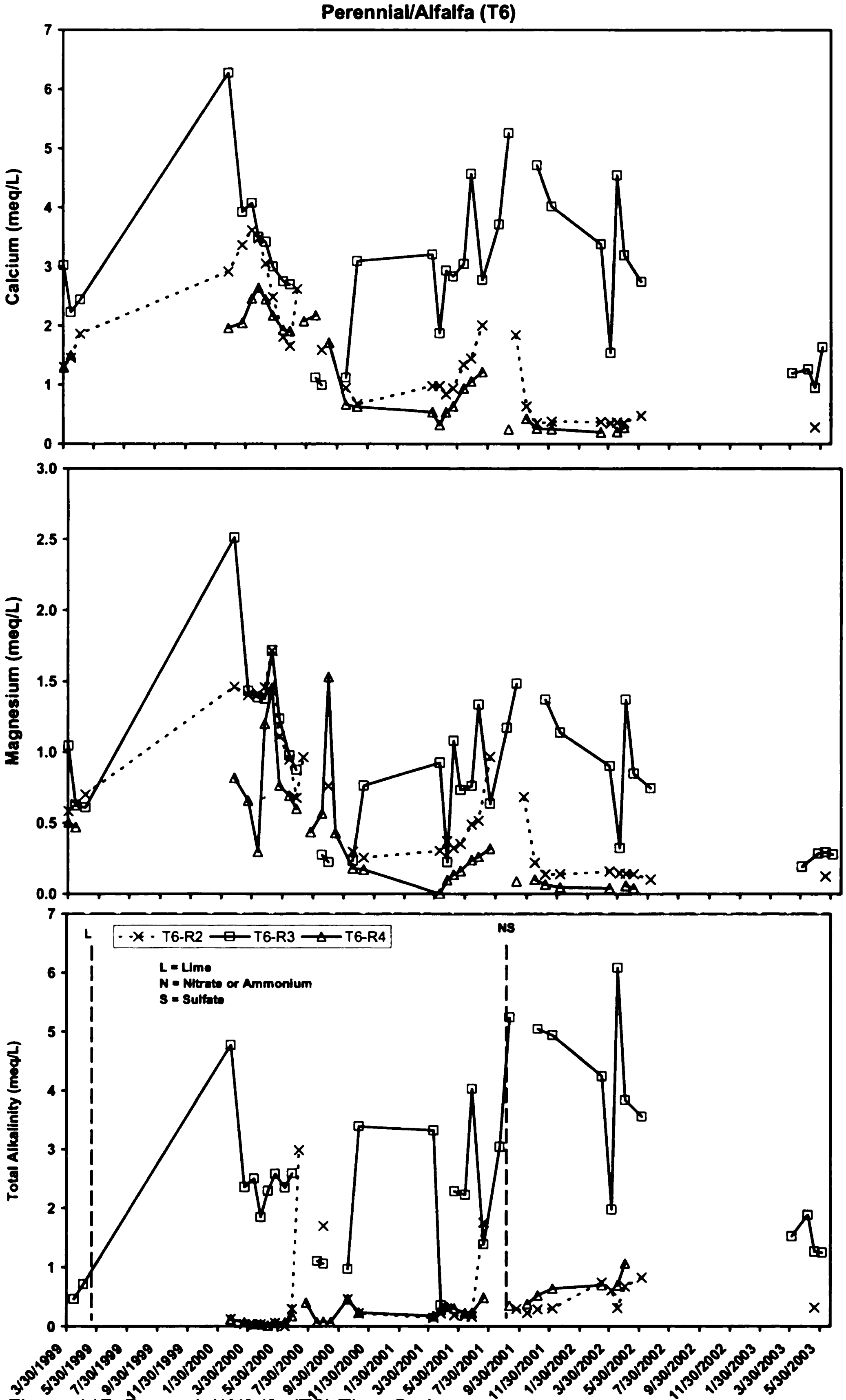


Figure 117: Perennial/Alfalfa (T6) Time Series

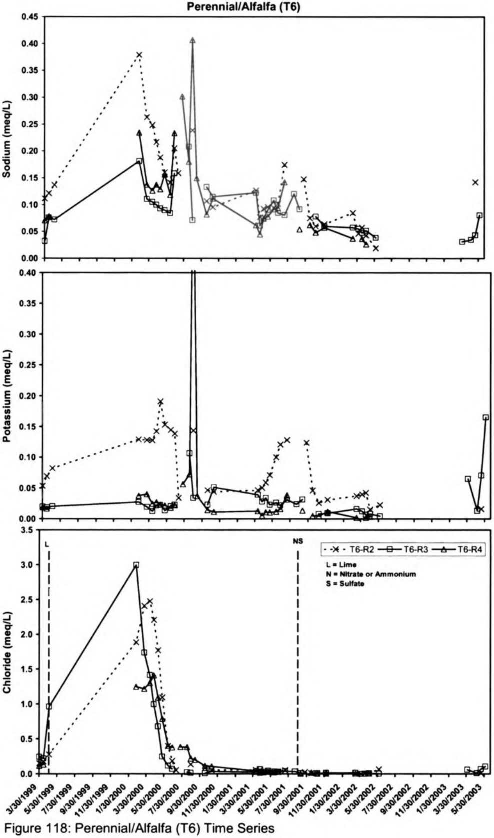


Figure 118: Perennial/Alfalfa (T6) Time Series

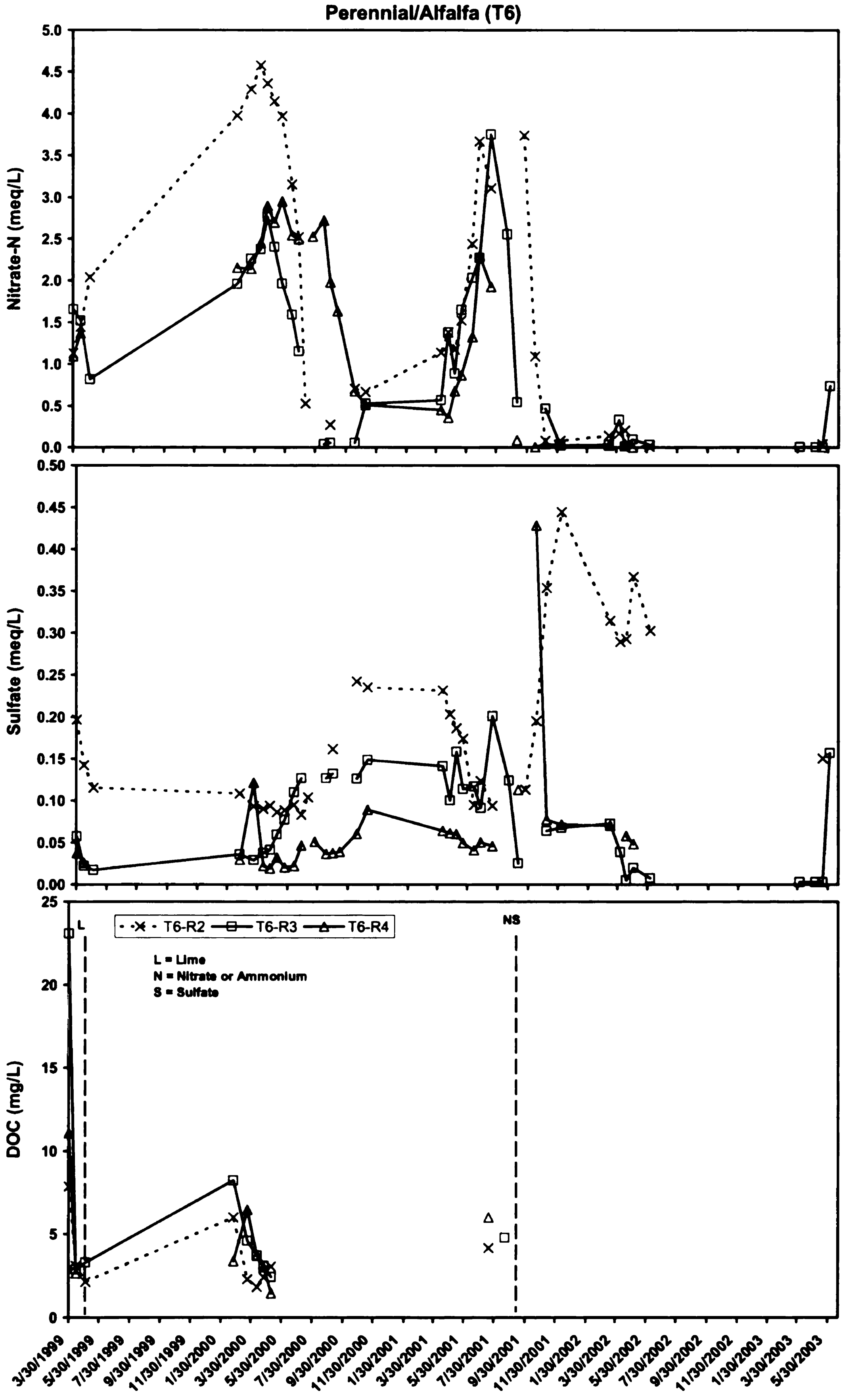


Figure 119: Perennial/Alfalfa (T6) Time Series

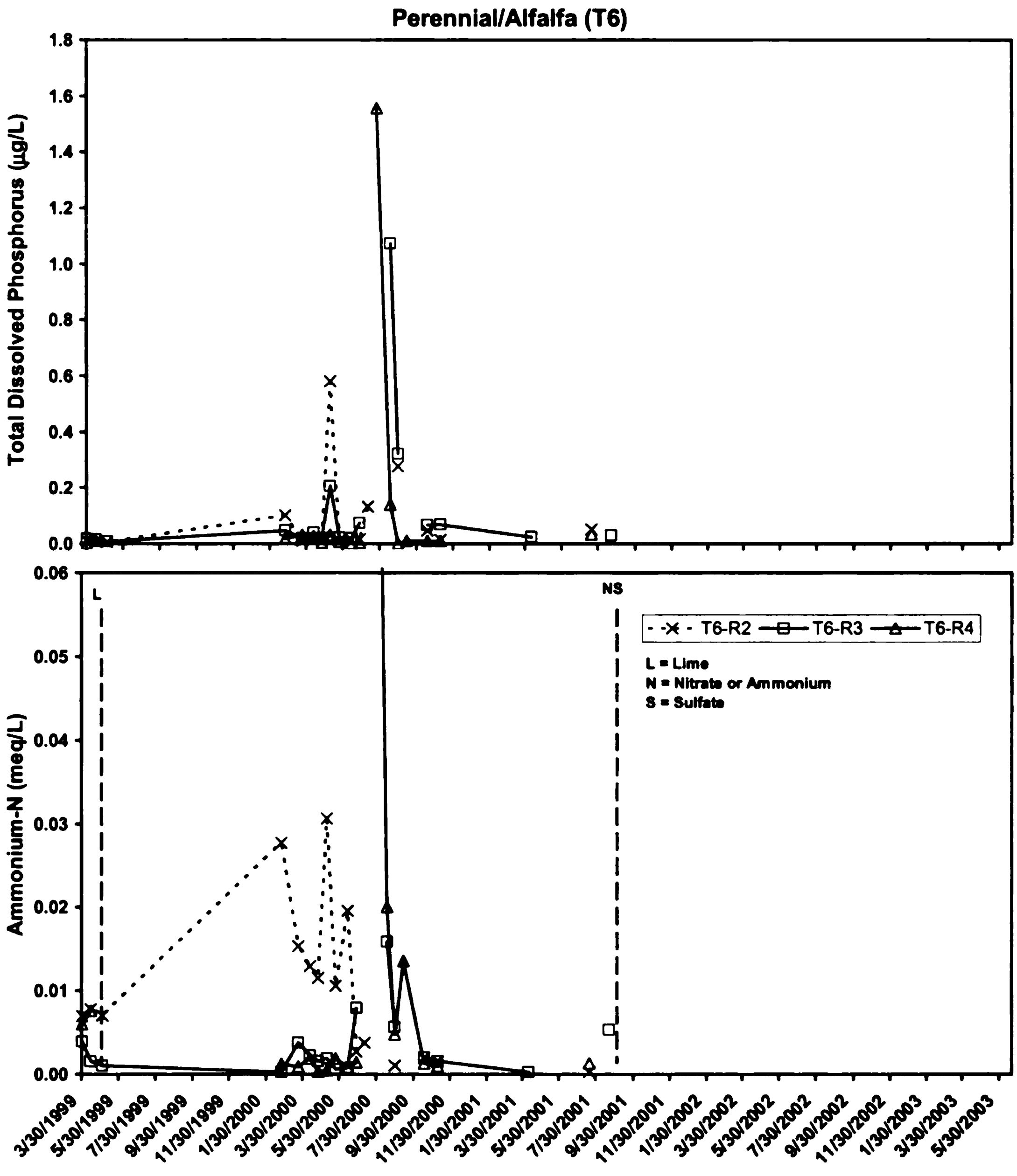


Figure 120: Perennial/Alfalfa (T6) Time Series

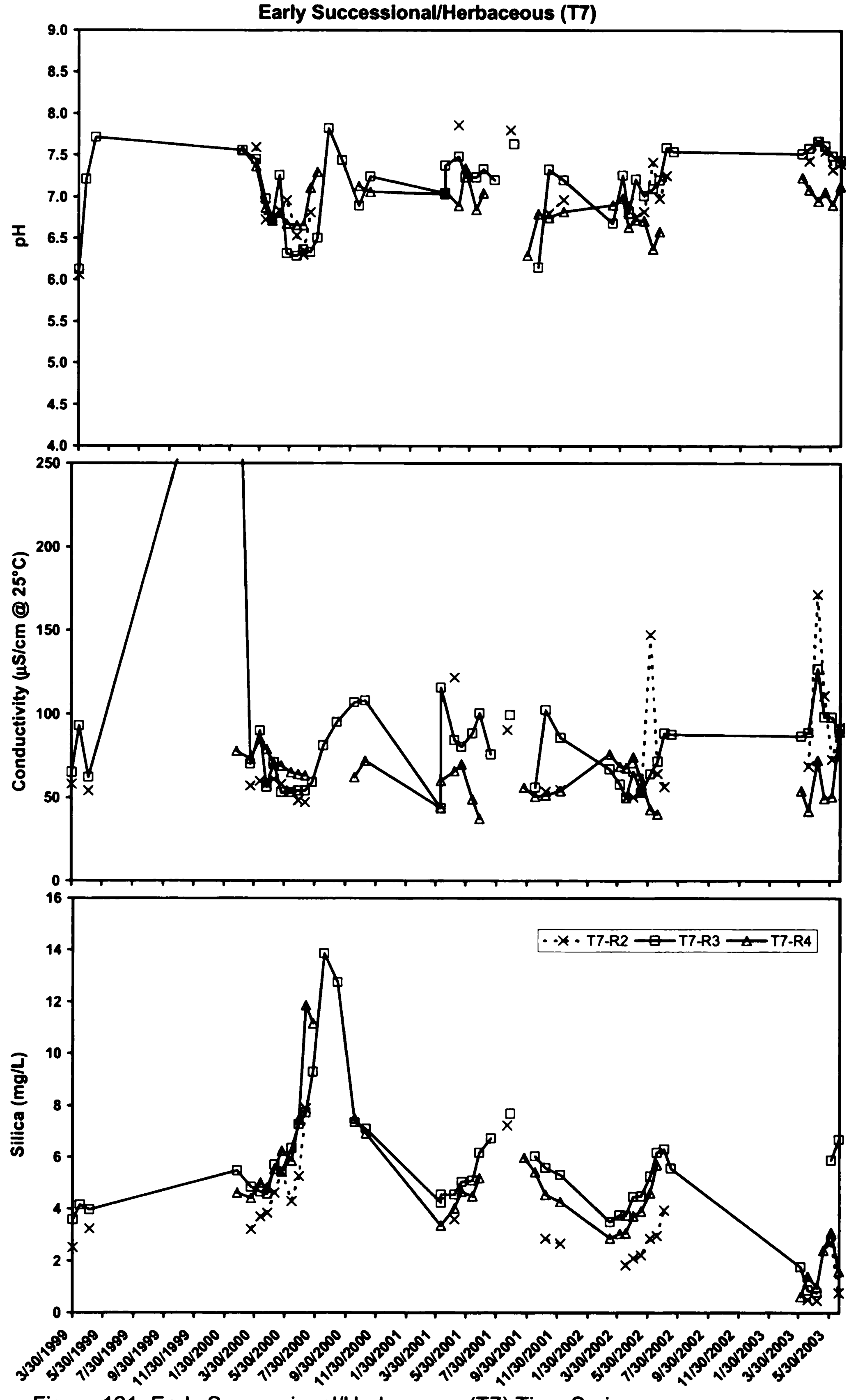


Figure 121: Early Successional/Herbaceous (T7) Time Series

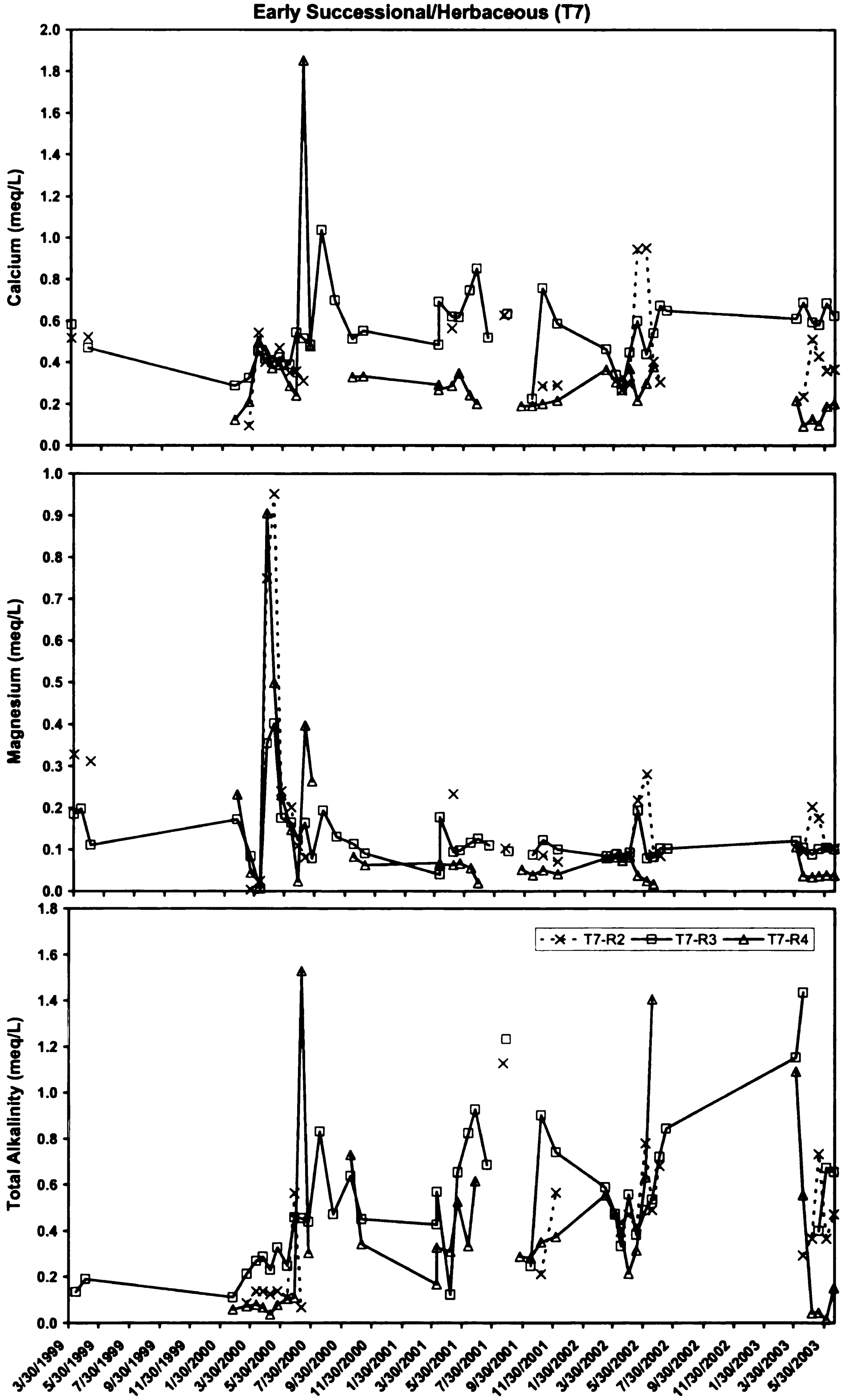


Figure 122: Early Successional/Herbaceous (T7) Time Series

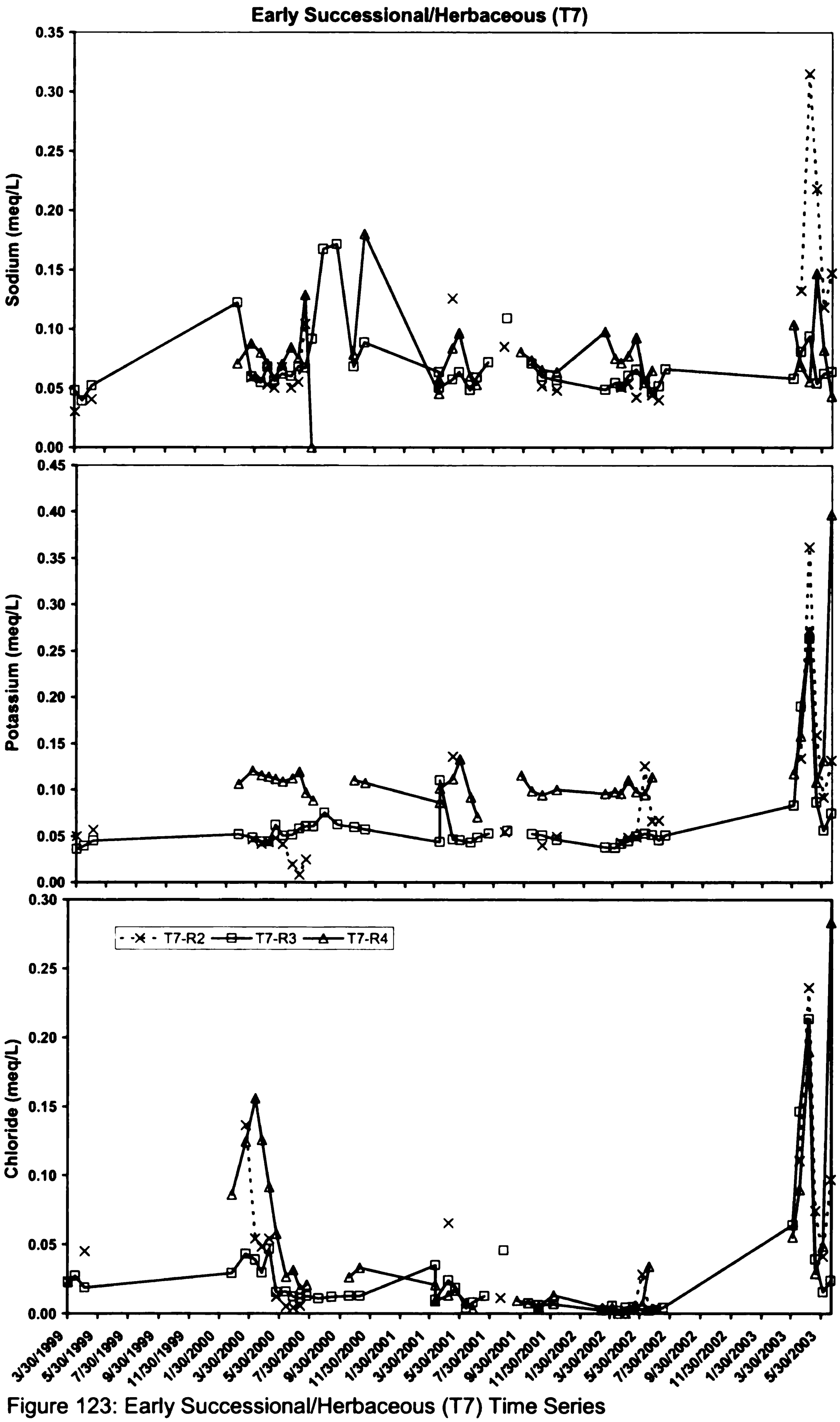


Figure 123: Early Successional/Herbaceous (T7) Time Series

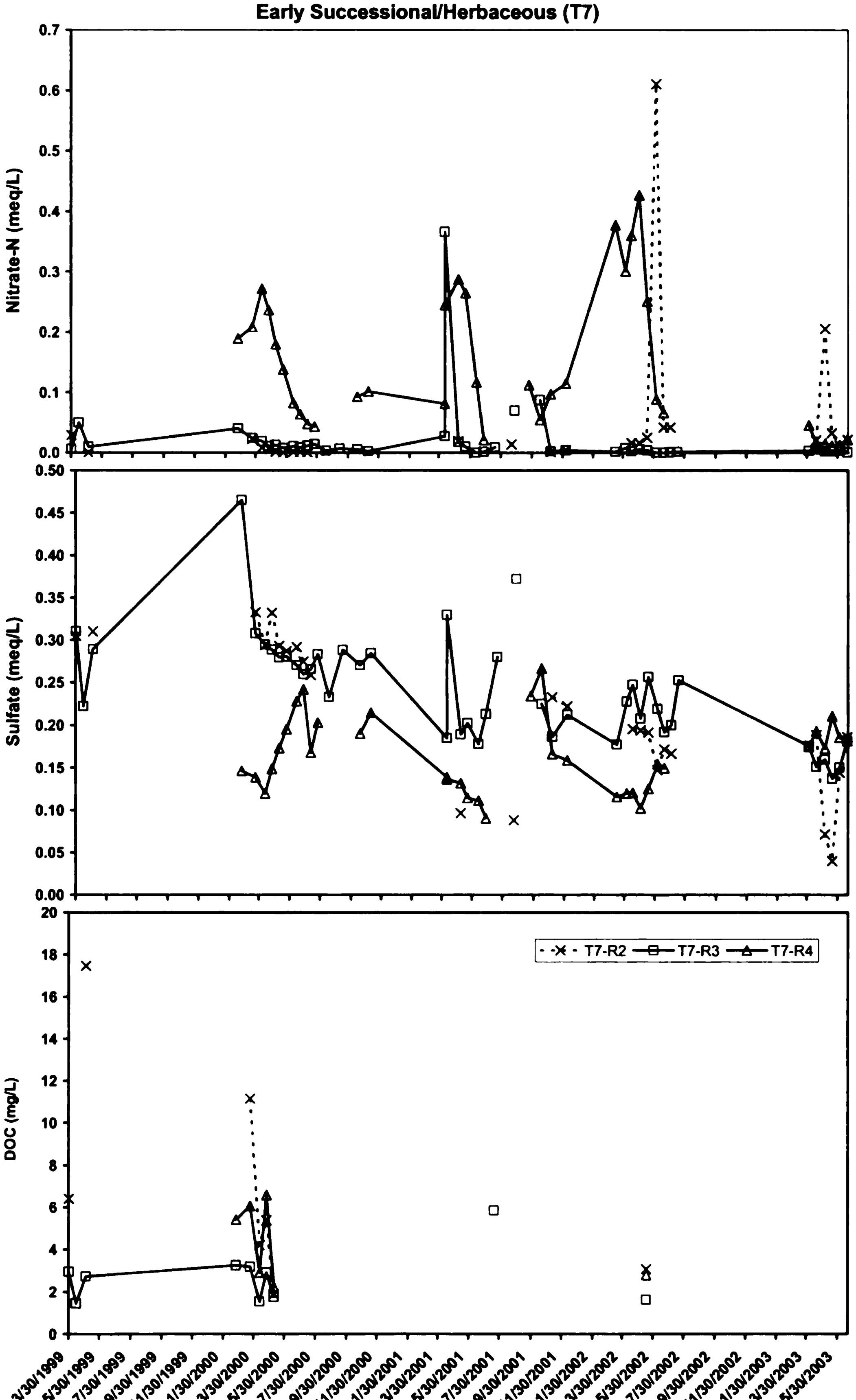


Figure 124: Early Successional/Herbaceous (T7) Time Series

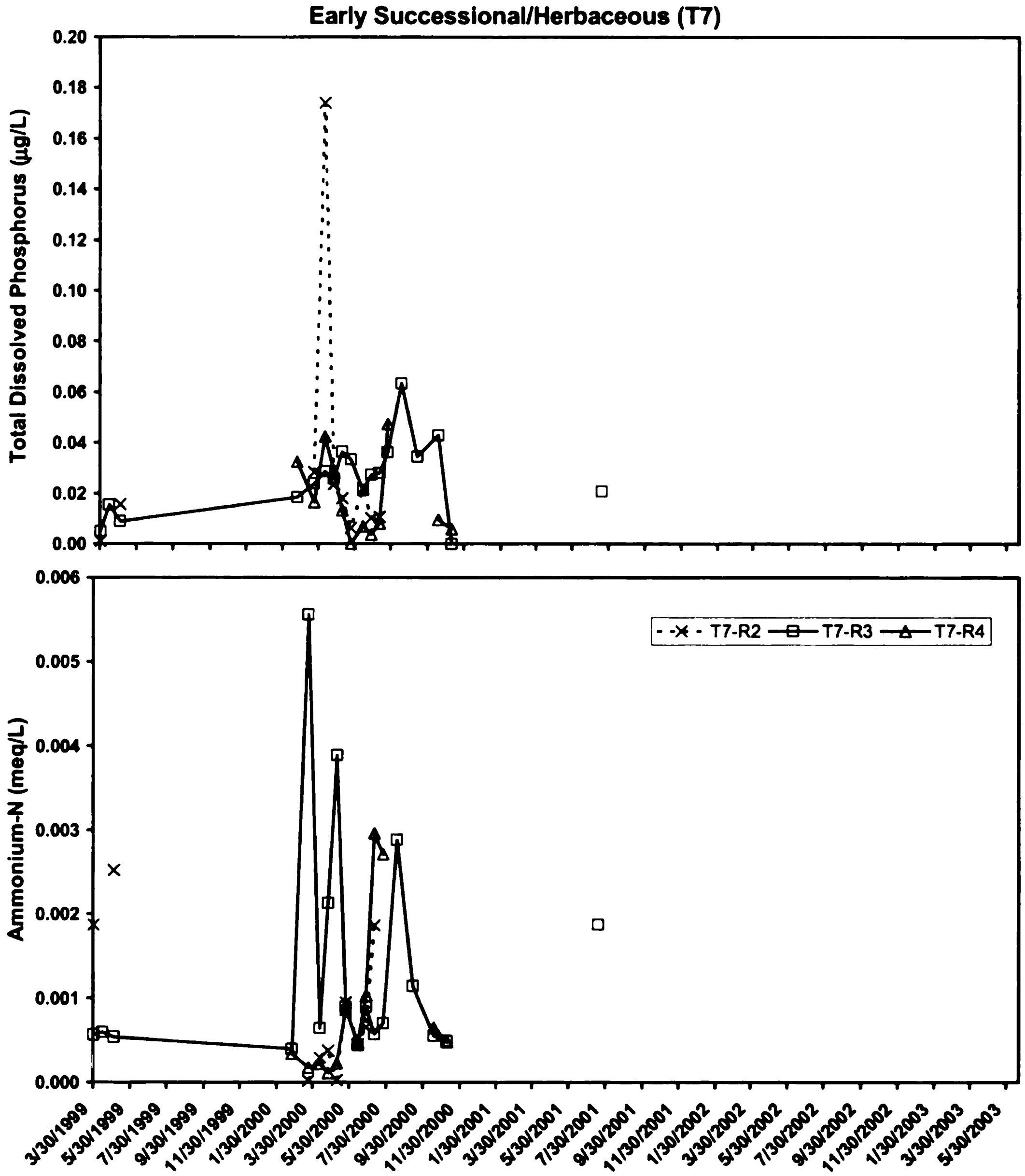


Figure 125: Early Successional/Herbaceous (T7) Time Series

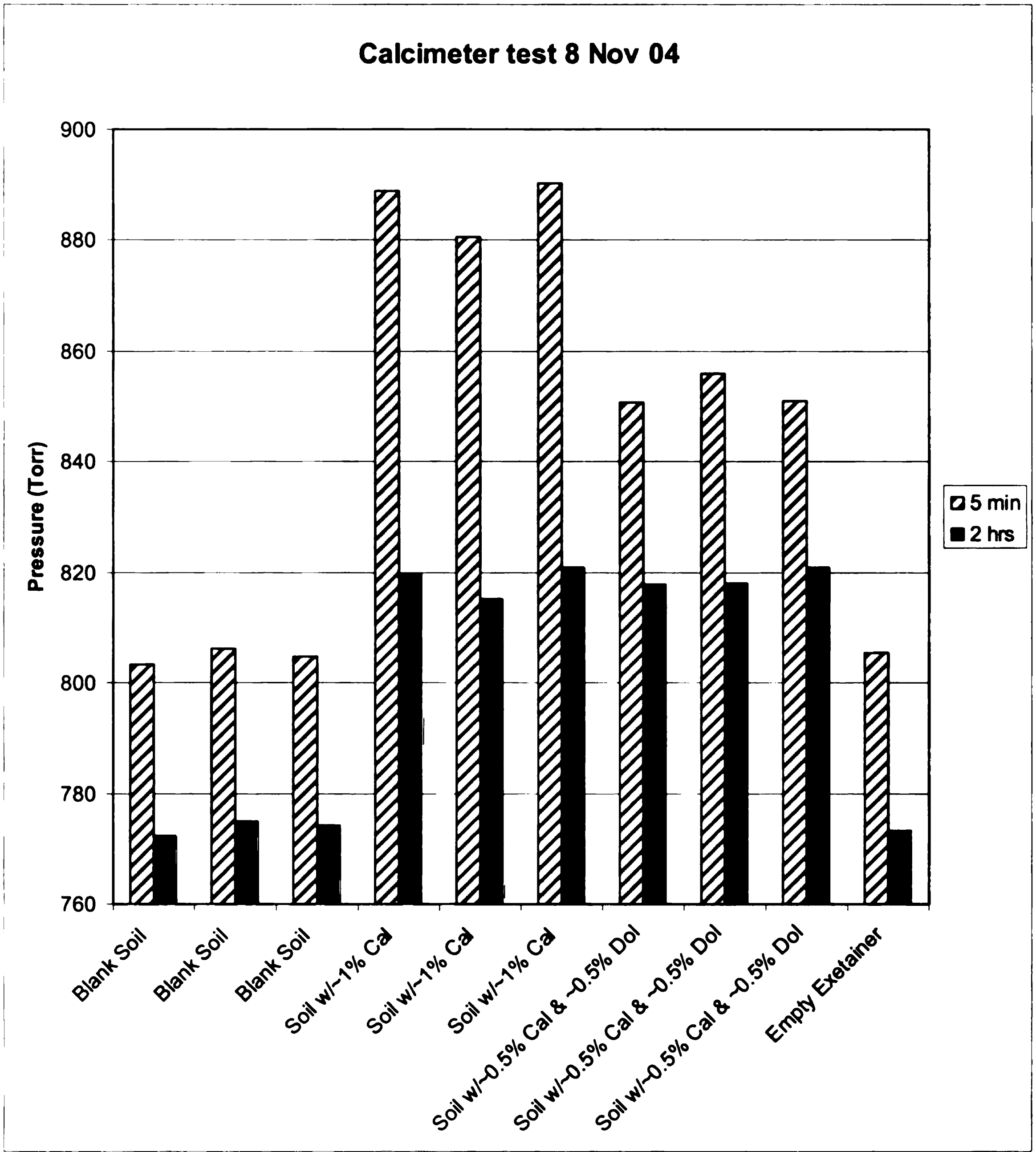
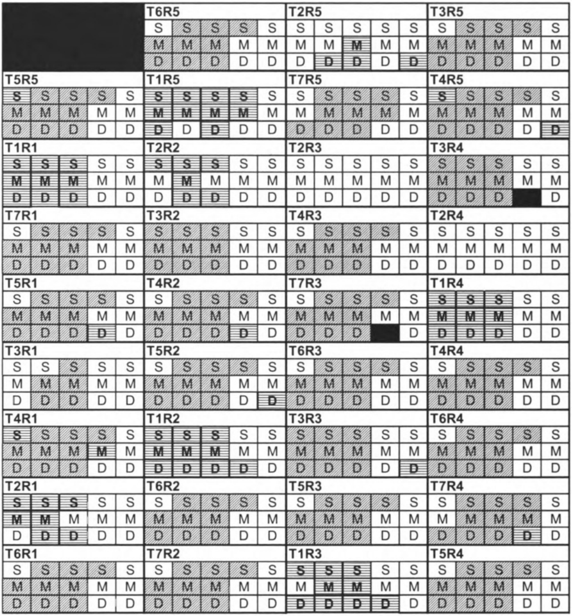


Figure 126: Soil core samples were screened for the presence of carbonate minerals by measuring the pressure response of acidified samples. Calcite is less resistant to acid breakdown than dolomite; therefore the pressure test was partitioned into two time intervals. It is expected that within the first 5 minutes, all of the calcite present in the sample was dissolved. Following the 5 minute measurement, the vial was opened to return the vial to atmospheric pressure. The pressure response after two hours is assumed to be the result of dolomite dissolution. The recovery for dolomite was similar as that for calcite.

Figure 127: Soil Carbonate Screening Results. Finely milled samples (< 0.5 mm diameter) from each horizon of the soil-core samples collected in 1999 from the KBS LTER main site were screened for the presence of carbonates by measuring the pressure response of acidified samples. In general, each core yielded three samples labeled by treatment and replicate as shallow, middle, or deep.

Based on the pressure response, I created a 95% Confidence Interval for the blanks and 0.25% $CaCO_3$ after normalizing the data to account for differences in soil weight and ambient pressure. The probability of an observation occurring that falls outside of the confidence interval is 5% or less.
The diagram at left is color-coded and the first row within each treatment corresponds to shallow, the second row within each treatment corresponds to middle, and the third row corresponds to deep. Note that lysimeters are only present in replicates 2, 3, and 4 of any given treatment.

Carbonates were observed in all replicates of Treatment 1, and in no replicates of T6, although both treatments receive dolomitic limestone as a soil amendment. Lime is also added to Treatments 2 and 3. Within Treatment 2, carbonates were only consistently observed in replicate 2 and in Treatment 3, carbonates were not consistently observed in any of the replicates. Carbonates were detected in some replicates of the unlimed treatments T4, T5, and T7; however, the sporadic detection makes it difficult to conclude that carbonates are present in those replicates as a whole.



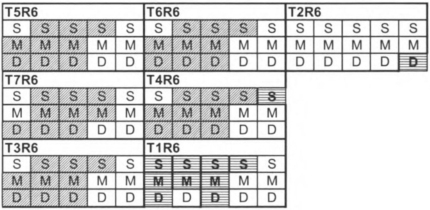
X Carbonate Present

X Sample not analyzed

Absence of color indicates that pressure response value fell within or below CI for blanks. Conclusion: No carbonate is present.

No sample collected

X Indicates sample depth within core



Carbonate Present

Sample not analyzed

Absence of color indicates that pressure response value fell within or below CI
Conclusion: No carbonate is present.

No sample collected

Indicates sample depth within

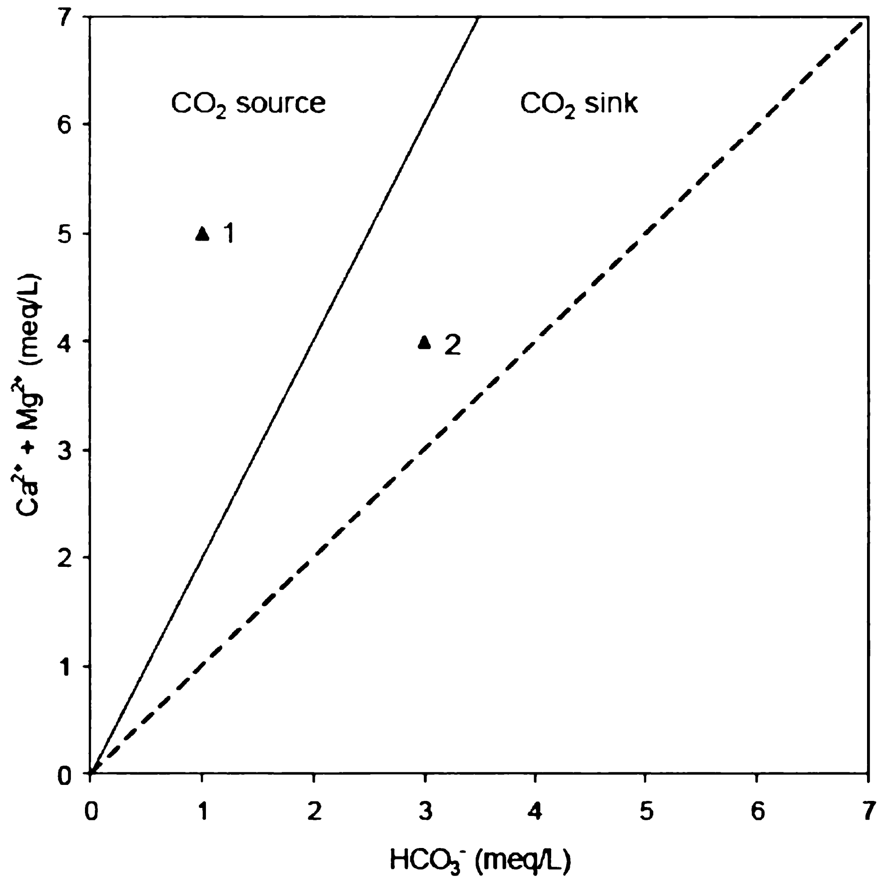


Figure 128: Conceptual model for carbonate mineral dissolution in soils. The dashed line depicts the expected 1:1 ratio of dissolved Ca^{2+} + Mg^{2+} to HCO_3^- produced by carbonic acid weathering. The solid line represents the elemental stoichiometry in the lime (calcite or dolomite). Hypothetical sample 1 demonstrates a case in which the lime has yielded CO_2 equivalent to 1.5 meq L-1, or 60% of its C content, thereby serving as a source of soil CO_2. Sample 2 has consumed soil CO_2 equivalent to 1 meq L-1, or 50% of its C content. Using Eq. 3, we thus define the "CO_2-C sink strength" as –60% for Sample 1 (i.e., a CO_2 source) and +50% for Sample 2 (a CO_2 sink).

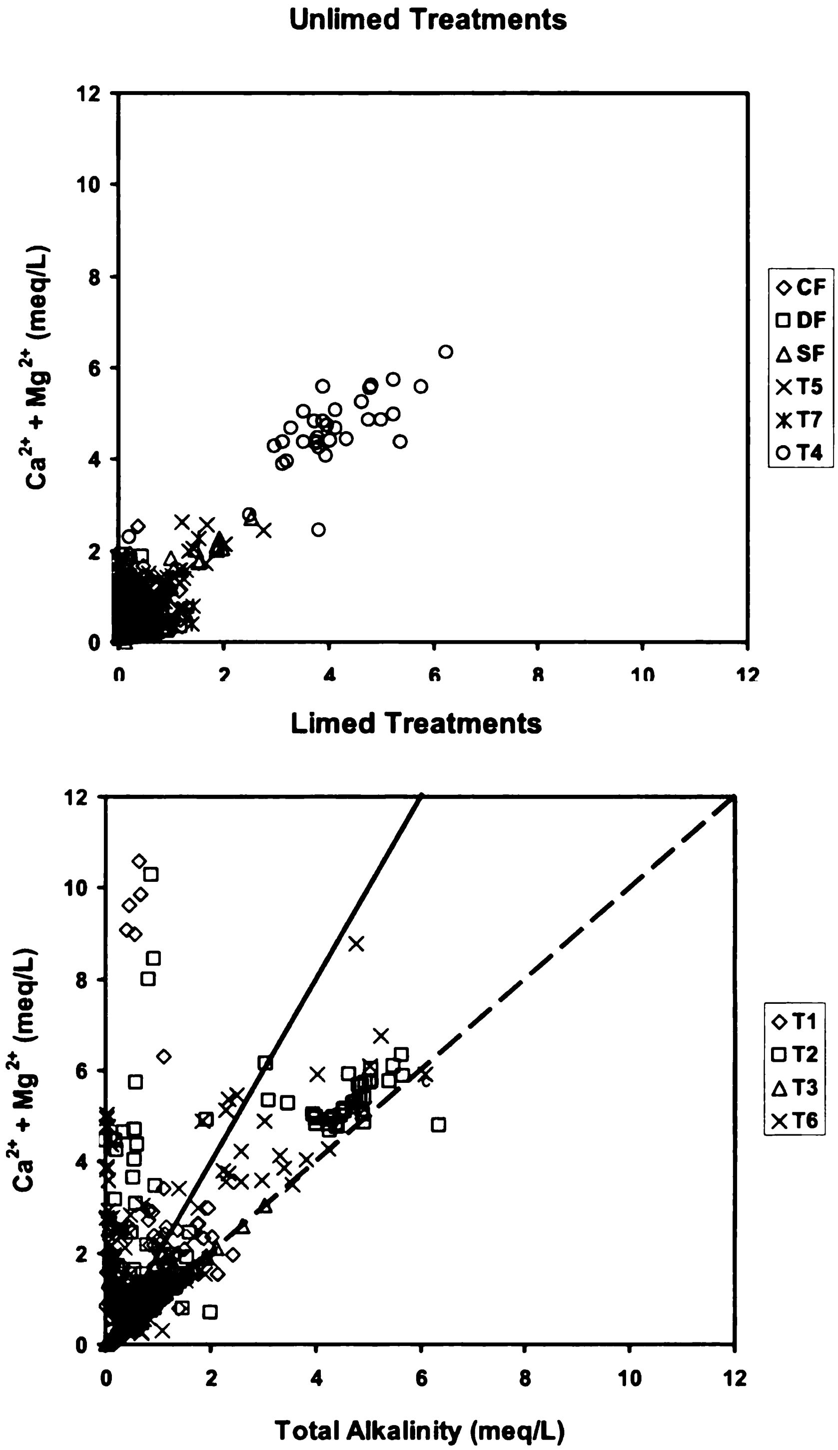
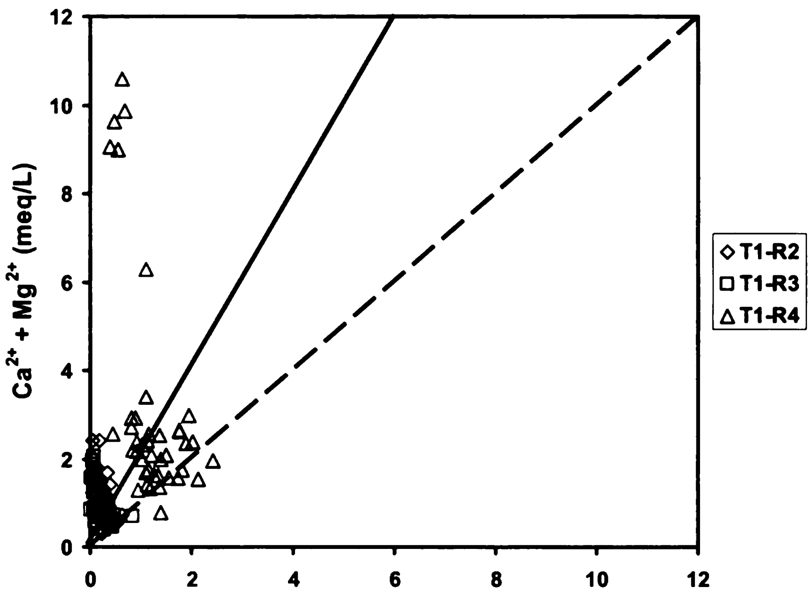


Figure 129. Evidence for carbonate mineral dissolution in soil solutions collected by low-tension samplers from 1-m depth in limed and unlimed treatments of the Long-Term Ecological Research Site at Kellogg Biological Station. Unlimed treatments show little or no carbonate mineral influence, with Ca^{2+} + Mg^{2+} usually below 2 meq/L, with the exception of Treatment 4: Organic Conventional Till. In contrast, limed treatments show evidence of carbonate mineral influence as a significant number of samples exhibit Ca^{2+} + Mg^{2+} above 2 meq/L. The solid line represents the source-sink dividing line; points to the right of the line indicate carbon sequestration.

T1: Conventional Input / Conventional Till



T2: Conventional Input / No Till

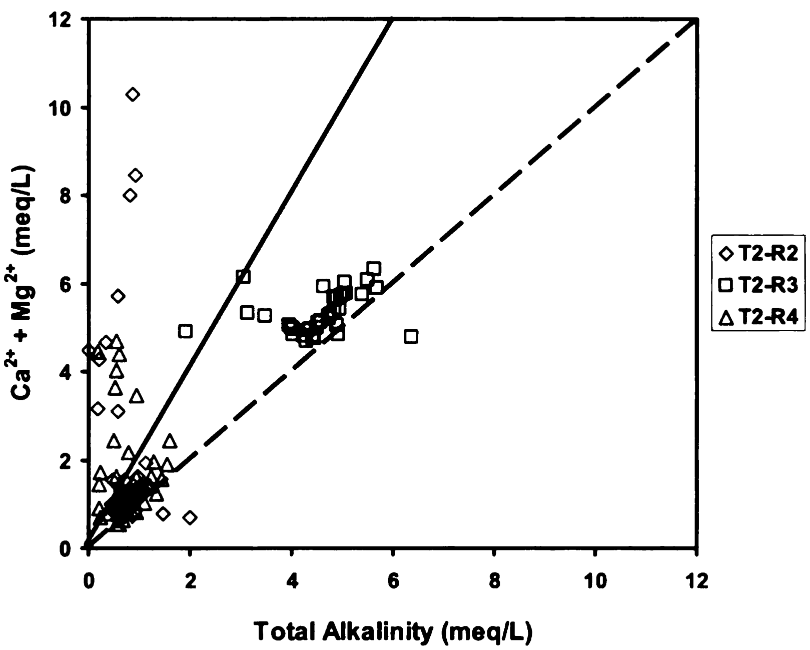
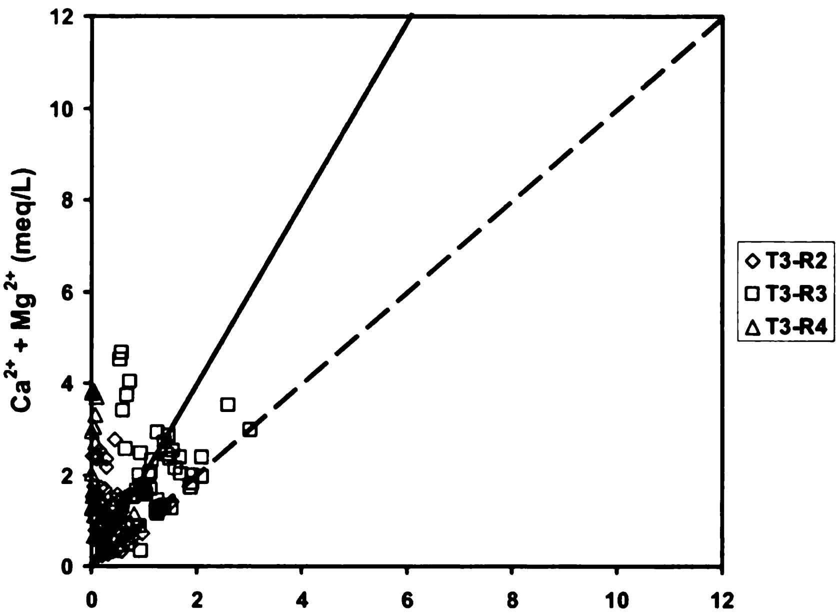


Figure 130: Calcium plus magnesium vs. total alkalinity plots for Treatments 1 and 2. Replicate T2-R2 and T2-R3 exhibits samples with higher concentrations of calcium and magnesium than Replicate T2-R4, but only T2-R3 has a samples above 2 meq/L falling to the right of the sink-source dividing line. The solid line represents the source-sink dividing line; points to the right of the line indicate carbon sequestration.

T3: Reduced Input / Conventional Till



T4: Organic / Conventional Till

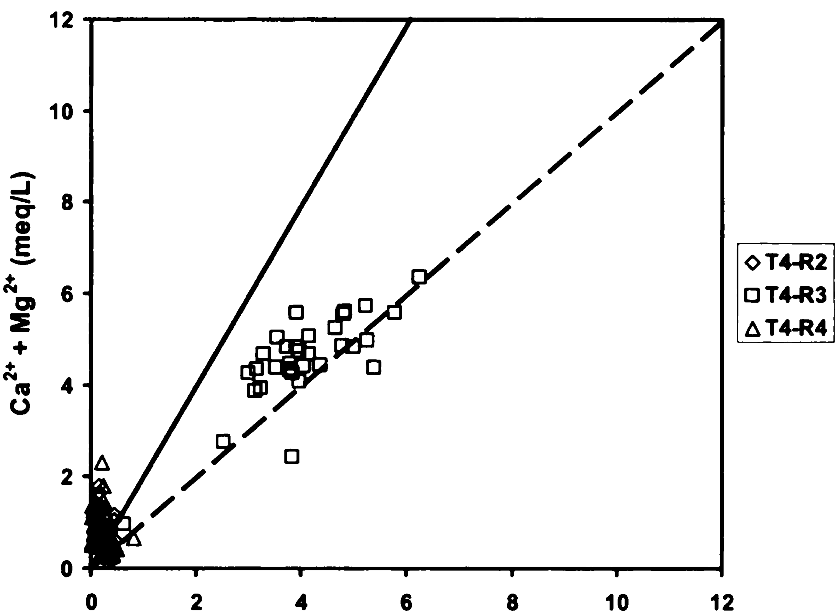


Figure 131: Calcium plus magnesium vs. total alkalinity plots for Treatments 3 and 4. Replicate T4-R3 exhibits samples with higher concentrations of calcium and magnesium than the other two replicates, and has more points falling to the right of the sink-source dividing line. The solid line represents the source-sink dividing line; points to the right of the line indicate carbon sequestration.

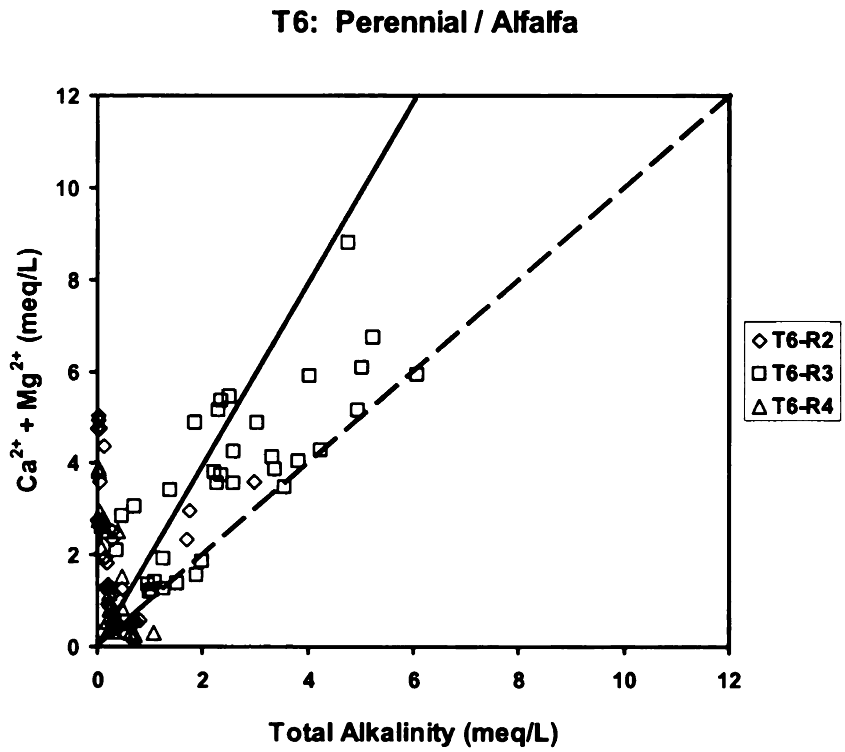


Figure 132: Calcium plus magnesium vs. total alkalinity plot for Treatment T6. Replicate T6-R3 exhibits samples with higher concentrations of calcium and magnesium than the other two replicates, and has more points falling to the right of the sink-source dividing line. The solid line represents the source-sink dividing line; points to the right of the line indicate carbon sequestration.

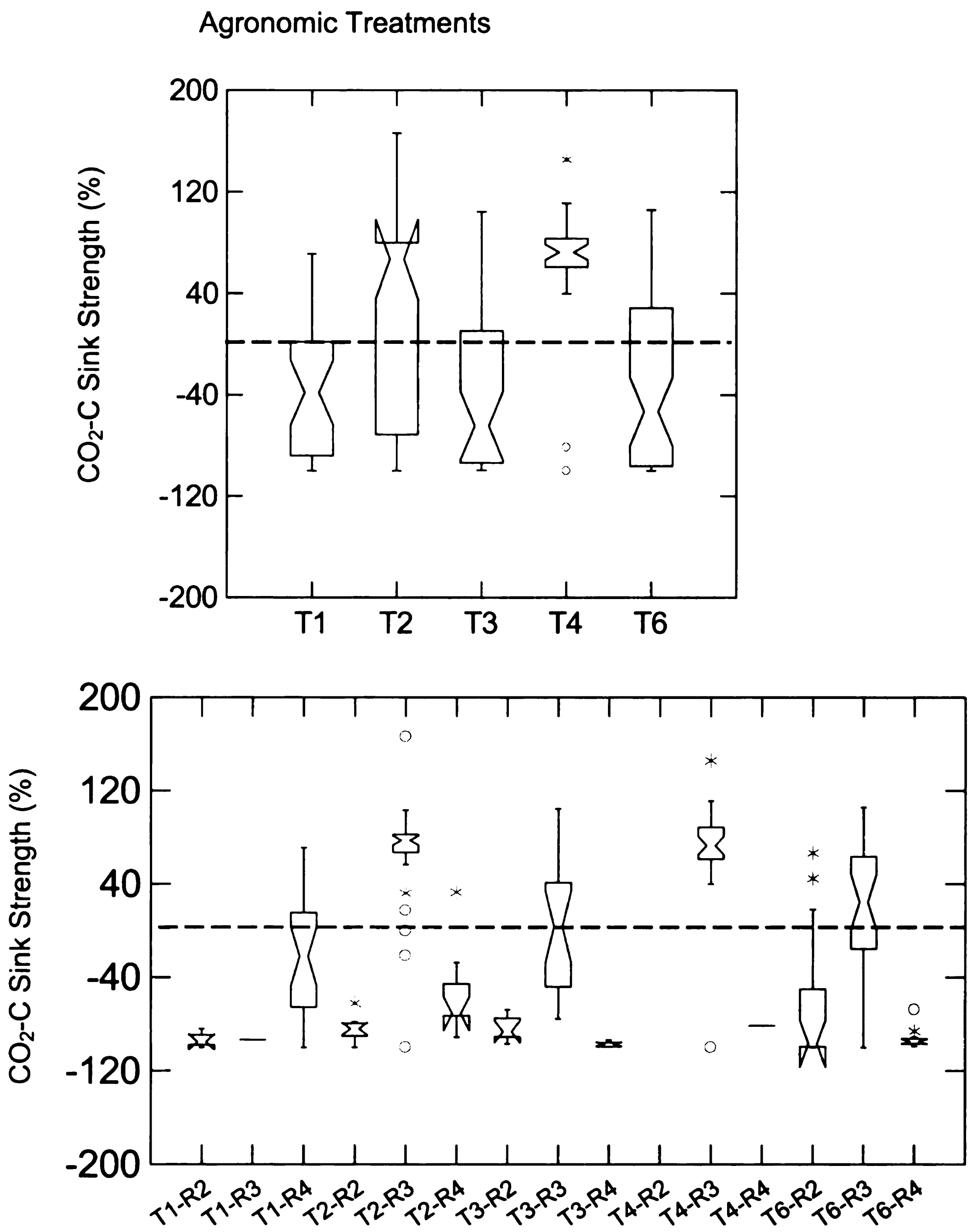


Figure 133: Notched box plots of CO2-C Sink Strength (%) in agronomic treatments by treatment and replicate. Notches represent approximate 95% confidence interval around the median.

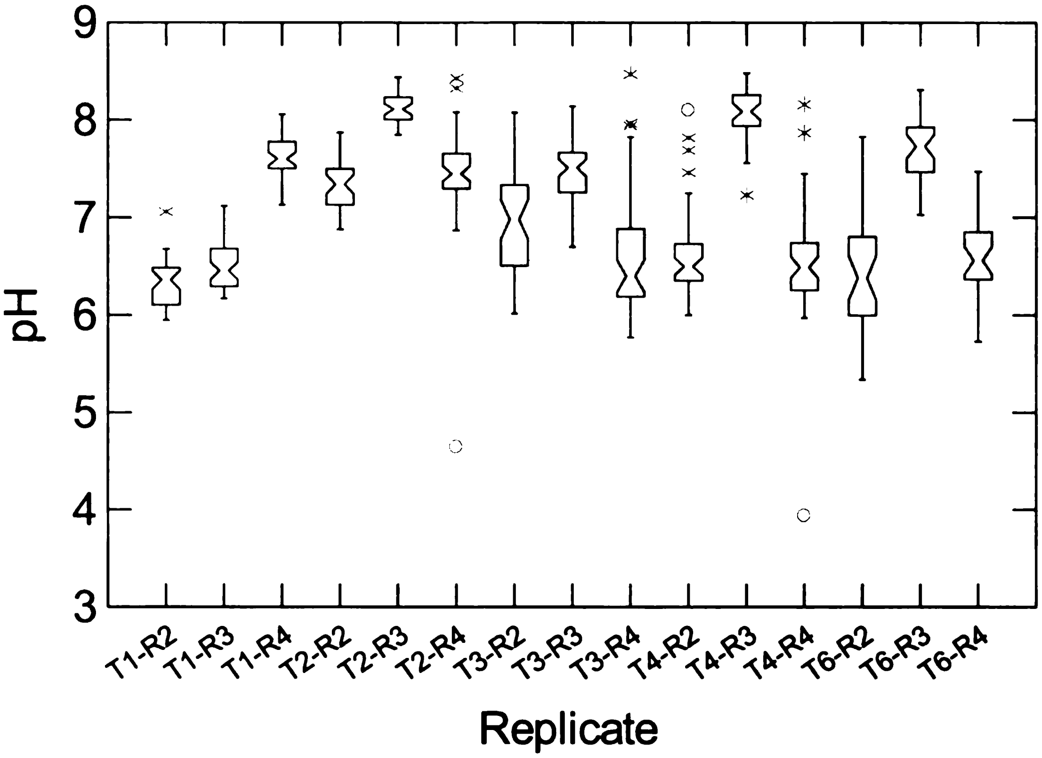


Figure 134: Notched box plots of pH among replicates of the agronomic treatments. Notches represent approximate 95% confidence interval around the median.

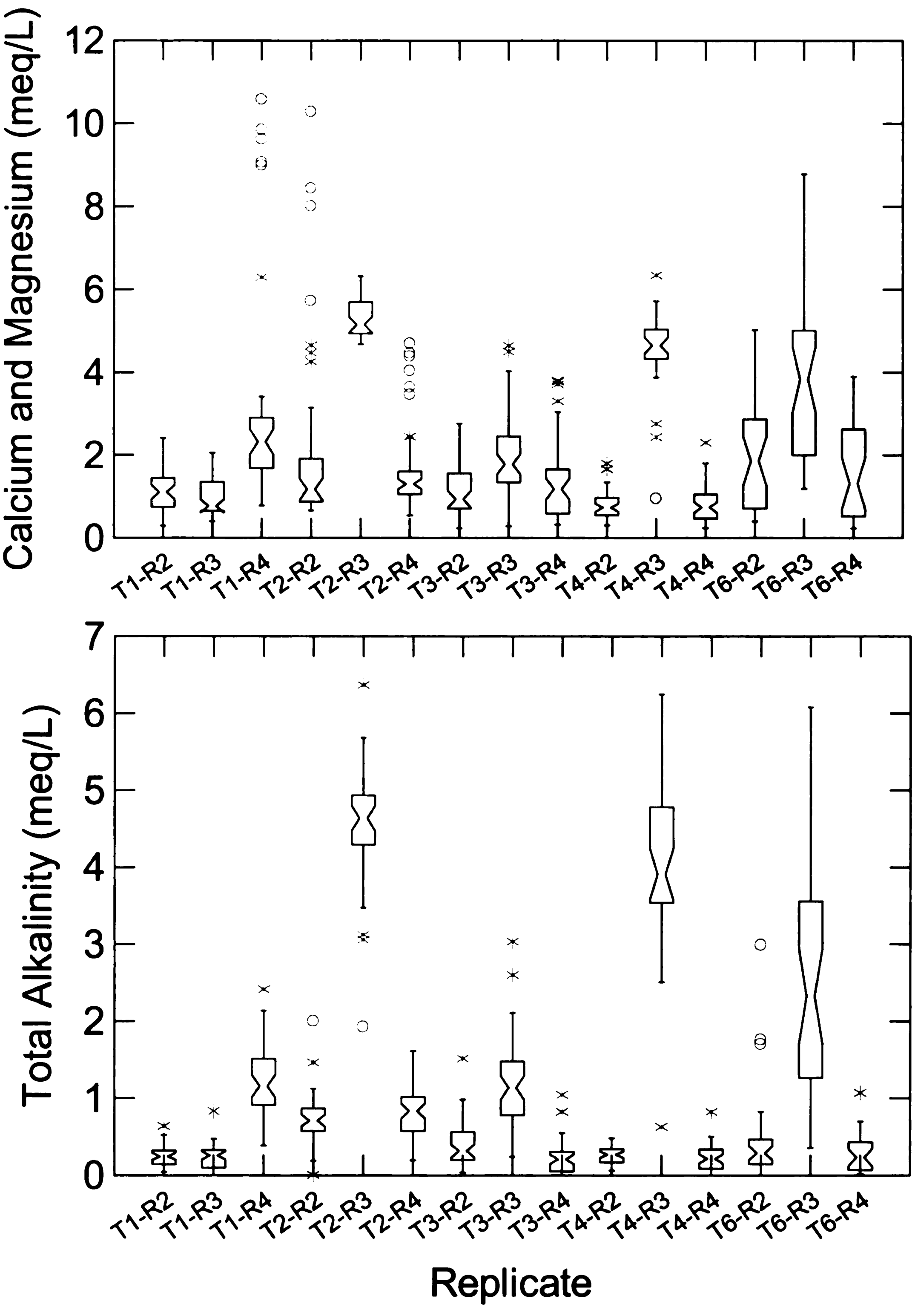


Figure 135: Notched box plots of calcium plus magnesium and total alkalinity concentrations among replicates of the agronomic treatments. Notches represent approximate 95% confidence interval around the median.

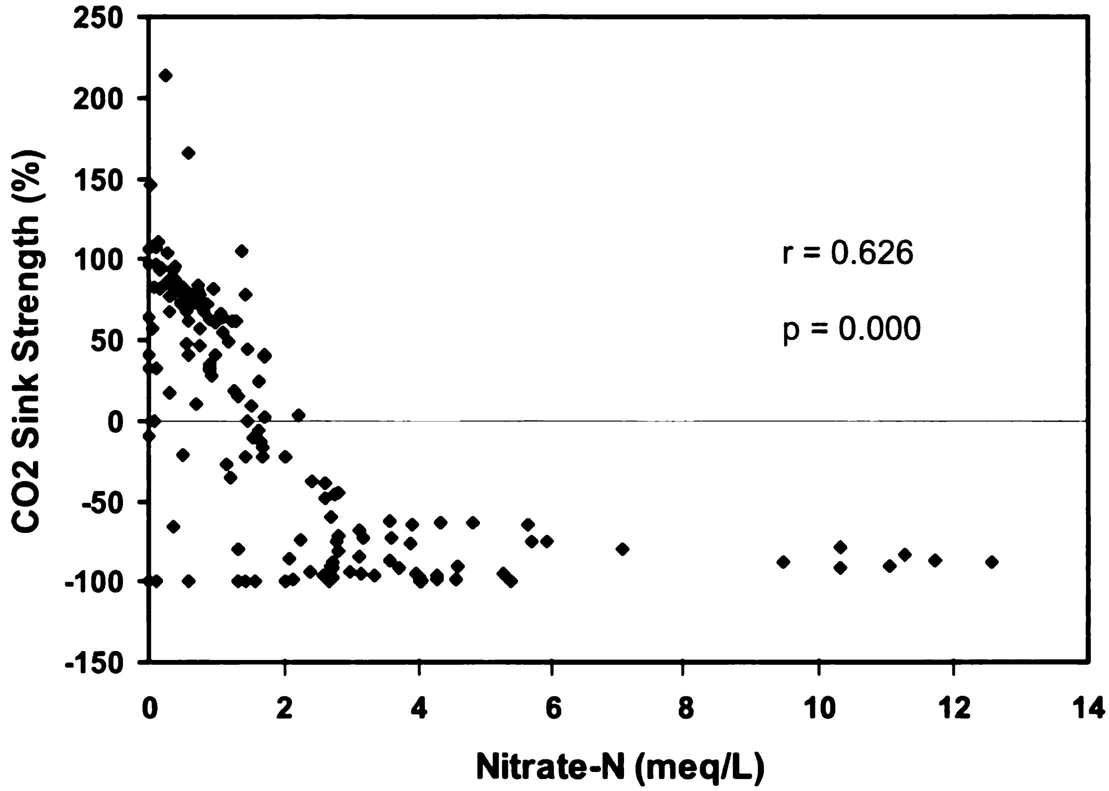


Figure 136: Relationship between CO_2-C Sink Strength (%) and Nitrate-N. The inverse relationship between nitrate-N concentrations and CO_2-C Sink Strength (%) is significant (Systat 8.0).

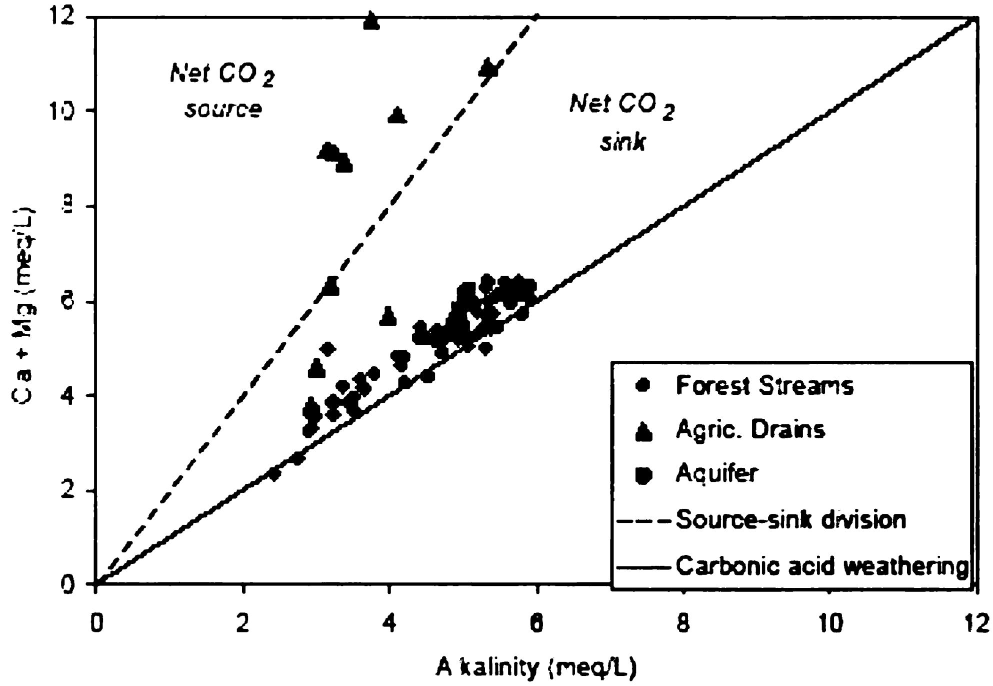


Figure 137: Calcium plus magnesium vs. alkalinity plots for surface waters in Michigan. (Hamilton, unpublished data). Note the concentration of calcium and magnesium (~6 meq/L) and total alkalinity (~6 meq/L), which are similar in concentration to Replicates T2-R3 and T4-R3 (Figure 132).

	T6-R5	T2-R5	T3-R5
T5-R5	T1-R5	T7-R5	T4-R5
T1-R1	T2-R2 (43)	T2-R3 (277)	T3-R4 (13)
T7-R1	T3-R2 (25)	T4-R3 (238)	T2-R4 (50)
T5-R1	T4-R2 (16)	T7-R3 (32)	T1-R4 (84)
T3-R1	T5-R2 (25)	T6-R3 (153)	T4-R4 (14)
T4-R1	T1-R2 (15)	T3-R3 (73)	T6-R4 (17)
T2-R1	T6-R2 (26)	T5-R3 (52)	T7-R4 (23)
T6-R1	T7-R2 (30)	T1-R3 (15)	T5-R4 (13)

(#) = mg/L HCO_3^-

T#-R# = Treatment - Replicate

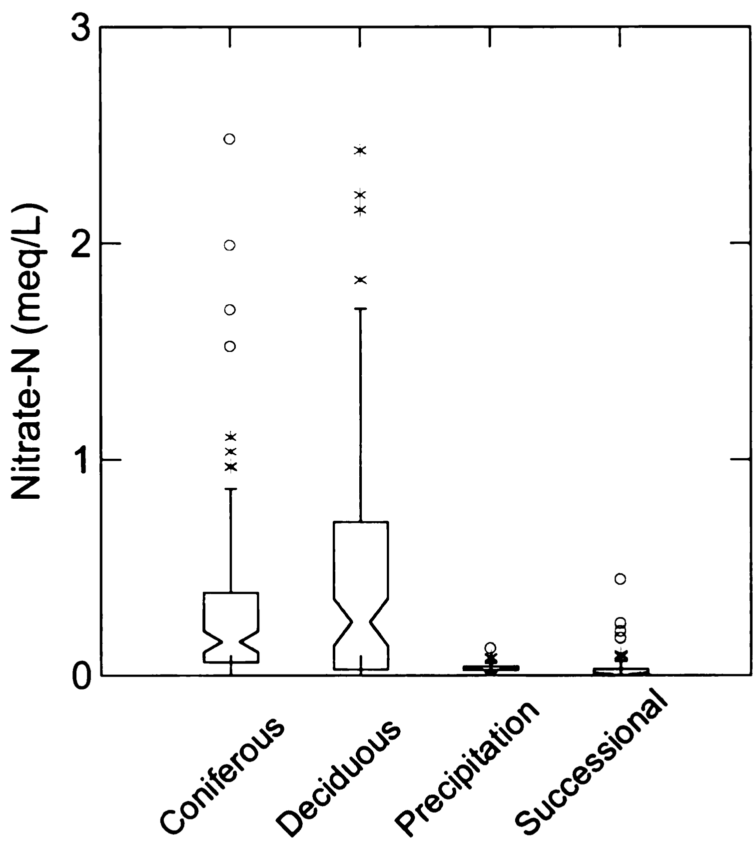
= Soil solution samplers are not present in these Treatment - Replicates; no soil solution sample available.

= Replicate exhibiting higher bicarbonate concentrations in soil solution samples relative to other two replicates within the same treatment.

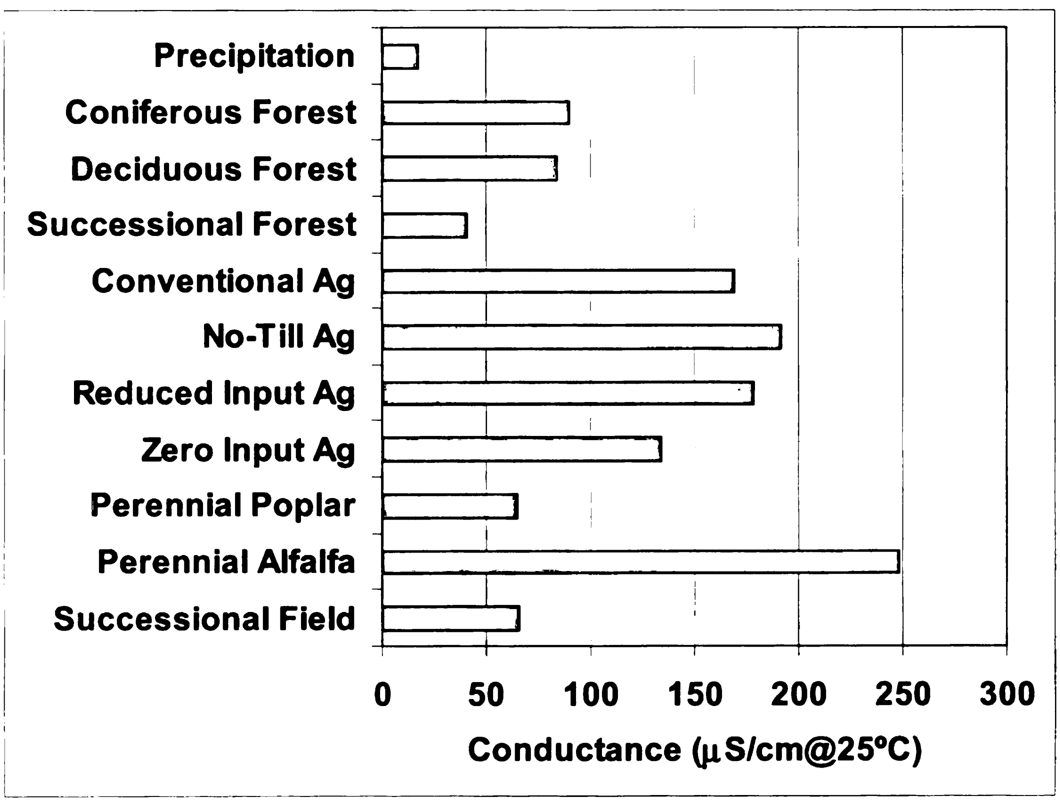
Figure 138: Median soil solution concentrations of alkalinity (mg/L) plotted spatially.

Figure 139, Top: Notched box plots for nitrate across forested treatments, including precipitation. The notches indicate the approximate 95% confidence intervals around the median.

Figure 139, Bottom: Bar chart of median conductivity for all treatments and precipitation.



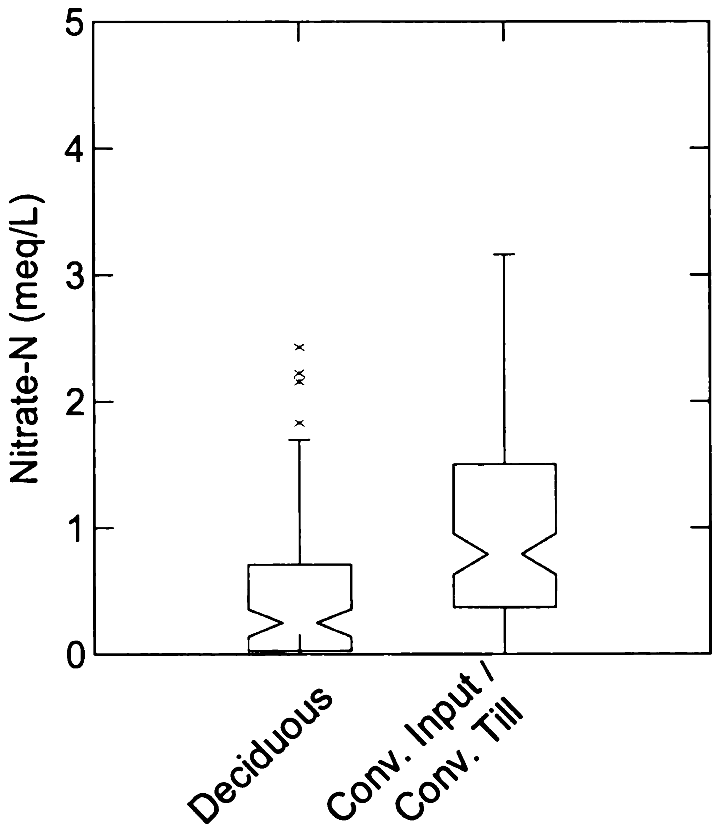
Nitrate-N (meq/L)
0
1
2
3
Coniferous
Deciduous
Precipitation
Successional



Precipitation
Coniferous Forest
Deciduous Forest
Successional Forest
Conventional Ag
No-Till Ag
Reduced Input Ag
Zero Input Ag
Perennial Poplar
Perennial Alfalfa
Successional Field
0
50
100
150
200
250
300
Conductance (μS/cm@25°C)

Figure 140, Top: Notched box plots for nitrate showing the Deciduous Forest treatment and the Conventional Input / Conventional Till treatment. The notches indicate the approximate 95% confidence intervals around the median. 6 cases were excluded by making the graph range less than the data range.

Figure 140, Bottom: Notched box plots for nitrate showing the Conventional Input / Conventional Till treatment and the Conventional Input / No-Till treatment. The notches indicate the approximate 95% confidence intervals around the median.


5
4
3
2
1
0
Nitrate-N (meq/L)
Deciduous
Conv. Input / Conv. Till

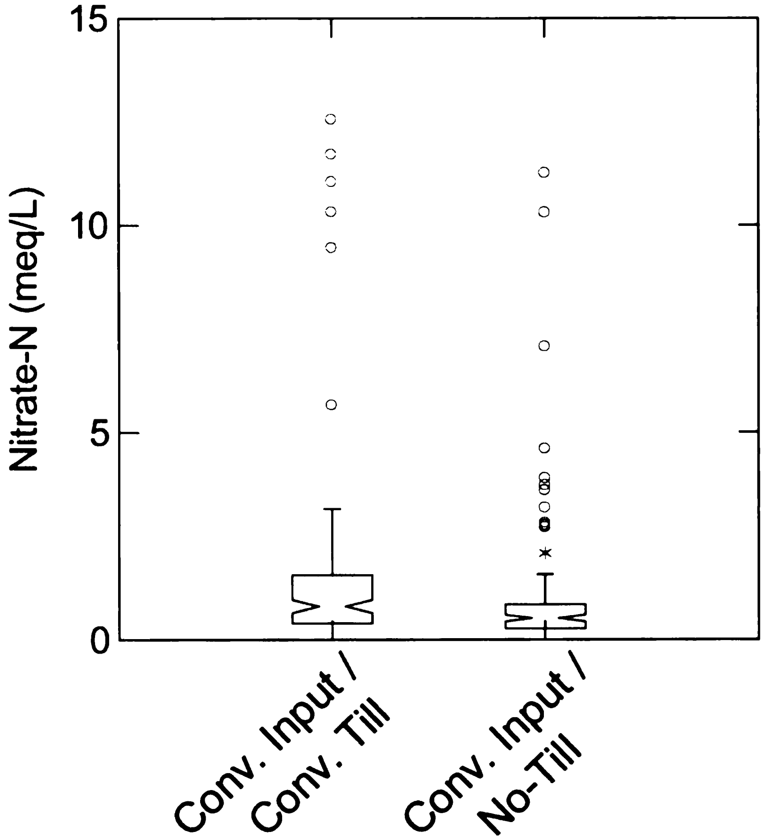
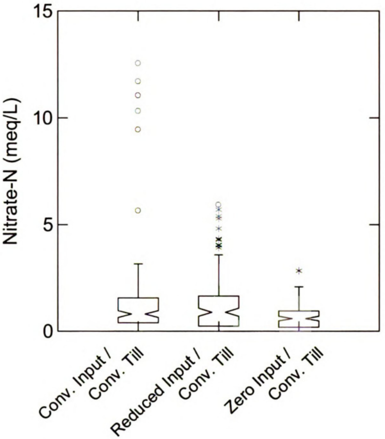
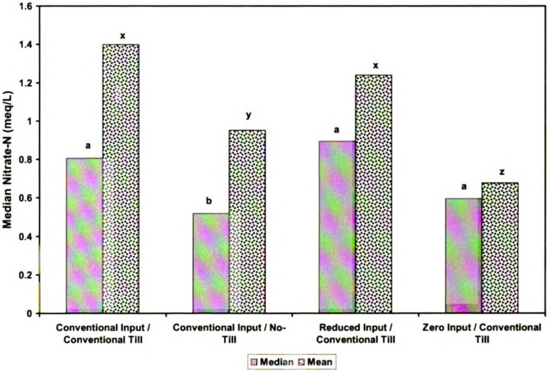

15
10
5
0
Nitrate-N (meq/L)
Conv. Input / Conv. Till
Conv. Input / No-Till

Figure 141, Top: Notched box plots showing the effect of varying levels of input on nitrate concentrations. The notches indicate the approximate 95% confidence intervals around the median.

Figure 141, Bottom: Column chart showing the elevation of treatment means relative to medians as a result of outliers. Where letters are different, significant differences between means or medians exist pursuant to the results of notched box plots (medians) or Fisher's (protected) LSD test (means).



Nitrate-N (meq/L)
15
10
5
0
Conv. Input / Conv. Till
Reduced Input / Conv. Till
Zero Input / Conv. Till



Median Nitrate-N (meq/L)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
a
x
b
y
a
x
a
z
Conventional Input / Conventional Till
Conventional Input / No-Till
Reduced Input / Conventional Till
Zero Input / Conventional Till
Median
Mean

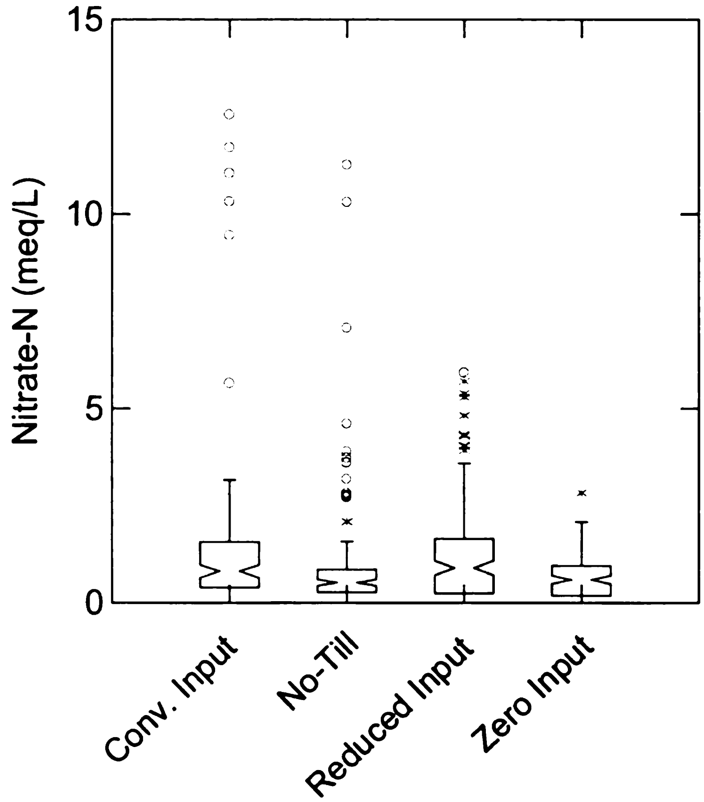


Figure 142: Notched box plots showing the effect of conventional, reduced input, zero input (organic), and no-till treatments on nitrate concentrations. The notches indicate the approximate 95% confidence intervals around the median.

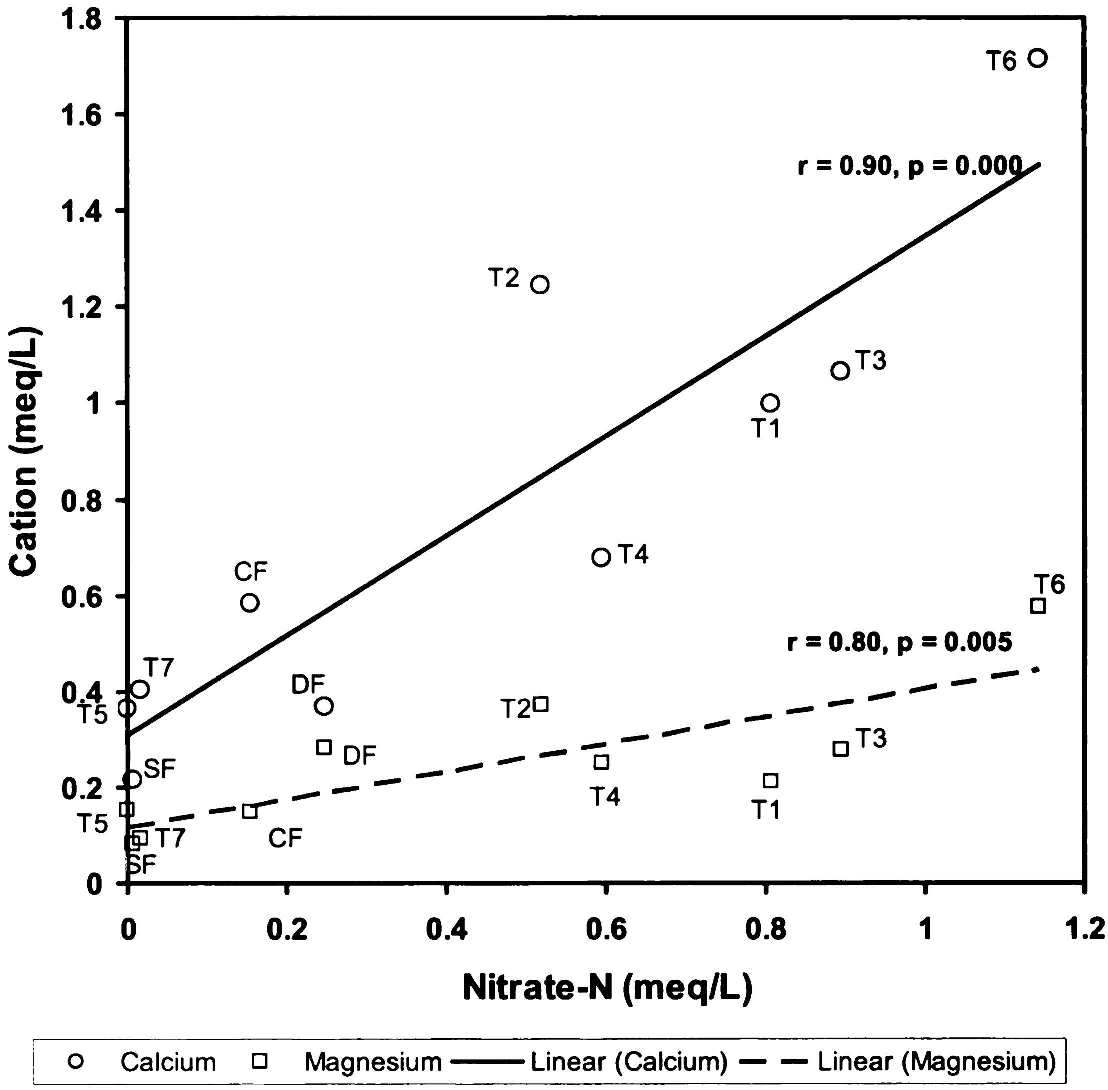


Figure 143: Median soil solution concentrations of calcium and magnesium plotted against nitrate-N by treatment. As the concentration of nitrate-N increase, the concentration of calcium and magnesium in the soil solution also increases.