



All Theses and Dissertations

2013-12-01

Importance of Placement Depth in Evaluating Soil Nitrogen, Phosphorus, and Sulfur Using Ion Exchange Resin Capsules in Semi-Arid, Low Fertility Soils

Rachel Lynn Buck

Brigham Young University - Provo

Follow this and additional works at: <https://scholarsarchive.byu.edu/etd>



Part of the [Animal Sciences Commons](#)

BYU ScholarsArchive Citation

Buck, Rachel Lynn, "Importance of Placement Depth in Evaluating Soil Nitrogen, Phosphorus, and Sulfur Using Ion Exchange Resin Capsules in Semi-Arid, Low Fertility Soils" (2013). *All Theses and Dissertations*. 4293.

<https://scholarsarchive.byu.edu/etd/4293>

This Thesis is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in All Theses and Dissertations by an authorized administrator of BYU ScholarsArchive. For more information, please contact scholarsarchive@byu.edu, ellen_amatangelo@byu.edu.

Importance of Placement Depth in Evaluating Soil Nitrogen, Phosphorus, and Sulfur Using Ion
Exchange Resin Capsules in Semi-Arid, Low Fertility Soils

Rachel L. Buck

A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of
Master of Science

Bryan Hopkins, Chair
Von Jolley
Richard Terry
Brad Geary

Department of Plant and Wildlife Sciences

Brigham Young University

December 2013

Copyright © 2013 Rachel L. Buck

All Rights Reserved

ABSTRACT

Importance of Placement Depth in Evaluating Soil Nitrogen, Phosphorus, and Sulfur Using Ion Exchange Resin Capsules in Semi-Arid, Low Fertility Soils

Rachel L. Buck

Department of Plant and Wildlife Sciences, BYU
Master of Science

Ion exchange resin capsules provide a possible alternative to conventional soil testing procedures. Previous studies with semi-arid, low fertility soils observed poor relationships with poorly mobile nutrients such as phosphorus (P). We propose that placement depth may improve those relationships. Our objective was to (1) determine if placement depth could improve resin capsule estimation of the bioavailability of nitrogen (N), P, and sulfur (S) and (2) to determine if resin capsules can effectively estimate S availability in semi-arid, low fertility soils. Field sites were established in Rush and Skull Valleys, Utah on loam and sandy loam soils, respectively. Fertilizer was surface applied as ammonium sulfate and triple superphosphate with six N, P and S treatments (0, 5.5, 11, 22, 44 and 88 kg ha⁻¹ of N and P₂O₅ and 0, 7, 14, 28, 56 and 112 kg ha⁻¹ of S). Thirty 4.0-m² plots were established at each field location. Resin capsules were placed three per plot at 0–5, 5–10, and 10–15 cm deep in the soil and soil samples taken at respective depths. The capsules were removed and replaced after approximately 90 d. Final removal and soil sampling occurred approximately 240 d later. For the second study, fertilizer was surface applied as ammonium sulfate with six S treatments (0, 7, 14, 28, 56 and 112 kg ha⁻¹ of S) with one resin capsule placed in each 4.0-m² plot at a depth of 5 cm in the soil. Resin capsules were removed and replaced approximately every 90 d for a total of four samplings. Soil samples were taken with every resin capsules install and removal.

In the first study, bicarbonate extractable P was significantly related to P application at all depths and times except the two lowest depths at the time of final sampling, and resin capsule P was only related to P application 398 days after application in the 0–5 and 5–10 cm depths. However, this is an improvement in estimates of bioavailability compared to a single placement depth. The 5–10 cm depth was the best for placement for determination of NH₄-N, and resin capsules improved upon soil test estimates. For NO₃-N, depth was not important, but resin capsules had a stronger relationship with N applied than the soil test 398 d after application. In addition, both resin capsules and the S soil test were related to S applied, but resin capsules were more able to pick up S cycling through the system. In the second study resin capsules and conventional soil tests were both effective in distinguishing between fertilizer rates, though only the conventional soil test was related to S applied at the last sampling (366 d after fertilizer application). Overall resin capsules were effective at reflecting application rates, and may be a good tool to estimate nutrient bioavailability. Correlation with plant uptake is required to determine if soil tests or resin capsules were a better estimate of bioavailable nutrients.

Keywords: adsorption, desert soil, nitrogen, phosphorus, sulfur, plant available nutrients, resin capsule

ACKNOWLEDGEMENTS

I would first like to thank Dr. Hopkins and my graduate committee for their advice, patience, and encouragement through my pursuit of a Master's degree. I am especially grateful for Bruce Webb, Von Jolley, and Mary Jones who were crucial to the design and completion of this project. Bruce Roundy and Nathan Cline provided the field sites we used, precipitation, and soil moisture data, without which this project would be impossible. Thanks also to the many lab employees who assisted in collecting samples in the field and completing laboratory analysis and the BYU Environmental Analytical Lab for providing funding and support. Finally, thanks to my husband Josh for being incredibly supportive throughout this program.

TABLE OF CONTENTS

TITLE PAGE	i
ABSTRACT	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
Chapter 1: Depth of ion exchange resin capsule placement impacts on estimation of nitrogen, phosphorus, and sulfur bioavailability in semi-arid, low fertility soils	1
Abstract	2
Introduction	3
Materials and Methods	6
<i>Field Experiments</i>	6
<i>Soil Nutrient and Statistical Analyses</i>	7
Results and Discussion	8
Conclusion	13
References	14
Chapter 2: Comparing traditional soil tests with ion exchange resin capsules for determination of bioavailability of sulfur in semi-arid, low fertility soils	23
Abstract	24
Introduction	25
Materials and Methods	27
<i>Field Experiment 1</i>	27
<i>Field Experiment 2</i>	28
<i>Soil Nutrient and Statistical Analyses</i>	28
Results and Discussion	29
<i>Field Experiment 1</i>	29
<i>Field Experiment 2</i>	30
Conclusion	32
References	33

APPENDIX.....	42
Laboratory Procedures	43
<i>Resin Capsules</i>	43
<i>Ammonium (NH₄-N) and Nitrate (NO₃-N) by Lachat</i>	44
<i>P Available (Olsen Bicarbonate Method)</i>	45
<i>Sulfate-S—500 ppm P Monocalcium Phosphate</i>	47

LIST OF TABLES

1.1 Selected characteristics of loam (Rush Valley) and sandy loam (Skull Valley) soils at the two field sites (Utah, USA).....	17
1.2 Precipitation distribution (in cm) during the period of experiments (May 2009–May 2011) at Rush Valley and Skull Valley (Toole County, Utah, USA).....	18
1.3 Number of days with soil water potential greater than -1.5 MPa (moist) at two depths (1–3 and 13–15 cm) during the field experiments (March 2010–May 2011) at Rush Valley and Skull Valley (Tooele County, Utah, USA).....	19
2.1 Selected characteristics of loam (Rush Valley) and sandy loam (Skull Valley) soils at the two field sites (Utah, USA).....	36
2.2 Precipitation distribution (in cm) during the period of experiments (May 2009–May 2011) at Rush Valley and Skull Valley (Toole County, Utah, USA).....	37
2.3 Wet days (soil water potential greater than -1.5 MPa) at the soil surface (1–3 cm) during the period of the first field experiment (May 2009–May 2010) at Rush Valley and Skull Valley (Toole County, Utah, USA).....	38
2.4 Wet days (soil water potential greater than -1.5 MPa) at two depths (1–3 and 13–15 cm) during the period of the second field experiment (March 2010–May 2011) at Rush Valley and Skull Valley (Toole County, Utah, USA).....	39

LIST OF FIGURES

1.1 Resin and KCl-extracted soil $\text{NH}_4\text{-N}$ measurements after application of 0, 5.5, 11, 22, 44, and 88 kg ha^{-1} N; fertilizer applied March 2010 (values represent the mean of two locations).....	20
1.2 Resin and KCl-extracted soil $\text{NO}_3\text{-N}$ measurements after application of 0, 5.5, 11, 22, 44, and 88 kg ha^{-1} N; fertilizer applied March 2010 (values represent the mean of two locations).....	21
1.3 Resin and NaHCO_3 -extracted soil P measurements after application of 0, 5.5, 11, 22, 44, and 88 kg ha^{-1} P; fertilizer applied March 2010 (values represent the mean of two locations).....	22
2.1 Resin (A) and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -extracted (B) S measurements after application of 0, 7, 14, 28, 56, and 112 kg ha^{-1} S; fertilizer applied 13 May 2009. Values represent the average of two locations (Rush Valley and Skull Valley).....	40
2.2 Resin and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -extracted S measurements after application of 0, 7, 14, 28, 56, and 112 kg ha^{-1} S; fertilizer applied 23 March 2010. Values represent the average of two locations (Rush Valley and Skull Valley).....	41

Chapter 1: Depth of ion exchange resin capsule placement impacts on estimation of nitrogen, phosphorus, and sulfur bioavailability in semi-arid, low fertility soils

Rachel L. Buck, Bryan G. Hopkins¹, Bruce L. Webb, and Von D. Jolley.

Department of Plant and Wildlife Sciences, Brigham Young University, Provo, UT 84602, USA

¹Corresponding author, 251 WIDB, Provo, Utah, 84602, USA, email: hopkins@byu.edu, Tel: 801-422-2185, Fax: 801-422-0008

Abstract

Ion exchange resin capsules provide a possible alternative method to conventional soil testing procedures. Previous studies with semi-arid, low fertility soils observed poor relationships with poorly mobile nutrients such as phosphorus (P). We propose that additional placement depths may improve those relationships. Field studies were established in Rush and Skull Valleys, Utah on loam and sandy loam soils, respectively. Nitrogen (N) and P (0, 5.5, 11, 22, 44 and 88 kg ha⁻¹ N and P₂O₅) were broadcast applied and lightly raked into soil on March 23, 2010 as ammonium sulfate and triple superphosphate. Resin capsules were placed in the soils on June 15, 2010 at depths of 0–5 cm, 5–10 cm, and 10–15 cm. The capsules were removed and replaced September 13, 2010 and removed for the last time on May 4, 2011. Soil samples were taken at the same depths and times whenever capsules were installed or removed. Overall, the 5–10 cm depth was the best for placement for determination of NH₄-N, and resin capsules improved upon soil test estimates. For NO₃-N, depth was not important, but resin capsules had a stronger relationship with N applied than the soil test 398 d after application. Bicarbonate extractable P was significantly related to P application at all depths and times except the two lowest depths at the time of final sampling, and resin capsule P was only related to P application 398 days after application in the 0–5 and 5–10 cm depths. However, this is an improvement in estimates of bioavailability compared to a single placement depth. Soil moisture should be carefully monitored when using resin capsules to access P availability in semi-arid soils.

Introduction

Nutrient uptake by plants is impacted by a wide variety of soil chemical, physical, and biological (plant and microbial) processes. These processes include solubilization of minerals, mineralization of soil organic matter (OM), biological organism decay, reduction, active ion pumping, exudation of chelates, protons, reductants, root interception, mass flow driven by transpiration rates, and diffusion. Traditional soil testing only partially mimics one of these processes (solubilization), but the soil testing thrives based on the idea is that a correlation can be established between the extraction and nutrient uptake. Despite imperfections of traditional soil testing in estimating nutrient availability, the correlation with plant nutrient status can be very good in some cases, but, very poor in others.

Ion exchange resin technology offers a potential improvement over traditional soil testing in that it theoretically simulates additional plant nutrient uptake processes, namely diffusion and some interactions with roots, microbes, and other soil organisms. Besides being impacted by actual soil physical and chemical properties, resin capsules make analysis procedures easy and cost effective because multiple nutrients can be extracted simultaneously (Qian and Schoenau, 2002). Additionally, Yang et al. (1991) stated that the majority of soil tests used for extracting nutrients with chemical solutions provide only an index of true nutrient availability, while resin capsules provide a better index of relative nutrient availability and consistency over a wider range of soil types.

Ion exchange resin capsules have been used for over four decades as an alternative method to conventional soil testing (Skogley, 1966; Vaidyanathan and Nye, 1966) and are of renewed interest in modern agriculture use as well (Laboratory Analysis Workshop, Prosser, Washington, May 2013). Mixed-bed ion exchange resin capsules (2 cm diameter) contain resin

beads encapsulated with an elliptical mesh screen. The internal surface area of resin beads can exceed $10^5 \text{ m}^2 \text{ kg}^{-1}$, giving resin capsules a higher cation exchange capacity than many soil colloids. But unlike soil colloids, which have high negative and low positive charge, this high surface area exhibits both positive and negative charges and, as such, acts as a sink for both cations and anions. In general, resin beads will function as a sink for any ion for which the capsule has a greater affinity than the counterion initially present on the resin (Skogley and Dobermann, 1996). Ion exchange counterions found in resin capsules vary, but common combinations include hydrogen/hydroxyl (H^+/OH^-), hydrogen/chloride (H^+/Cl^-), and sodium/bicarbonate ($\text{Na}^+/\text{HCO}_3^-$) (Sherrod et al., 2003).

Because resin capsules act as a continuous sink for nutrients, it is possible to assess the nutrient supplying capacity of a soil over either short, intermediate or long periods of time, in contrast to conventional soil testing which characterize a single point in time (Jones et al., 2012). Since almost no soil is removed with the resin capsule unlike soil sampling, their use allows for multiple placements at specific points (i.e. depths or locations) in the soil over time (Johnson et al., 2005). In addition, *in situ* use of resin capsules minimizes physical and chemical disturbance of the soil after initial placement (Dobermann et al., 1997). Resin capsules placed in the field would be impacted by biological functions (such as microbial and plant root exudates) as well as actual soil physical and chemical properties. Ion exchange occurs through both film diffusion and particle diffusion. Film diffusion occurs when ions in the soil solution surrounding the resin bead exchange for counterions on the surface of the resin bead. In response to ions exchanging at the resin surface, particle diffusion will occur through the countermovement of ions within the resin beads. It is important to recognize that besides diffusion through soil media, final resin capsule nutrient concentrations will reflect differences in initial solute concentrations, nutrient

release rates from solid phases (soil minerals and organic matter), movement of ions toward the resin via gravitational solution transfer, mass flow (if capsule is near roots drawing in water), and other dynamics (Skogley and Dobermann, 1996).

As with any technology used to assess nutrient availability, there are a number of disadvantages with resin capsule use to determine nutrient availability for plants: two trips to field sites for placement and then removal, possible interference by burrowing/digging organisms, and each capsule only represents a finite spatial measurement. In contrast, traditional soil sampling requires just one trip to a field site and more easily allows measurement of an average spatial value across a landscape and by depth. In addition, resin capsules are sensitive to soil water status and temperature, as well as possible competition from microorganisms and roots for nutrients. In an incubation study, Johnson et al. (2005) found that both higher temperature and moisture conditions resulted in significant, positive effects on resin capsule mineral nitrogen (N). They suggested that because the soil solution is a major vector of contact between soil exchange sites and resin surfaces, resin capsules will not be especially accurate indices of soil mineral N in dry conditions.

Additionally, research on the use of resin capsules in field conditions has focused on evaluating N, phosphorus (P), potassium (K), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) in highly fertile soils, which creates questions about the validity of their use in low fertility or dry soils (Sherrod et al., 2002). In a field study conducted on low fertility, semi-arid soils, Jones et al. (2013b) found that resin capsule nitrate-N ($\text{NO}_3\text{-N}$) and ammonium-N ($\text{NH}_4\text{-N}$) had predictable relationships with N application rates, but the traditional soil test procedure of KCl-extraction of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ better predicted N availability. Furthermore, resin P did not reflect P application rates. It is suspected that the most likely explanation is the lack of

movement of P into the soil layer containing the resin capsule (five cm placement depth) due to poor mobility of P and low moisture levels. Before recommending against use of resin capsules in semi-arid, low fertility soils, an evaluation of shallower placement of resin capsules than used by Jones et al. (2013b) needs to be tested for P determination. Spatial variation is highest for nutrients affected by redox processes and microbial transformations, such as N, P, and Fe (Dobermann et al., 1997), thus, placement depth could be an important factor in resin capsule absorption of these elements.

Our objective was to determine if depth of placement could improve resin capsule estimates of P and N in low fertility, semiarid zone soils. We hope to find a methodology for field use of resin capsules in semi-arid zone soils that is effective and repeatable in reference to N and P determination.

Materials and Methods

Field Experiments

Field studies were conducted southwest of the Great Salt Lake in Rush Valley (40°8'16"N and -112°30'26"W, 1676 m) and Skull Valley (40°18'27"N and -112°50'3"W, 1524 m), Tooele County, Utah, USA on low fertility loam and sandy loam soils, respectively (Table 1.1). Annual precipitation classifies these areas as semi-arid (Table 1.2). Use of previously fenced field sites prevented free range livestock from disturbing the study area. Each site was divided into thirty 4.0-m² plots per site which received surface application of N and P at six rates (0, 5.5, 11, 22, 44, and 88 kg ha⁻¹ N and P₂O₅) with five replications of each treatment in a completely randomized block design. Nitrogen was applied as granular ammonium sulfate [(NH₄)₂SO₄; 21-0-0-24(S)] and P as granular triple superphosphate [Ca(H₂PO₄)₂; 0-45-0] on 23

March 2010. Light raking was used to incorporate the fertilizer into the soil to a depth of approximately 0.5 to 1.0 cm.

Resin capsules were prepared for placement in the field by attaching plastic string (60 cm in length) to which colored plastic (3 cm²) was attached to make capsules easier to find after burial (Jones et al., 2013b). Three mixed bed (H⁺/OH⁻) resin capsules were placed into each plot at depths of 0–5, 5–10, and 10–15 cm on 15 June 2010 (84 d after fertilization). Resin capsules were removed and a majority of surrounding soil was detached on 13 September 2010 (166 d after fertilization; 82 d after resin capsule insertion); for analysis and replaced at similar depths with fresh capsules. Soil samples were also taken at 0–5, 5–10, and 10–15 cm depths. Resin capsules were again removed and a final set of soil samples taken on 4 May 2011 (398 d after initial fertilization and 233 d after resin capsule insertion).

Soil Nutrient and Statistical Analyses

After field removal and initial soil detachment, capsules were placed in sealed plastic bags and stored at ~5°C until analyses were performed. After 14 to 21 d storage, soil was removed from each capsule by rinsing briefly with distilled water. The P, NO₃-N, and NH₄-N were extracted from resin capsules by washing each capsule three times successively using 20 mL of 2 M hydrochloric acid (HCl) (Skogley et al., 1997; Jones et al., 2012). The extract (total of 60 mL) was then analyzed using flow injection analysis (Quick Chem 8500, Lachat Instruments, Loveland, Colorado, USA) for NO₃-N and NH₄-N and inductively coupled plasma spectroscopy (Iris Intrepid II XSP, ICP-OES, Thermo Electron Corporation, Franklin, Maryland, USA) for P. Concentration of NO₃-N was determined using the cadmium reduction method (Keeney and Nelson, 1982) and concentration of NH₄-N was determined by the sodium salicylate–sodium nitroprusside method (Rowland, 1983).

Immediately after transport to the laboratory, conventional soil samples were air dried and flail ground to pass a 2 mm sieve. The soil $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were extracted with 2 M potassium chloride (KCl, referred to as KCl-extracted $\text{NO}_3\text{-N}$ and KCl-extracted $\text{NH}_4\text{-N}$) and the concentration determined as described above. Phosphorus was extracted with 0.5 M sodium bicarbonate (NaHCO_3) and quantified using the ammonium molybdate–ascorbic acid method (Olsen et al., 1954).

Field location was designated as a random variable for statistical analysis. Statistical analysis by generalized liner model (GLM) with mean separation by Duncan-Waller K Ratio Test was performed using SAS 9.3 (SAS Institute, 2011, Cary, North Carolina, USA). Means were subjected to regression analysis (PROC REG) also with SAS.

Results and Discussion

Resin capsule $\text{NH}_4\text{-N}$ was significantly correlated to N application during the first sampling period at all depths (Figure 1.1A). The effect continued through the next sampling period for the upper two depths, however, the quantity of $\text{NH}_4\text{-N}$ measured in resin capsules declined considerably by May 2011 and relationship between applied N and resin $\text{NH}_4\text{-N}$ was not as strong (Figure 1.1B). The KCl-extracted $\text{NH}_4\text{-N}$ was also significantly related to N applied at all depths on June and September 2010 (the days when resin capsules were placed at the beginning of both sampling periods (Figure 1.1C and 1.1D). Soil quantities and correlations had declined considerably by May 2011 (Figure 1.1E). One might expect relationships between N applied and $\text{NH}_4\text{-N}$ in soil or resin capsule to decline in later sampling periods, especially in these highly alkaline conditions. Nitrification would convert $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ as soon as warm, moist soil conditions prevail. Also, in calcareous soils, resin- H^+ reacts with CaCO_3 to form CO_2

and HCO_3^- . A large quantity of Ca^{2+} accumulated by the resin will affect both K^+ and NH_4^+ adsorption when the resin is in the soil for long periods of time (Qian and Shoenau, 2002). However, there were still significant relationships between resin capsule $\text{NH}_4\text{-N}$ with N application through the September–May sampling period (Figure 1.1B) in the 0–5 and 5–10 cm depths. A few of the regressions between N rate and $\text{NH}_4\text{-N}$ were improved by curvilinear expression of those relationships (Figure 1.1A, 1.1C, and 1.1D); however the majority are best and adequately predicted using linear regression and to be consistent with the majority of the other graphs, all were presented linearly. This curvilinear relationship is seen only with $\text{NH}_4\text{-N}$ (not $\text{NO}_3\text{-N}$ or P with either resin or soil sampling) which could be due to nitrification and release of native N augmenting N to keep up with the rate of N applied, except at the highest rate (88 kg N ha^{-1}). The spike in $\text{NH}_4\text{-N}$ concentration at the highest treatment only occurred at the surface (Figure 1.1A, 1.1C, and 1.1D) which is not surprising as $\text{NH}_4\text{-N}$ is not as mobile as $\text{NO}_3\text{-N}$ in the soil and there was very little precipitation during this time (Table 1.2).

Potassium chloride-extracted $\text{NH}_4\text{-N}$ from the soil samples taken in May 2011 was not related to N application rate (Figure 1.1E). The sampling took place 398 d after fertilizer application, and the soil test $\text{NH}_4\text{-N}$ represents only a single point in time. It is likely that by May 2011 the NH_4^+ applied was used by plants and/or converted to NO_3^- via nitrification or, less likely, lost to volatilization. In contrast, resin capsule $\text{NH}_4\text{-N}$ represents a cumulative amount adsorbed during the sampling period, explaining why there were still significant relationships in the resin capsules taken out a year after fertilizer was applied (Figure 1.1B). Similarly, Johnson et al. (2005) found that while soil mineral N either remained constant or declined slightly during the second and third incubation periods (56 and 84 d, respectively) in their study, resin capsules showed increases in ammonium-N recovery. Additionally, in an irrigated glasshouse study with

native Utah soils and squirreltail grass, Jones et al. (2013a) found that $\text{NH}_4\text{-N}$ extracted from resin capsules was related closely to yield, total N removal of squirreltail grass, and rate of fertilizer N applied while KCl-extractable $\text{NH}_4\text{-N}$ was not. In our current study, resin capsule $\text{NH}_4\text{-N}$ improved upon KCl-extracted estimates of $\text{NH}_4\text{-N}$ to reflect N application rates, giving a good correlation to N applied even a year after fertilizer application. While significant relationships were found at all depths, the 5–10 cm depth (middle) clearly produced the best correlation to N applied at both sampling times and, as such, is recommended for use in semi-arid soils.

Resin capsule $\text{NO}_3\text{-N}$ was low in all three depths in the June to September 2010 sampling period yet also highly correlated to N application rate (Figure 1.2A). Surprisingly the $\text{NO}_3\text{-N}$ values were high as well as highly correlated to N application rate at all three depths in the September 2010 to May 2011 sampling period (Figure 1.2B). The low $\text{NO}_3\text{-N}$ and concurrent high $\text{NH}_4\text{-N}$ measured in resin capsules in June to September sampling period and the high $\text{NO}_3\text{-N}$ and low $\text{NH}_4\text{-N}$ may be explained by low precipitation June to September 2010 (Table 1.2) and the relatively few days with moisture content above -1.5 MPa (Table 1.3). Active plant growth would have begun as early as April 2010 and continued, albeit slowly, through September 2010 and that growth could have absorbed $\text{NO}_3\text{-N}$ released by nitrification during that period resulting in low resin $\text{NO}_3\text{-N}$ and high resin $\text{NH}_4\text{-N}$. There could have been rapid nitrification and conversion of NH_4^+ to NO_3^- in fall of 2010 resulting in low resin $\text{NH}_4\text{-N}$ and high resin $\text{NO}_3\text{-N}$ by May 2011. There was not a curvilinear relationship with $\text{NO}_3\text{-N}$ responses as there was for $\text{NH}_4\text{-N}$ (Figure 1.2 and 1.2). The KCl-extracted $\text{NO}_3\text{-N}$ was related to N application in June and September 2010 at all depths (Figure 1.2C and 1.2D) but only at the lowest depth by May 2011 (Figure 1.2E). This is not surprising because the final soil sampling

occurred a year after fertilizer application, giving the $\text{NO}_3\text{-N}$ ample time to be utilized by plants, leached from the soil profile, and/or denitrified. In contrast, resin capsules were able to capture NO_3^- over the time frame measured. In a study about detecting NO_3^- leaching through bypass flow, Pampolino et al. (2000) found that resin capsules were able to continuously intercept a representative amount of NO_3^- and suggested that resin capsules were a promising technique for NO_3^- leaching measurements. In our study, it is interesting that, while the concentration of KCl-extracted soil $\text{NO}_3\text{-N}$ decreases over the three sampling times, the resin capsule $\text{NO}_3\text{-N}$ increases dramatically from the first (June–September 2010) to the second sampling period (September 2010–May 2011; Figure 1.2A and 1.2B). Perhaps this can be explained by the fact that there was more available soil moisture from Sept 2010–May 2011 than from June–Sept 2010 (Table 1.3), and soil moisture has significant, positive effects on resin capsule $\text{NO}_3\text{-N}$ (Johnson et al., 2005). There was more KCl-extracted $\text{NO}_3\text{-N}$ in the surface than the lower depths at the June 2010 sampling (Figure 1.2C); however, the resin capsule $\text{NO}_3\text{-N}$ was very close in concentration at all three depths (Figure 1.2A). Our results are in agreement with Jones et al. (2013b) who found that resin $\text{NO}_3\text{-N}$ was strongly correlated to N application rates—suggesting that resin capsules may be effective in assessing mobile nutrient status in semi-arid land soils even if the nutrient is not mixed directly into the zone of placement.

Resin capsule P was not related to P application rates at any depth for the resin capsules buried from June–Sept 2010 (Figure 1.3A), but was highly correlated to P application in the 0–5 and 5–10 cm depths during the September 2010 to May 2011 sampling period (Figure 1.3B). The poor early relationship may be associated with low precipitation (Table 1.2; June–Sept 2010; Rush Valley, 4.1 cm; Skull Valley, 2.7 cm) and, thus, minimal dissolution and/or diffusion of P to promote adsorption of P from solution by resin capsules. The high correlations observed over

a period of relatively higher precipitation (September 2010–May 2011) in the 0–5 and 5–10 cm depths supports resin capsule use in semi-arid soils but also points out the need to follow moisture relationships when interpreting resin capsule P data in such environments. This suggests that moisture is an important factor for P diffusion into resin capsules. In a laboratory incubation study, Pampolino and Hatano (2000) found a decrease in P adsorption on the resin due to reduced soil moisture. In a previous study with resin capsules buried at 5 cm, Jones et al. (2013b) found that P extracted from resin capsules never reflected P application levels and proposed that the most likely cause was that the P was not moving from the surface where placed into the soil layer containing the resin capsule due to known poor mobility of P and low moisture levels. Our current study supports that conclusion. Additional research is required to find the minimum amount of available moisture required for P to move into resin capsules. The bicarbonate extractable P was highly correlated to P applied in our study at all depths at the first two sampling times (Figure 1.3C and 1.3D) with much lower P tests observed in the 5–10 and 10–15 cm depths than 0–5 cm surface depth where this immobile nutrient was placed. Bicarbonate extractable P declined in the intermediate samplings taken September 2010 and again in the samples taken May 2011 (Figure 1.3C, 1.3D and 1.3E). Bicarbonate extractable P was only related to P rate in the 0–5 cm depth only by May 2011 (Figure 1.3E). This would be expected as soluble applied P is normally fixed by soil chemical reactions that reduce soluble to insoluble or adsorbed forms (Hemwall, 1957). It is interesting that at all three sampling timings, there was clearly more P found at the surface (0–5 cm) than at deeper depths. The high correlation between bicarbonate P and P application rates in the 0–5 cm depth is in complete agreement with a previous study that sampled only the 0–5 cm depth (Jones et al., 2013b).

Conclusion

Resin capsule $\text{NH}_4\text{-N}$ improved upon soil test (KCl-extracted) estimates of $\text{NH}_4\text{-N}$ to reflect N application rates, giving a good correlation to N applied even a year after fertilizer application. The middle depth (5–10 cm) clearly produced the highest correlation to N applied and is recommended for use in semi-arid soils for $\text{NH}_4\text{-N}$ detection. In contrast, placement depth was not an important factor for estimating $\text{NO}_3\text{-N}$ with resin capsules (all depths sampled produced predictable relationships with N applied). Resin capsule $\text{NO}_3\text{-N}$ did improve upon soil test (KCl-extracted) estimates of $\text{NO}_3\text{-N}$ to reflect N application rates when samples were taken 398 d after fertilizer was applied. Placing resin capsules nearer to the surface did improve estimates of P, but only after the soils were moist enough for P mobility to promote equilibrium. Overall, bicarbonate extractable P was better at reflecting rates of P applied, although correlation with plant uptake would be required to determine which of the two would be a better estimate of bioavailable P. Further research is required to define the minimum amount of available moisture required for P movement into resin capsules. Precipitation as well as soil moisture should be carefully monitored if resin capsules are used to assess P availability in semi-arid soils.

References

- Dobermann, A., M. A. A. Adviento, and M. F. Pampolino. 1997. Resin capsules for on-site assessment of soil nutrient supply in lowland rice fields. *Soil Sci. Soc. Am. J.* 61:1202–1213.
- Hemwall, J. B. 1957. The fixation of phosphorus by soils. *In: Advances in Agronomy, Volume 9.* A. G. Norman (ed.). Academic Press Inc, New York, pp. 95–112.
- Johnson, D. W., J. A. Arnone, and P. S. J. Verburg. 2005. Soil extraction, ion exchange resin, and ion exchange membrane measures of soil mineral nitrogen during incubation of a tallgrass prairie soil. *Soil Sci. Soc. Am. J.* 69:260–265.
- Jones, M. P., B. L. Webb, D. A. Cook, and V. D. Jolley. 2012. Comparing nutrient availability in low fertility soils using ion exchange resin capsules. *Commun. Soil Sci. Plant Anal.* 43:368–376.
- Jones, M. P., B. L. Webb, V. D. Jolley, B. G. Hopkins, and D. A. Cook. 2013a. Evaluating nutrient availability in semi-arid soils with resin capsules and conventional soil tests. I. Native plant bioavailability under glasshouse conditions. *Commun. Soil Sci. Plant Anal.* 44:971–986.
- Jones, M. P., B. L. Webb, V. D. Jolley, M. D. Vickery, R. L. Buck, and B. G. Hopkins. 2013b. Evaluating nutrient availability in semi-arid soils with resin capsules and conventional soil tests. II. Field studies. *Commun. Soil Sci. Plant Anal.* 44:1764–1775.
- Keeney, D. R., and D. W. Nelson. 1982. Nitrate by colorimetric methods. *In* A. L. Page (ed.). *Methods of Soil Analysis, Part 2, 2nd Ed.* ASA, CSSA and SSSA, Madison, WI, pp. 676–682.

- Olsen, S. R., C. V. Cole, F. S. Watanabe, and L. A. Dean. 1954. Estimation of available phosphorus in soil by extraction with sodium bicarbonate. USDA Cir. No. 939.
- Pampolino, M. F., and R. Hatano. 2000. Comparison between conventional soil tests and the use of resin capsules for measuring P, K, and N in two soils under two moisture conditions. *Soil Sci. Plant Nutr.* 46:461–471.
- Pampolino, M. F., T. Urushiyama, and R. Hatano. 2000. Detection of nitrate leaching through bypass flow using pan lysimeter, suction cup, and resin capsule. *Soil Sci. Plant Nutr.* 46:703–711.
- Qian, P., and J. J. Schoenau. 2002. Practical applications of ion exchange resins in agricultural and environmental soil research. *Can. J. Soil Sci.* 82:9–21.
- Rowland, A. P. 1983. An automated method for the determination of ammonium-N in ecological materials. *Commun. Soil Sci. Plant Anal.* 14:49–63.
- Sherrod, S. K., J. Belnap, and M. E. Miller. 2002. Comparison of methods for nutrient measurement in calcareous soils: Ion-exchange resin bag, capsule, membrane, and chemical extractions. *Soil Sci.* 167:666–679.
- Sherrod, S. K., M. E. Miller, and J. Belnap. 2003. Comparison of ion-exchange resin counterions in the nutrient measurement of calcareous soils: Implications of correlative studies of plant-soil relationships. *Commun. Soil Sci. Plant Anal.* 34:1981–2001.
- Skogley, E. O. 1966. Ion-exchange resin media: micronutrient levels and response of tomatoes. *Soil Sci.* 102:167–172.
- Skogley, E. O., and A. Dobermann. 1996. Synthetic ion-exchange resins: Soil and environmental studies. *J. Environ. Qual.* 25:13–24.

Skogley, E. O., A. Dobermann, J. E. Yang, B. E. Schaff, M. A. A. Adviento, and M. F.

Pampolino. 1997. Methodologies for resin capsules: capsule storage and ion recovery. *Sci Soils*, 2, <http://www.hintze-online.com/sos/1997/Articles/Art3>.

Vaidyanathan, L. V. and P. H. Nye. 1966. The measurement and mechanism of ion diffusion in soils. II. An exchange resin paper method for measurement of diffusive flux and diffusion coefficient of nutrient ions in soils. *J. Soil Sci.* 17:175–183.

Yang, J. E., B. E. Schaff, A. H. Ferguson, E. O. Skogley, and S. J. Georgitis. 1991.

Phytoavailability soil test: Development and verification of theory. *Soil Sci. Soc. Am. J.* 55:1358–1365.

Table 1.1. Selected characteristics of loam (Rush Valley) and sandy loam (Skull Valley) soils at the two field sites (Utah, USA).

Soil characteristic	Rush Valley, UT	Skull Valley, UT
Textural classification	Loam	Sandy loam
Sand, %	39	65
Silt, %	38	20
Clay, %	23	15
Organic matter, %	2.2	1.0
pH	7.7	7.8
Electrical conductivity, dS m ⁻¹	0.75	0.57
Sodium bicarbonate P, mg kg ⁻¹	13.4	8.4
Sodium bicarbonate K, mg kg ⁻¹	340	220
NO ₃ -N, mg kg ⁻¹	2.0	1.6
Calcium phosphate SO ₄ -S, mg kg ⁻¹	4.4	3.6
Calcium carbonate, %	19.8	9.8

Table 1.2. On site precipitation distribution (cm) during the two field experiments (March 2010–May 2011) at Rush Valley and Skull Valley (Tooele County, Utah, USA).

Period of precipitation	Rush Valley*	Skull Valley*
	---- cm ----	
March to June 2010	5.1	10.2
June to September 2010	1.5	2.3
September 2010 to May 2011	13.1	13.1

*Bruce Roundy, personal communication, 2013

Table 1.3. Number of days with soil water potential greater than -1.5 MPa (moist) at two depths (1–3 and 13–15 cm) during the field experiments (March 2010–May 2011) at Rush Valley and Skull Valley (Tooele County, Utah, USA).

Period of experiments	Rush Valley*		Skull Valley*	
	Depth, cm			
	1–3	13–15	1–3	13–15
	---- d, % of d in period ----			
March to June 2010	41, 48%	49, 58%	57, 67%	79, 93%
June to September 2010	30, 33%	35, 38%	42, 46%	64, 70%
September 2010 to May 2011	171, 73%	176, 75%	168, 72%	185, 79%

*Bruce Roundy, personal communication, 2013

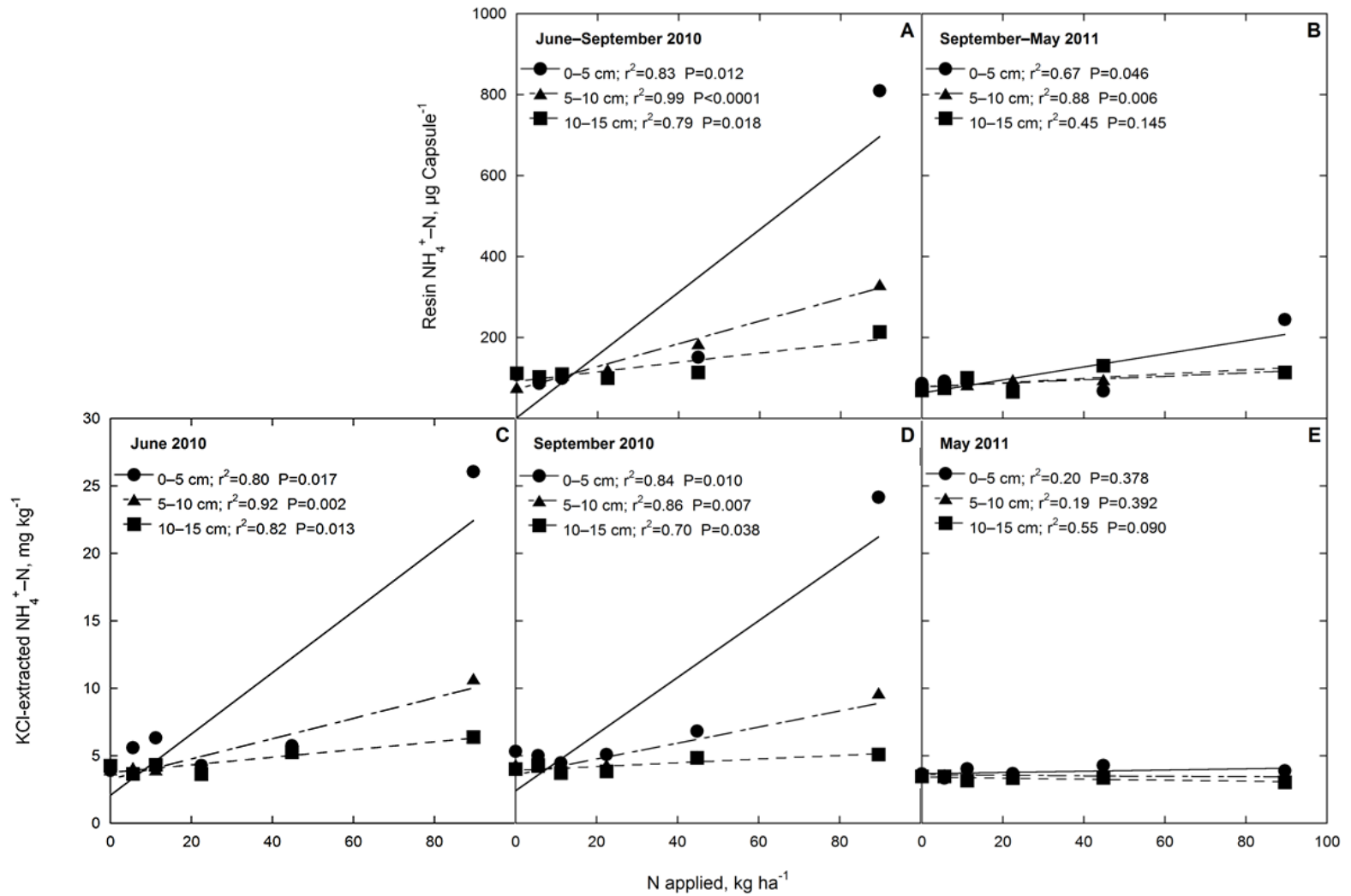


Figure 1.1. Resin and KCl-extracted soil $\text{NH}_4\text{-N}$ measurements after application of 0, 5.5, 11, 22, 44, and 88 kg ha^{-1} N; fertilizer applied March 2010 (values represent the mean of two locations).

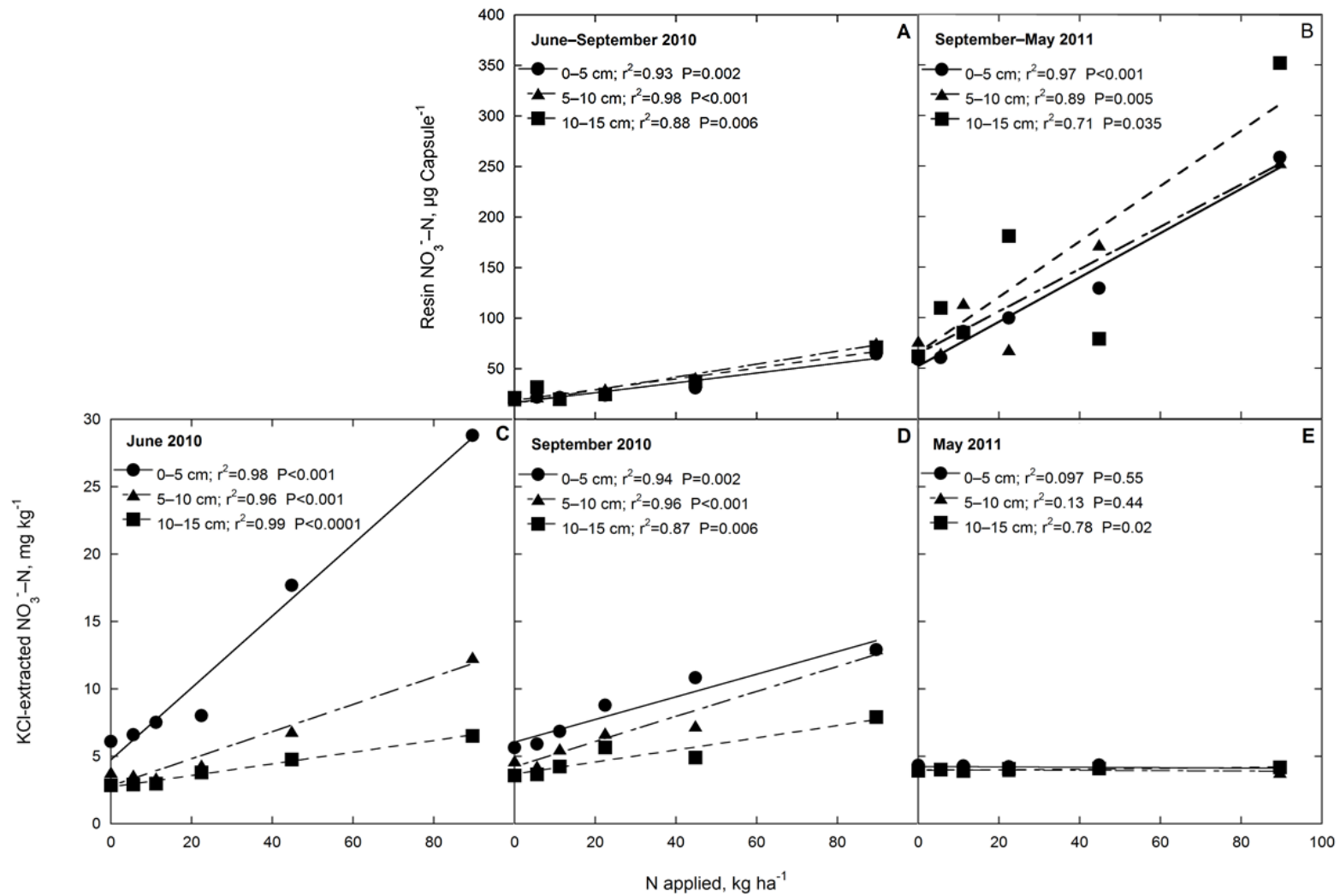


Figure 1.2. Resin and KCl-extracted soil $\text{NO}_3\text{-N}$ measurements after application of 0, 5.5, 11, 22, 44, and 88 kg ha^{-1} N; fertilizer applied March 2010 (values represent the mean of two locations).

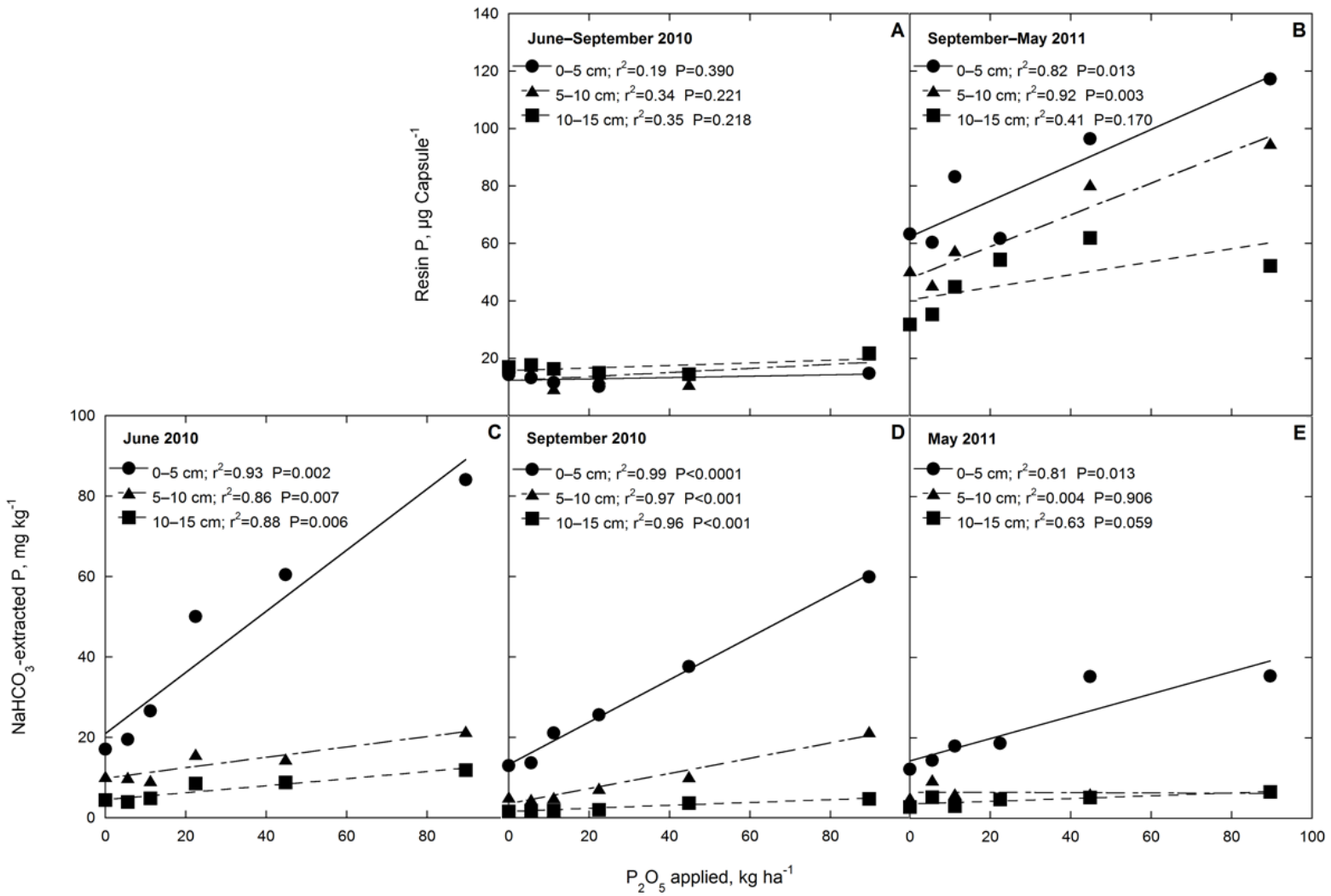


Figure 1.3. Resin and NaHCO_3 -extracted soil P measurements after application of 0, 5.5, 11, 22, 44, and 88 kg ha⁻¹ P; fertilizer applied March 2010 (values represent the mean of two locations).

Chapter 2: Comparing traditional soil tests with ion exchange resin capsules for determination of
bioavailability of sulfur in semi-arid, low fertility soils

Rachel L. Buck, Bryan G. Hopkins¹, Bruce L. Webb, and Von D. Jolley.

Department of Plant and Wildlife Sciences, Brigham Young University, Provo, UT 84602, USA

¹Corresponding author, 251 WIDB, Provo, Utah, 84602, USA, email: hopkins@byu.edu, Tel:
801-422-2185, Fax: 801-422-0008

Abstract

Sulfur (S) is an essential plant element found in most soils primarily in the organic matter phase; consequently, predicting plant bioavailability is difficult. Ion exchange resin capsules provide a viable alternative to chemical soil tests in evaluating the S status of fertilized soils, however their validity in desert ecosystems is not known. Two field studies were established at two locations—Rush Valley and Skull Valley, Utah on loam and sandy loam soils, respectively. In the first study, fertilizer was applied with six S treatments (0, 7, 14, 28, 56 and 112 kg ha⁻¹). Resin capsules were installed at a depth of 5 cm at fertilization and then removed and replaced approximately every 90 days with soil samples taken at the same times. Sulfate-S was determined on both the soil samples and resin capsules. Resins capsules and conventional soil tests are both effective in distinguishing between fertilizer rates on most dates, although at the last sampling, only the conventional soil test was related to S applied. The second field study used the same fertilizer rates as previously described, but three resin capsules were placed with one per plot at 0–5, 5–10, and 10–15 cm deep in the soil. Resin capsules were removed and replaced after 90 d, and final removal occurred 398 d after fertilizer application. Depth was not too important a factor as all depths yielded significant correlation to S applied, except the surface depth through the first sampling period. For both field studies, resin capsule correlation to S applied was good, but soil test S estimates were slightly better. Overall, resin capsules would be recommended for use in estimating S availability in semi-arid, low fertility conditions. Further research is needed to relate resin capsule S to plant uptake.

Introduction

Sulfur (S) is an essential plant nutrient involved in the synthesis of amino acids (cysteine, cystine, and methionine) and proteins, enzyme activity, vitamin production, and nitrogen (N) fixation (Sinclair and Saunders, 1982). Sulfur deficiency in plants has become more prevalent in recent years due to increased crop removal [decreased organic matter (OM) pool], mitigation of sulfur dioxide (SO₂) air pollution, and reduced S contamination in N or phosphorus (P) fertilizers. There can be both yield and crop quality benefits to using S fertilizers, and therefore it is important to assess the S status of soils and crops (Jensen, 2013).

However, most soil S tests do a poor job of estimating bioavailable S. Anderson et al. (1998) observed that potassium chloride (KCl)-100 (0.25 M KCl heated at 100°C for 3 h) and 0.5 M sodium bicarbonate (NaHCO₃) are unsuitable as soil S tests as they overestimate the availability of S from the organic fraction in soil. In contrast, monocalcium phosphate, H₂O, and KCl-40 (0.25 M KCl heated at 40°C for 3 h) appeared to have potential as soil S tests but had a relatively low correlation with plant S response due to an underestimation of the availability of soil organic S. Blair et al. (1991) also found that monocalcium phosphate, the most commonly used extractant, is unable to extract the organic S pool where 95% of the total S resides (Fenster, 1978).

Among the factors that complicate S soil tests are conversion of sulfate to insoluble sulfides, accretion of S from irrigation water and rain, volatilization of hydrogen sulfide, and mineralization of organic S (Islam and Ponnampereuma, 1982). As the amount of S in soils is depleted, additional S is dissolved from the inorganic pool and mineralized from the organic pool (Barrow, 1967; Till and May, 1971). The rate at which this mineralization occurs is controlled by soil moisture and temperature (Williams, 1967). This process is similar to N mineralization as

most of the N in the soil is in the organic form. However, the concentration of S is less than 10% of the total amount of N in soils and plants. Consequently, the inorganic soil N tests are not effective in assessing S availability to plants. In addition, the concentration of inorganic S in soils varies seasonally (Ghani et al., 1991) and is affected by the activity of microbial biomass, leaching and surface run off, fertilizer, and plant uptake. Any analytical value on sulfate concentration of a soil sample is more or less only for the moment the sample has been taken (Scherer, 2001; Schnug and Haneklaus, 1998).

Because of these complicating factors, resin capsules may be better suited to estimate bioavailable nutrients. Resin capsules are elliptical mesh balls approximately 2 cm in diameter that act as sinks for ions in soil solution in a manner similar to plant absorption of nutrients (Jones et al., 2012). Because resin capsules have the ability to act as a sink over time and are buried for specific periods of time, they may be estimates related to the amount of S that becomes available through mineralization of OM than soil tests. It is also important to realize that the form of S taken up by resin capsules could be any mobile form, though most would be SO_4^{2-} .

Some researchers have already reported promising data regarding the estimation of S availability using resin technology (Prochnow et al., 1998). Anion exchange resin strip estimates of S were significantly correlated to S uptake in corn and rice (Li et al., 2001). In addition, Matula (1999) found that resin capsules successfully predicted the availability of S from soils with a surplus of gypsum while multiple soil extractions failed to do so. Under laboratory and saturated conditions, Yang and Skogley (1992) found that resin capsule S was significantly related to S extracted by a standard soil test. In an incubation study with two semi-arid soils, Jones et al. (2013a) assessed the ability of resin capsules to estimate available iron (Fe) and zinc

(Zn) applied at low rates as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. While Fe and Zn levels were not found to be significantly different between treated and untreated soils, significant differences in sulfate-S ($\text{SO}_4\text{-S}$) were measured. Thus, resin capsules adsorbed $\text{SO}_4\text{-S}$, even at very low application rates (Jones et al., 2013a).

Additionally, the amount of soil that actually contributes to delivering ions to the resin capsule is not known (Skogley, 1994) and is likely dependent on the mobility of the ion, temperature, and moisture. It is therefore currently unknown if placement depth for resin capsules used *in situ* is important for capturing specific elements. Buck et al. (in preparation) found that placing resin capsules near the soil surface (0–5 cm) improved resin capsule phosphorus (P) correlation to applied P while a deeper depth of placement (5–10 cm) best related resin capsule ammonium-nitrogen ($\text{NH}_4\text{-N}$) to N applied. Because S is mobile in the SO_4^{2-} form, lower depths may be an effective measure of available S. Finally, research with resin capsules outside the laboratory has been done almost exclusively in highly fertile soils, which creates questions about the validity of their use in low fertility or dry soils (Sherrod et al., 2002).

Our objectives were to study S availability in low fertility semi-arid soils treated with six rates of surface applied S by (1) assessing resin capsule sulfate or soil test sulfate, taken at four sampling dates over a 12-month period, and (2) assessing if varying depth of placement could improve such estimates.

Materials and Methods

Field Experiment 1

Field studies were conducted southwest of the Great Salt Lake in Rush Valley ($40^\circ 8' 16''\text{N}$ and $-112^\circ 30' 26''\text{W}$, 1676 m) and Skull Valley ($40^\circ 18' 27''\text{N}$ and $-112^\circ 50' 3''\text{W}$, 1524

m), Tooele County, Utah, USA on low fertility loam and sandy loam soils, respectively (Table 2.1). Annual precipitation classifies these areas as semi-arid (Table 2.2). Previously fenced field sites prevented free range livestock from disturbing the study area. Each site was divided into thirty 4.0-m² plots per site which received surface application of S at six rates (0, 7, 14, 28, 56, and 112 kg ha⁻¹ S) with five replications of each treatment in a completely randomized block design on 18 May 2009. Sulfur was applied as granular ammonium sulfate [(NH₄)₂SO₄; 21-0-0-24]. Light raking was used to incorporate the fertilizer into the soil to a depth of approximately 0.5 to 1.0 cm.

Resin capsules were prepared for placement in the field by attaching plastic string (60 cm in length) to which colored plastic (3 cm²) was attached to make capsules easier to find after burial (Jones et al., 2013b). One mixed bed (H⁺/ OH⁻) ion exchange resin capsule was placed to a depth of 5 cm in each plot (18 May 2009). Resin capsules were removed and replaced, and soil samples taken in 18 August and 17 November 2009, as well as 23 March and 18 May 2010.

Field Experiment 2

Additional plots were established with identical S rates and experimental design adjacent to those described in Experiment 1. Sulfur was applied on 23 March 2010 with three mixed bed (H⁺/ OH⁻) resin capsules placed as previously described into each plot at depths of 0–5, 5–10, and 10–15 cm beginning 15 June 2010 and continuing with removal and installation of fresh capsules 13 September 2010 with final removal 4 May 2011. Soil samples were taken corresponding with each of these dates.

Soil Nutrient and Statistical Analyses

After field removal, capsules were placed in sealed plastic bags and stored at 5 °C until analyses were performed. After 14 to 21 d in storage, remaining soil was washed from each

capsule by rinsing with distilled water just prior to analysis. Sulfur was extracted from the resin capsules by washing each capsule successively three times using 20 mL of 2 M HCl (Skogley et al., 1997; Jones et al., 2012). The extract (total of 60 mL) was then analyzed for S using inductively coupled plasma spectroscopy (Iris Intrepid II XSP, ICP-OES, Thermo Electron Corporation, Franklin, Maryland, USA).

Immediately after transport to the laboratory, conventional soil samples were air dried and then ground to pass a 2-mm sieve. Sulfate-S was extracted from soils with monocalcium phosphate (Fox et al., 1964). Sulfur in solution was quantified as described above.

Field location was designated as a random variable for statistical analysis. Statistical analysis by generalized linear model (GLM) with mean separation by Duncan-Waller K Ratio Test was performed using SAS 9.3 (SAS Institute, 2011, Cary, North Carolina, USA). Means were subjected to regression analysis (PROC REG) also with SAS.

Results and Discussion

Field Experiment 1

Resin capsule S was significantly related to fertilizer S applied through the first three sampling periods (Figure 2.1A). However, by the end of the fourth sampling period (Mar–May 2010), there was no significant relationship (Figure 2.1A). This was somewhat surprising because there was more available moisture during this time period (Table 2.2; Table 2.3) and resin capsules are better at absorbing soluble ions with high soil moisture (Yang et al., 1991; Buck et al., in preparation). Perhaps this can be explained by microorganisms taking advantage of the increased available moisture and more S being taken up these organisms and subsequently released from soil OM (confounding the amount of S applied).

Values from the traditional soil test, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -extracted, for $\text{SO}_4\text{-S}$ were highly correlated to S applied at all four sampling dates (Figure 2.1B). In contrast to the resin capsule results where the $\text{SO}_4\text{-S}$ was highest through the first sampling period (May–Aug 2009), $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -extracted $\text{SO}_4\text{-S}$ was highest at the second sampling (November 2009). This may be related to some $\text{SO}_4\text{-S}$ leaching below the zone of the resin capsule in later sampling periods (or all leached below in the case of the last sampling period) or due to S cycling between microbes, the soil organic fraction, and soil solution. Soil sampling might pick up the $\text{SO}_4\text{-S}$ slightly below the resin capsule and thus giving better relationships even at later sampling periods. It is important to note that S was applied as sulfate, and the soil test used quantifies $\text{SO}_4\text{-S}$, while resin capsule S could represent any form of S that can move to the resin capsule. Other researchers have also found positive relationships using resin technology to estimate S bioavailability. In a study comparing different soil extractants and resin strips, Li et al. (2001) found that that extractable S by $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and KH_2PO_4 in soils with a pH below 6.0 was more than that extracted by CaCl_2 . However, all three extractants produced similar amounts of extractable S from the soils with a pH greater than 6.0. In contrast, the anion resin strips value for S was not affected by pH but depended more on the mineralization potential of the soil. This suggests that resin technology may be a better estimator of available S over a wide range of soil types and conditions.

Field Experiment 2

In the second field experiment, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -extracted $\text{SO}_4\text{-S}$ was also significantly correlated to S applied at every time and depth from which samples were taken, even by May 2011 which was 398 days after fertilizer application. It is interesting to note that the most $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -extracted $\text{SO}_4\text{-S}$ was found at the lowest depth (10–15 cm) in both June 2010 (soil

samples taken when resin capsules were placed in the soil) and September 2010 (soil samples taken when first set of resin capsules were extracted). However, the quantity of $\text{SO}_4\text{-S}$ measured was very low in May 2011 compared to earlier sampling periods (in which similar amounts and similar patterns of accumulation were observed). There was ample precipitation between March and June 2010 to provide the moisture necessary for sulfate leaching (Table 2.2; Table 2.4).

Resin capsule S was not significantly related to S applied at the end of the first sampling period in the top depth ($P=0.085$, Figure 2.2A) but was significantly related at all other points sampled. These relationships were generally significant at lower values than with $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extracted $\text{SO}_4\text{-S}$ (Figure 2.2). It is clear from the $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extraction that there was S in the top depth; perhaps the poor relationship with resin capsule $\text{SO}_4\text{-S}$ at that depth and date could be explained by evaporation at the surface resulting in less available moisture at that depth and reducing the ability of $\text{SO}_4\text{-S}$ to come in contact with resin capsules. Yang and Skogley (1992) found that movement of S, K, P, and NH_4 to a sink is highly dependent on ion activities in soil solution. In our study, the best relationship with resin capsules was found in the 0–5 cm and the 10–15 cm depths at the end of the second sampling period (Figure 2.2B). Although resin capsules were slightly less effective than $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extracted $\text{SO}_4\text{-S}$ at relating soil applied S levels, there were strong relationships between resin S and application rates at all but one date/depth in these relatively dry semi-arid conditions. In addition, soil tests for S can measure how much available S was present in the soil when sampled, but such tests cannot forecast how much S will be released in an available form by the decay of soil OM and crop residues (Ratanalert, 1978). These strong relationships warrant further study of the potential for resin capsule S and plant S nutrition relationships.

Conclusion

Both ion exchange resin capsules and the $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extract were able to predict available S based on application rates. However, the $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (traditional soil test) had a stronger correlation to fertilizer application rates. Resin capsules were more able to pick up the sulfur cycling through the system during the second time period, suggesting that they may be a better indicator of nutrient availability over time and are a promising method for estimating soil S as they show a more complete picture of the amount of S released from OM. Overall, resin capsules would be recommended for use in estimating S availability in semi-arid, low fertility conditions. Further research is needed to relate resin capsule S to plant uptake.

References

- Anderson, G. C., G. J. Blair, and R. D. B. Lefroy. 1998. Soil-extractable sulfur and pasture response to applied sulfur. 1. Studies under glasshouse conditions. *Aust. J. Exp. Agric.* 38:567–574.
- Barrow, N. J. 1967. Studies on extraction and on availability to plants of adsorbed plus soluble sulfate. *Soil Sci.* 104:242–249.
- Blair, G. J., G. C. Anderson, G. J. Crocker, N. Chinoim, and R. D. B. Lefroy. 1991. A soil sulfur test for pastures and crops. *Aust J. Soil Res.* 29:619–626.
- Buck, R. L., B. G. Hopkins, B. L. Webb, and V. D. Jolley. *In preparation*. Depth of ion exchange resin capsule placement impacts on estimation of nitrogen, phosphorus, and sulfur bioavailability in semi-arid, low fertility soils.
- Fenster, W. E. 1978. Sulfur soil tests for Minnesota. *Agric. Ext. Serv. Univ. Minn. Spec. Rep.* 70–71.
- Fox, R. L., R. A. Olson, and H. F. Rhoades. 1964. Evaluating the sulfur status of soils by plants and soil tests. *Soil Sci. Soc. Am. Proc.* 28:243–246.
- Ghani, A., R. G. McLaren, and R. S. Swift. 1991. Sulphur mineralization in some New Zealand soils. *Biol. Fert. Soils* 11:68–71.
- Islam, M. M. and F. N. Ponnampuruma. 1982. Soil and plant tests for available sulfur in wetland rice soils. *Plant Soil.* 68:97–133.
- Jensen, T. L. 2013. Protein quality enhancement with sulfur fertilization. *Plant Nutrition Today: International Plant Nutrition Institute*, 2. <http://www.ipni.net/pnt>
- Jones, M. P., B. L. Webb, D. A. Cook, and V. D. Jolley. 2012. Comparing nutrient availability in Low fertility soils using ion exchange resin capsules. *Commun. Soil Sci. Plant Anal.*

43:368–376.

- Jones, M. P., B. L. Webb, V. D. Jolley, B. G. Hopkins, and D. A. Cook. 2013a. Evaluating nutrient availability in semi-arid soils with resin capsules and conventional soil tests, I: Native plant bioavailability under glasshouse conditions. *Commun. Soil Sci. Plant Anal.* 44:971–986.
- Jones, M. P., B. L. Webb, V. D. Jolley, M. D. Vickery, R. L. Buck, and B. G. Hopkins. 2013b. Evaluating nutrient availability in semi-arid soils with resin capsules and conventional soil tests. II. Field studies. *Commun. Soil Sci. Plant Anal.* 44:1764–1775.
- Li, S., B. Lin, and W. Zhou. 2001. Soil sulfur supply assesment using anion exchange resin strip-plant root simulator probe. *Commun. Soil Sci. Plant Anal.* 32:711–722.
- Matula, J. 1999. Use of multinutrient soil tests for sulphur determination. *Commun. Soil Sci. Plant Anal.* 30:1733–1746.
- Prochnow, L. I., F. S. Pismel, H. Cantarella, G. C. Vitti, J. E. Corrente, and J. C. Kiehl. 1998. Use of ion-exchange resin to evaluate the bioavailability of sulfur in the soil. *Commun. Soil Sci. Plant Anal.* 29:1833–1841.
- Ratanalert, P., C. F. Bentley, and J. M. Crepin. 1978. Soil tests for sulfur: Importance and limitations. Alberta University College of Agriculture. *Agriculture Bulletin.* 1:16–21.
- Scherer, H. W. 2001. Sulphur in crop production – invited paper. *Eur. J. Agron.* 14:81–111.
- Sherrod, S. K., J. Belnap, and M. E. Miller. 2002. Comparison of methods for nutrient measurement in calcareous soils: Ion-exchange resin bag, capsule, membrane, and chemical extractions. *Soil Sci.* 167:666–679.
- Sinclair, A. G. and W. M. H. Saunders. 1982. The importance of sulphur, and a soil test for it. *Ruakura Farmers' Conference Proceedings.* 34:41–44.

- Skogley, E. O. 1994. Reinventing soil testing for the future. p. 187–201. *In* J. L. Havlin et al. (ed.) Soil testing: Prospects for improving nutrient recommendations. SSSA Spec. Publ. 40. ASA and SSSA, Madison, WI.
- Skogley, E. O., A. Dobermann, J. E. Yang, B. E. Schaff, M. A. A. Adviento, and M. F. Pampolino. 1997. Methodologies for resin capsules: capsule storage and ion recovery. *Sci. Soils*, 2, <http://www.hintze-online.com/sos/1997/Articles/Art3>.
- Schnug, E. and S. Haneklaus. 1998. Diagnosis of sulphur nutrition. *In* Schnug, E. (ed.), Sulphur in Agroecosystems. Kluwer Academic Press, The Netherlands, pp. 1–38.
- Till, A. R., and May, P. F. 1971. Nutrient cycling in grazed pastures. 4. The fate of sulphur-35 following its application to a small area in a grazed pasture. *Aust. J. Agric. Res.* 22:391–400.
- Williams, C. H. 1967. Some factors affecting the mineralisation of organic sulphur in soils. *Plant Soil* 26:205–223.
- Yang, J. E., B. E. Schaff, A. H. Ferguson, E. O. Skogley, and S. J. Georgitis. 1991. Phytoavailability soil test: Development and verification of theory. *Soil Sci. Soc. Am. J.* 55:1358–1365.
- Yang, J. E. and E. O. Skogley. 1992. Diffusion kinetics of multinutrient accumulation by mixed bed ion-exchange resin. *Soil Sci. Soc. Am. J.* 56:408–414.

Table 2.1. Selected characteristics of loam (Rush Valley) and sandy loam (Skull Valley) soils at the two field sites (Utah, USA).

Soil characteristic	Rush Valley, UT	Skull Valley, UT
Textural classification	Loam	Sandy loam
Sand, %	39	65
Silt, %	38	20
Clay, %	23	15
Organic matter, %	2.2	1.0
pH	7.7	7.8
Electrical conductivity, dS m ⁻¹	0.75	0.57
Sodium bicarbonate P, mg kg ⁻¹	13.4	8.4
Sodium bicarbonate K, mg kg ⁻¹	340	220
NO ₃ -N, mg kg ⁻¹	2.0	1.6
Calcium phosphate SO ₄ -S, mg kg ⁻¹	4.4	3.6
Calcium carbonate, %	19.8	9.8

Table 2.2. Precipitation distribution (in cm) during the period of experiments (May 2009–May 2011) at Rush Valley and Skull Valley (Toole County, Utah, USA).

Period of experiments	Rush Valley*	Skull Valley*
	---- cm ----	
May to August 2009	3.2	3.8
August to November 2009	2.4	1.1
November 2009 to March 2010	3.2	7.0
March to June 2010	5.1	10.2
June to September 2010	1.5	2.3
September 2010 to May 2011	13.1	13.1

*Bruce Roundy, personal communication, 2013

Table 2.3. Wet days (soil water potential greater than -1.5 MPa) at the soil surface (1–3 cm) during the period of the first field experiment (May 2009–May 2010) at Rush Valley and Skull Valley (Toole County, Utah, USA).

Period of experiments	Rush Valley*	Skull Valley*
	---- d ----	
May to August 2009	6	7
August to November 2009	8	6
November 2009 to March 2010	66	63
March to May 2010	41	57

*Bruce Roundy, personal communication, 2013

Table 2.4. Wet days (soil water potential greater than -1.5 MPa) at two depths (1–3 and 13–15 cm) during the period of the second field experiment (March 2010–May 2011) at Rush Valley and Skull Valley (Toole County, Utah, USA).

Period of experiments	Rush Valley*		Skull Valley*	
	1–3 cm	13–15 cm	1–3 cm	13–15 cm
Depth				
		---- d, % of period ----		
March to June 2010	41, 48%	41, 48%	41, 48%	41, 48%
June to September 2010	30, 33%	30, 33%	30, 33%	30, 33%
September 2010 to May 2011	171, 73%	171, 73%	171, 73%	171, 73%

*Bruce Roundy, personal communication, 2013

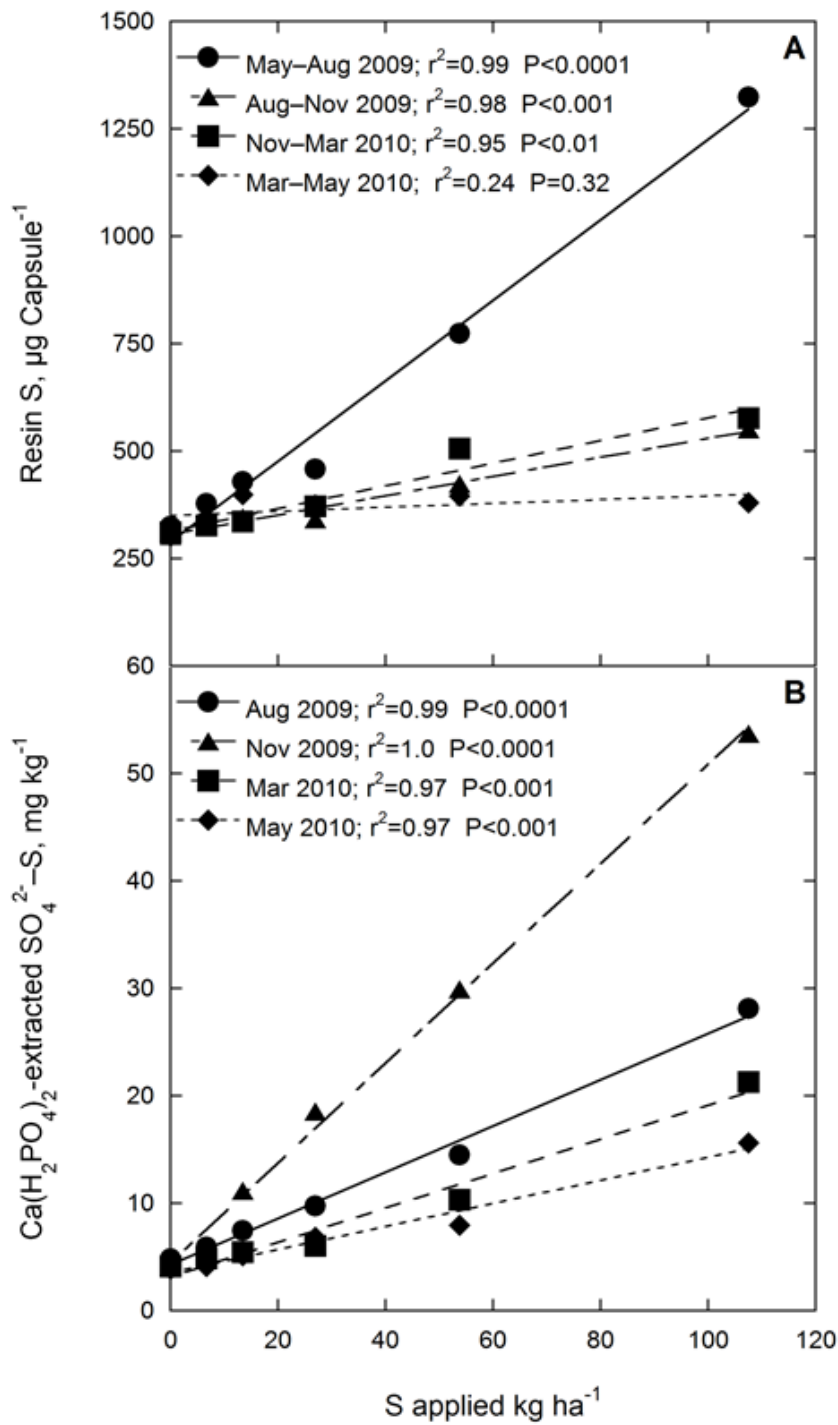


Figure 2.1. Resin (A) and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -extracted (B) S measurements after application of 0, 7, 14, 28, 56, and 112 kg ha^{-1} S; fertilizer applied 13 May 2009. Values represent the average of two locations (Rush Valley and Skull Valley).

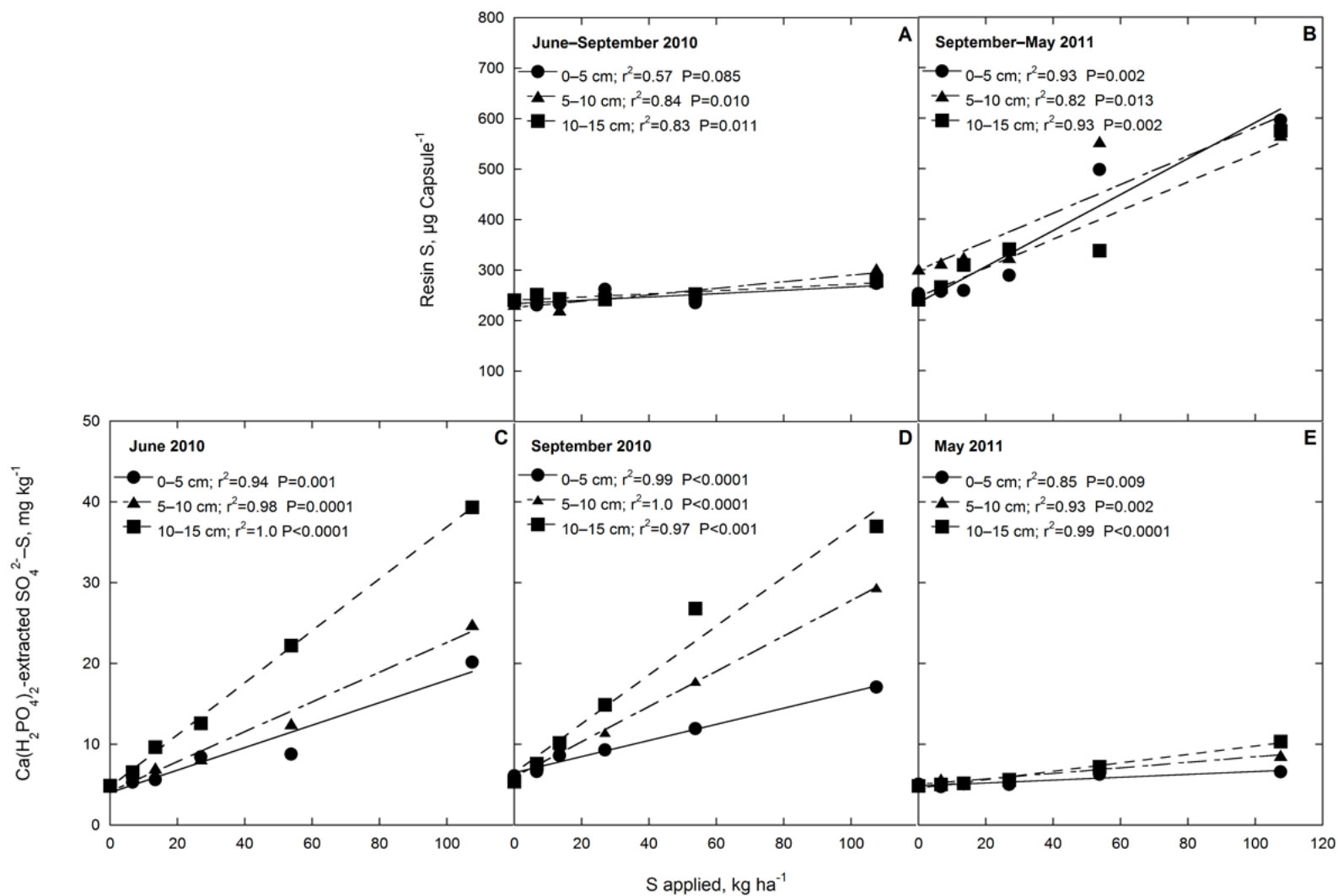


Figure 2.2. Resin and Ca(H₂PO₄)₂-extracted S measurements after application of 0, 7, 14, 28, 56, and 112 kg ha⁻¹ S; fertilizer applied 23 March 2010. Values represent the average of two locations (Rush Valley and Skull Valley).

APPENDIX

Laboratory Procedures

Resin Capsules

Additional PPE: gloves, safety goggles, fume hood

Extraction:

1. Remove capsule with tweezers and rinse thoroughly with distilled water using the pressurized nozzle from the tap.
2. Place capsule in 50 ml centrifuge tube.
3. Add 20 ml 2N HCL. To make: 333.3 ml concentrated HCl for 2 L distilled water
4. Shake for 20 minutes.
5. Filter through 12.5 cm filter paper into 125 ml plastic bottles.
6. Repeat steps 6-8 two more times, for a total of three times ending with a total of 60 ml.
7. Run on the ICP using the Resin method with 2N HCl as the blank.

Lachat:

Ammonium: samples MUST be neutralized before running. First, add 0.5 ml of 50% NaOH to the tubes you will be using of an ICP rack. Next, pipette 5 ml of sample into each tube (don't forget to neutralize the standards also). Place silicon or neoprene (green) stoppers, size zero, over each tube. Invert several times to mix.

Nitrate: Use the neutralized samples and neutralize the nitrate standards.

Reference:

Mary P. Jones, Bruce L. Webb, Daniel A. cook & Von D. Jolley (2012): Comparing Nutrient Availability in Low-Fertility Soils using Ion Exchange Resin Capsules, *Communications in Soil Science and Plant Analysis*, 43:1-2, 368-376.

Ammonium (NH₄-N) and Nitrate (NO₃-N) by Lachat

Additional PPE: gloves, safety goggles, fume hood

Standards:

- 1,000 ppm NH₄-N stock solution should be remade every 6 months. To make: Add 4.717 g of ammonium sulfate (NH₄)₂SO₄ to a 1 L volumetric flask. Add about 500 ml of deionized water, then add 1 ml of concentrated HCl and fill to volume with deionized water.

Reagents:

- 2 M KCl. Add 149 g of KCl to a 1 L volumetric flask. Fill to volume with deionized water.

Extraction:

1. Weigh 2.5 grams of soil into a 50 ml centrifuge tube and add 25 ml of 2M KCl. Cap the tubes and shake for 1 hour.
2. Centrifuge the samples for approximately 5 minutes and filter into a 125 ml plastic bottle. This extract is used to determine both ammonium and nitrate. Ammonium samples need to be analyzed the same day.
3. Run samples on the Lachat (see Lachat instructions). If you are running biosolids, the extract will need to be diluted 1:16 before running the ammonium on the Lachat (it does not need to be diluted for nitrate). Use the clear dilutor on the far right.

Reference:

Ammonium and Nitrate extracted with KCl. Analyzed by Rapid Flow Analyzer

Kenny, D.R., and D.W. Nelson. Nitrogen - Inorganic forms. pp. 643-698. In: A.L. Page (ed.), Methods of Soil Analysis Part 2. 1982. American Society of Agronomy, Inc. Madison, WI.

P Available (Olsen Bicarbonate Method)

Additional PPE: gloves

Reagents:

0.5 molar sodium bicarbonate: Add 1 liter of distilled water to 42 g of NaHCO₃. Let the solution equilibrate overnight. Store the solution in a plastic container. The pH in the 2 liter bottle needs to be adjusted with each use. To make 18 liters, use 756 g of NaHCO₃.

Reagent A: Dissolve 12 g of ammonium molybdate in 250 ml of distilled water. Dissolve 0.2908 g of antimony potassium tartrate in 100 ml of distilled water. Make 1000 ml of 5 N H₂SO₄ by adding 141 ml of concentrated H₂SO₄ to water and bringing to a volume of 1 liter. Add these three solutions together and bring to a volume of 2000 ml with distilled water. Store in a Pyrex bottle in a dark, cool place.

Reagent B: Dissolve 0.528g of ascorbic acid in 100 ml of reagent A (for 25 ml use 0.132g ascorbic acid, for 50ml use 0.264g ascorbic acid and for 200 ml use 1.056 g ascorbic acid). This solution needs to be made every day.

Procedure:

- Place 2.5 g of soil in a 250 ml Erlenmeyer flask. Use the racks with 9 flasks in a row. Adjust the pH of the NaHCO₃ in the 2 liter bottle using 6 N NaOH or 6 N HCl. to read between 8.28 and 8.30. Add 50 ml of 0.5 molar NaHCO₃ to the flasks using the orange dispenser (2 pumps). Place the rack on the reciprocating shaker and shake at low speed for 30 minutes.
- After shaking, immediately filter the suspension through 15 cm medium fast filter paper. To accomplish this, fold the filter paper so it will sit on top of the 100 ml plastic cups which are in racks of 9. Pour the suspension through the filter paper into the cups. The filtrate will be used for both phosphorus and potassium, so do not discard it.
- Use the 1:3 dilutor to take a 5 ml aliquot of the filtrate and add 10 ml of distilled water. Make this dilution in the large plastic tubes. Add 5 ml of reagent B (directions are above) with a pipettor and then swirl vigorously.
- Let the solution stand for 15 minutes and then read the color intensity on the Spectronic7 20 GenesysJ Spectrophotometer at a wavelength of 880 nm. Use your blank to set the transmittance at 100 %, and then read the transmittance on the samples.
- The ppm phosphorus are determined by comparing the samples with a standard curve. This curve is obtained by making working standards of 0.25, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 ppm from the stock solution. Develop the color in these standards just as was

done with the soil extract. The curve is made by plotting the transmittance of the standard against the concentration.

- The curve follows Beer's law, so the log of transmittance falls in a straight line. This means a regression equation can be calculated and the results computed on a calculator.

Reference:

Phosphorus extracted with sodium bicarbonate

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L.A. Dean. 1954. Estimation of available phosphorus in soil by extraction with sodium bicarbonate. USDA Cir. No. 939.

Sulfate-S—500 ppm P Monocalcium Phosphate

Reagents:

500 ppm P monocalcium phosphate: Add 2.03 g of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to a 1 L volumetric flask. Fill to volume with deionized water.

Procedure:

1. Weigh out 10 grams of sample into 25 ml centrifuge tubes.
2. Add 25 ml of 500 ppm P monocalcium phosphate extracting solution.
3. Shake for 30 minutes.
4. Centrifuge for 5 minutes, and filter the samples into small plastic bottles.
5. Run on the ICP with the sulfates method.

Reference:

Fox, R.L., R.A. Olson, and H.F. Rhoades. 1964. Evaluating the sulfur status of soils by plants and soil tests. *Soil Sci. Soc. Am. Proc.* 28:243-246.