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Variation in mineral content of prairie forb species and content changes over winter related to slagging potential

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VARIATION IN MINERAL CONTENT OF PRAIRIE FORB SPECIES AND
CONTENT CHANGES OVER WINTER RELATED TO SLAGGING POTENTIAL

An Abstract of a Thesis
Submitted
in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Jennifer Nyla Wahl Rupp
University of Northern Iowa

May 2015

ABSTRACT

Coal fired power plants are responsible for more than 75 percent of the energy produced in Iowa. Burning coal releases large amount of carbon dioxide and other chemical compounds into the atmosphere.

A variety of types of biomass, including prairie vegetation, are being proposed as biofuel alternatives for electrical generation. Tilman et al. (2006) determined that biofuels from mixtures of prairie vegetation of increasing diversity provide more usable energy, reduce greenhouse gases and produce less agriculture pollutants. The Prairie Power Project of the Tallgrass Prairie Center is testing four mixtures of prairie species for maximum production of biomass. A primary concerns regarding burning prairie biomass for electrical generation is the potential for slag production from trace metals and other minerals during the combustion process (Skrifvars et al. 1998). Adler et al. (2006) observed that the mineral content of switchgrass declined from summer to fall harvest and dropped further the following spring. Little is known about the slagging potential of prairie forbs.

This study examined the concentration of three minerals, potassium, sodium, and silicon, in nine prairie forb species in relation to their potential for slagging. Samples of the prairie forbs were collected during late fall and early spring-near the beginning and the end of the winter dormancy period from five different prairie sites. Mineral concentrations of the prairies forbs were compared to determine whether some species had higher potential for slagging than others. Also, concentrations of the minerals were

sampled fall and spring to determine if there were changes during the winter dormancy period that would affect slagging potential of the plants.

The energy production per unit weight was similar for all the species. The slag-inducing chemicals in the prairie forbs varied from species to species. *Solidago canadensis*, *Solidago rigida* and *Silphium laciniatum* exhibited high potential for slagging and should be avoided as biofuels. *Desmodium canadensis* showed low potential for slagging. Concentrations in *Monarda fistulosa*, *Lespedeza capitata*, and *Heliopsis helianthoides* declined during the winter dormancy. Delaying harvest until spring would improve their candidacy for biomass production.

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This Study by: Jennifer Nyla Wahl Rupp

Entitled: Variation in Mineral Content of Prairie Forb Species and Content Changes Over Winter Related to Slagging Potential

has been approved as meeting the thesis requirement for the

Degree of Master of Science

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DEDICATION

For my family.

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TABLE OF CONTENTS

	PAGE
LIST OF TABLES	vii
LIST OF FIGURES	x
CHAPTER 1. INTRODUCTION	1
Literature Review.....	5
Research Questions.....	16
Hypotheses.....	17
CHAPTER 2. MATERIALS AND METHODS	18
Site Descriptions	18
Species Sampled	29
Mineral Sampling and Analysis.....	31
Weather Component	35
Analysis Methods of External Laboratories	39
Statistical Analysis.....	41
CHAPTER 3. RESULTS	43
Biomass and Species Richness	43
Dormant Biomass.....	45
Potassium	47
Sodium	51
Silicon	55
Energy and Slagging.....	60
CHAPTER 4. INTERPRETATION AND DISCUSSION	69
Biomass and Species Richness	69
Variability of Minerals between Species	71
Changes in Mineral Concentration during Dormancy	74

Slagging Potential	78
Summary	79
Conclusion	81
LITERATURE CITED	82
APPENDIX A. COMPARISON OF MINERAL CONCENTRATIONS OF INDIVIDUAL SPECIES DURING TWO WINTER DORMANCY PERIODS	88
APPENDIX B. CORRELATION BETWEEN VEGETATION AND SOIL MINERAL CONTENT	113

LIST OF TABLES

TABLE	PAGE
1. Mineral content of ash from hybrid poplar, pine, and switchgrass.....	9
2. Slagging potential as indicated by calculations of Slagging Index A and Slagging Index B (Magasiner et al. 2001)	11
3. Fouling potential as indicated by calculations of TES Index and DOE Index (Magasiner et al. 2001)	12
4. Forb species studied.....	29
5. Temperature and precipitation at the Waterloo Municipal Airport 2007-2009	36
6 a. Year 1: Temperature and precipitation weekly in sample time at the Waterloo Municipal Airport	37
6 b. Temperature and precipitation weekly in sample time at the Waterloo Municipal Airport	38
7. Mean biomass of vegetation adjacent to selected forb species sampled August, 2008.....	44
8. Mean species richness of vegetation sampled adjacent to selected species sampled in August, 2008.....	44
9. Mean flowering stalk biomass (g) and standard error of selected forbs sampled in 2007-08 and 2008-09.....	46
10. Mean concentration (ppm) of potassium in selected forbs sampled during dormancy in fall 2007, spring 2008, fall 2008 and spring 2009.....	48
11. Mean concentration (ppm) of sodium in selected forbs sampled fall 2007, spring 2008, fall 2008 and spring 2009	52
12. Mean concentration (ppm) of silicon in selected forbs sampled during dormancy in fall 2007, spring 2008, fall 2008 and spring 2009.....	57
13. Percentage mineral levels of ash of combusted composite samples.....	61

14. Percent dry ash and energy output of composite samples of species per sample time	62
15 a The potassium and sodium concentrations of composite samples of species per sample time	64
15 b Slagging potential value of selected species calculated from potassium and sodium ash concentrations using Miles et al. (1995).....	65
B1. Mean concentration (ppm) of plant available potassium in soil surrounding selected forbs sampled during dormancy in fall 2007, spring 2008, and fall 2008 and spring 2009.....	114
B2. Mean concentration (ppm) of plant available sodium in soil surrounding selected forbs sampled during dormancy in fall 2007, spring 2008, and fall 2008 and spring 2009	119
B3. Mean concentration (ppm) of plant available silicon in soil surrounding selected forbs sampled during dormancy in fall 2007, spring 2008, and fall 2008 and spring 2009	124
B4. Concentration of minerals present in composite samples from soils adjacent to selected forbs	128
B5 a. Percent of potassium in ash and plant available potassium in composite soil samples.....	130
B5 b. Percent of sodium in ash and plant available sodium in composite soil samples.....	131
B5 c. Percent of silicon in ash and plant available silicon in composite soil samples.....	132
B6. Change in concentration (ppm) of potassium in composite samples from forbs and adjacent soils from fall 2007 to spring 2008 and fall 2008 to spring 2009.....	133
B7. Change in concentration (ppm) of sodium in composite samples from forbs and adjacent soils from fall 2007 to spring 2008 and fall 2008 to spring 2009.....	134

- B8. Change in concentration (ppm) of silicon in composite samples from forbs and adjacent soils from fall 2007 to spring 2008 and fall 2008 to spring 2009..... 135
- B9. Correlation between mineral concentrations of plant species and adjacent soils of individual sites..... 136

LIST OF FIGURES

FIGURES	PAGE
1. Map of research site locations within Black Hawk County, Iowa.....	19
2. View of Dunkerton Prairie site during fall sampling.....	21
3. The same area of Dunkerton Prairie, before the second sampling (winter) the first year	22
4. Different view, standing on the train tracks, of the same area of Dunkerton prairie site during spring sampling	23
5. Big Woods Lake Prairie after the flood, April 2008; between years 1 and 2	25
6. UNI Campus Prairie, after sampling time 1, year 1	26
7. UNI Museum Prairie, after sampling time 1, year 1	27
8. Pheasant Ridge Prairie, after sampling time 1, year 1	28
9. Mean concentration (ppm) of potassium of selected forbs sampled fall 2007 and spring 2008.....	49
10. Mean concentration (ppm) of potassium of selected forbs sampled fall 2008 and spring 2009.....	50
11. Mean concentration (ppm) of sodium of selected forbs sampled 2007 and spring 2008.....	53
12. Mean concentration (ppm) of sodium of selected forbs sampled fall 2008 and spring 2009.....	54
13. Mean concentration (ppm) of silicon of selected forbs sampled fall 2007 and spring 2008.....	58
14. Mean concentration (ppm) of silicon of selected forbs sampled fall 2008 and spring 2009.....	59
15. Potential for slagging of selected species as indicated by slag index	66
16. Change in slag index value of sampled forbs from fall to spring in 2007-08 and 2008-09	68

A1 a-i. Changes in concentration of potassium in nine species in fall 2007, spring 2008, fall 2008 and spring 2009	89-91
A2 a-i. Concentration of sodium in nine species in fall 2007, spring 2008, fall 2008, and spring 2009.....	93-95
A3 a-i. Concentration of silicon in nine species in fall 2007, spring 2008, fall 2008, and spring 2009.....	96-98
A4 a-i. Concentration of plant available potassium in soil surrounding nine species in fall 2007, spring 2008, fall 2008, and spring 2009	100-102
A5 a-i. Concentration of plant available sodium in soil surrounding nine species in fall 2007, spring 2008, fall 2008, and spring 2009	105-107
A6 a-i. Concentration of plant available silicon in soil surrounding nine species in fall 2007, spring 2008, fall 2008, and spring 2009	110-112
B1. Mean concentration (ppm) of plant available potassium of selected soil samples near forbs sampled fall 2007 and spring 2008	115
B2. Mean concentration (ppm) of plant available potassium of selected soil samples near forbs sampled fall 2008 and spring 2009	117
B3. Mean concentration (ppm) of plant available sodium of selected soil samples near forbs sampled fall 2007 and spring 2008	120
B4. Mean concentration (ppm) of plant available sodium of selected soil samples near forbs sampled fall 2008 and spring 2009	122
B5. Mean concentration (ppm) of plant available silicon of selected soil samples near forbs sampled fall 2007 and spring 2008	125
B6. Mean concentration (ppm) of plant available silicon of selected soil samples near forbs sampled fall 2008 and spring 2009	127
B7. Scatter plot of potassium concentration in vegetation and plant available potassium in the soil from individual sites	137
B8. Scatter plot of sodium concentration in vegetation and plant available sodium in the soil from individual sites.....	138

B9. Scatter plot of silicon concentration in vegetation and plant available silicon in the soil from individual sites.....	139
B10. Scatter plot comparing potassium concentrations in plant species and adjacent soils of composite samples.....	141
B11. Scatter plot comparing sodium concentrations in plant species and adjacent soils from composite samples	142
B12. Scatter plot comparing silicon concentrations of plant species and adjacent soils from composite samples	143

CHAPTER 1

INTRODUCTION

Iowa has relied upon coal fired power plants for the bulk of its energy production since the 1880s (Energy Information Administration 2008). In 1999, burning coal released 1.8×10^6 metric tons of carbon dioxide in the United States alone. Low-sulfur coal is commonly used to reduce air pollution. Currently, the state of Iowa produces more than 75 percent of its energy using low-sulfur coal (Energy Information Administration 2008). Coal, as a fossil fuel, is not an unlimited resource. The environmental impact of burning any fossil fuel leaves a mark on the Earth. Not only does coal cause air quality issues, it produces a host of other environmental concerns, including water pollution and land disturbance (World Coal Association 2015).

Renewable fuel resources are increasingly being considered as a means of reducing the carbon footprint (Energy Information Administration 2008). Biofuels have been gaining popularity as a viable source of renewable energy to reduce our dependence on fossil fuels. Iowa, with a high production rate of corn, is the leading producer of ethanol (Energy Information Administration 2008). In 2008, the state produced about three-tenths (30%) of our nation's supply. In 2012, according to the Iowa Renewable Fuels Association (2012), Iowa's ethanol plants produced 3.7 billion gallons of ethanol. The United States produced 13.3 billion gallons of ethanol in 2013 (Renewable Fuels Association 2013).

A wide variety of different types of biomass are being pursued as biofuels. The different types of biomass include single species of grasses, sawdust and other wood

products, railroad ties, plant residue from sugar processing, alfalfa, rice hulls, straws, stone fruit pits, mill sludges and other natural products to name a few. Biomass fuels are more carbon neutral than fossil fuels (McKendry 2002). Neutrality in this sense means that a growing plant sequesters the same amount of CO₂ as is released during its combustion. Therefore, no excess CO₂ is released during combustion than is incorporated into the plant. Fossil fuels are carbon positive. All of the CO₂ produced by fossil fuels when burned is released into the atmosphere. The CO₂ they sequestered was taken from an ancient atmosphere millions of years ago, and therefore adds to that of the current atmosphere.

McKendry (2002) lists the following characteristics of the ideal crop species for energy production:

- high yield (maximum production of dry matter per hectare)
- low energy input to produce
- low cost
- composition low in contaminants
- low nutrient requirements

Other environmental requirements for ideal energy crops include appropriate climate conditions for the growth of specific species and the effective use of available moisture and naturally available fertilizers (McKendry 2002). While this study by McKendry (2002) relates to United Kingdom climates, these considerations apply to biomass crops in general.

In an effort to find ways to reduce greenhouse gasses and become less dependent on fossil fuel, Governor Culver recommended to the Iowa Legislature that they establish an Office of Energy Independence. Culver indicated, “The goal is to wean Iowa from its

dependence on foreign oil by 2025,” (Clayworth 2007). To provide funding to meet the goal, he further recommended the creation of the Iowa Power Fund in 2007 (Bevill 2011). The bill was signed May 23, 2007 with the intention of providing funding for various alternative energy projects.

The Iowa Power Fund was initiated with \$100 million dollars to be spent in 4 years (Bevill 2011). “Culver predicted the fund would leverage ‘hundreds of millions, if not billions of dollars’ of additional investments in the state from private and federal sources,” according to an article in the Des Moines Register (Clayworth 2007). Within the first two years, \$51.6 million dollars was used to fund 39 projects, 13 of which were focused on biofuels (Bevill 2011).

The first project funded by the Iowa Power Fund Board was proposed by the Tallgrass Prairie Center (TPC) at the University of Northern Iowa (UNI). The Prairie Power project was designed to (1) determine the best mixture of prairie species for maximum biomass production to burn for electrical generation and (2) test at an agronomic (crop scale) level the findings of Tilman et al. (2006) that energy production increased with greater species richness (Smith 2008b). The applied research project compared four different mixes of prairie species (1) a switchgrass monoculture, (2) a mixture of five species of native warm season grasses including switchgrass, (3) a mixture of 16 native species, five warm season grasses and cool season grasses, plus forbs, and (4) a mixture of 32 species (including the previous 16 species) plus 16 more species of native grasses, forbs and sedges (Smith 2008b).

Several ongoing studies, including those at Iowa State University and the University of Texas, involve the use of monocultures of native prairie grasses, such as switchgrass, for alternative energy production (Price 2009). However, very few are studying mixed plantings of prairie grasses and/or forbs. Ancillary benefits of using prairie plants for biomass production include improved habitat for wildlife, reduced storm water runoff and soil erosion, decreased greenhouse gases, increased carbon sequestration, less fuel usage for tillage and increased biodiversity (Smith 2008a).

One of the concerns of burning prairie biomass for electrical generation is the production of slag during the combustion process from trace metals and other minerals within plants (Skrifvars et al. 1998). Timing of harvest of switchgrass has been observed to affect both switchgrass yield and biofuel quality. The ash concentration of switchgrass decreases as it matures during the growing season (Sanderson and Wolf 1995). If harvest is delayed until the following spring, mineral concentration as well as yield decreased in *Miscanthus* sp. (Lewandowski et al. 2003) and reed canary grass (*Phalaris arundinaceae* L.) (Burvall 1997).

Adler et al. (2006) studied chemical changes in selected plants to determine if mineral concentrations were affected by different harvest times. They examined how harvest time affected switchgrass biomass yield and biofuel quality. They observed that mineral content within switchgrass decreased from summer to fall harvests as others observed in reed canary grass (*Phalaris arundinaceae*) and *Miscanthus* sp. (Burvall 1997 and Lewandowski and Kitcherer 1997). The mineral concentrations dropped even further when harvest was delayed to the following spring (Adler et al. 2006). However, later

harvest times could affect the quantity of biomass gathered from a site. Although Adler et al. (2006) determined that switchgrass yield generally decreased when harvest was delayed from fall to spring, they observed that fuel quality was improved with reduced concentrations of slagging and fouling minerals and lower water content.

Literature Review

Giant strides toward developing renewable fuel sources are being made in the United States every day. The State of Iowa, through the Office of Energy Independence and the Power Fund, provides opportunities to pursue alternative energy sources. Iowa State University (ISU) and several other universities across the country are investigating monoculture stands of native grasses, while other organizations have invested in more exotic species such as sugar cane, corn, sugar beets, grains, elephant grass, silver plume grass, and kelp (Demirbas 2005). ISU has focused on combinations of native species and agronomic crops. In the process, they have studied cover crops, weed suppression and management strategies (Picasso et al. 2008, Wilsey and Blong 2007). There has been extensive study of the energy and biomass output of crops grown exclusively for energy production (Demirbas 2005).

Growth and productivity of monoculture stands are being extensively investigated. Switchgrass, for instance, exhibits a strong correlation between the latitude of its native origin and the rate that it reproduces (Rinehart 2006). Lowland ecotypes from the southern latitudes have higher yield potential than upland ecotypes from the north, but are not as cold tolerant (Casler et al. 2004). Cultivars moved north from more

southerly latitudes have higher yields, producing more biomass than cultivars originally from those northern latitudes (Rinehart 2006).

Co-firing plant biomass with coal is gaining considerable attention. For over 10 years, Chariton Valley Resource and Conservation Development, a non-profit corporation, studied the feasibility of co-firing switchgrass biomass with coal for electrical generation (Florine et al. 2006). Programs testing the co-firing of coal and plant biomass in large utility boilers show beneficial results for the utility by reducing fuel costs and minimizing waste while benefiting the environment with reduced pollution from NO_x, SO_x and CO₂ (Sami et al. 2001). The degree of benefit depends on the type of biomass used and the biomass/coal blend. When burned, each type of biomass material produces ash of a specific quantity and composition, and different quantity of energy from one to the next. While cofiring seems beneficial, experiments investigating the interactions between coal particles and biomass during the combustion process need further research (Sami et al. 2001).

Demirbas (2005) suggests that an area of future study for biofuel production would be the use of polycultures, rather than monocultures. Polyculture mixtures yield much more biomass and subsequently more energy than monoculture stands. Tilman et al.'s (1996) research indicates that as species richness increases energy production increases due to greater biomass. The Prairie Power Project of the Tallgrass Prairie Center was designed to verify the findings of Tilman et al. (2006) at an agronomic level and determine the best mixture of native biofuels for optimal energy production. The TPC project was initiated in 2008.

According to Tillman and Prinzing (1995), the use of vegetative biofuel “requires an understanding that these materials are fundamentally different” than coal. Structure, specific gravity, bulk density, porosity and void volume, chemical composition and characteristics of ash and reactivity are all widely varying physical characteristics. Ash produced from living plant matter typically has a tendency to be very alkaline ash with high levels of potassium oxide. Their study suggests that the alkalinity in the plant matter is influenced by soil conditions and mineral uptake during growth properties (Tillman and Prinzing 1995). A logical and important step in moving from monocultures to polycultures is the testing of mineral properties of the species included in a biomass mix (Tilman et al. 1996).

Harvest time is a big factor to be considered in all the studies of biomass quality. According to Adler et al. (2006), harvest time directly affects quality (mineral content) and quantity of biomass from switchgrass and a variety of other grasses.

Florine et al. (2006) evaluated twenty-six cool-season grassland species including forbs from ten fields of pasture, hay or Conservation Reserve (CRP) plantings in the Chariton Valley Biomass Project area. This evaluation was to determine the plants’ potential for energy production for co-firing with coal for electrical generation. Biomass accumulation in cool-season pastures was greatest in spring and early summer while in switchgrass it was greatest in late spring and summer. Due to the diversity of herbaceous plant species in the sampled sites, chemical composition was variable. Vegetation harvested for burning with coal was more suitable from some areas than from other areas because of lower ash, sulfur, and chloride content. The ash levels of a majority of cool-

season species from pastures were higher than switchgrass and were more comparable to coal. However, sulfur levels were similar to switchgrass and lower than coal. The major component of ash from grasses is silica. Warm season (C4) grasses typically have lower silica levels than cool-season (C3) grasses because they utilize water 50% more efficiently (Samson and Mehdi 1998).

According to Demirbas (2005) ash compositions of plant biomass and coal are fundamentally different, as “Biomass fuel properties vary significantly more than those of coal...” Consequently, the deposition rate of biomass ash has the potential to be widely variable relative to coal (Demirbas 2005).

There are thirteen mineral nutrients that are important to a plant’s growth and survival. Most plants grow by absorbing nutrients that come from the soil. Presumably plants can only absorb those minerals accessible to them. Therefore, variations in mineral concentrations in plants are related to concentrations in the soil. In the absorption process, chemicals in addition to mineral nutrients may be taken up from the soil. Consequently, a number of different minerals may be present in plants when they are harvested for burning to generate electricity. All species utilize similar minerals to grow, but they may require different amounts. An example of varying levels of minerals within different plant species is presented in Table 1 (Klaas 1998).

Table 1: Mineral content of ash from hybrid poplar, pine, and switchgrass*

Component	Hybrid poplar (dry wt%)	Pine (dry wt %)	Switchgrass (dry wt %)
CaO	47.20	49.20	4.80
K ₂ O	20.00	2.55	15.00
P ₂ O ₅	5.00	0.31	2.60
MgO	4.40	0.44	2.60
SiO ₂	2.59	32.46	69.92
Al ₂ O ₃	0.94	4.50	0.45
BaO	0.70		0.22
Fe ₂ O ₃	0.50	3.53	0.45
TiO ₂	0.26	0.40	0.12
Na ₂ O	0.18	0.44	0.10
Mn ₂ O ₄	0.14		0.15
SrO	0.13		0.04
CO ₂	14.00		
SO ₃	2.74	2.47	1.90
Total:	98.78	96.30	98.35

*Presence of carbon and sulfur likely due to insufficient temperature and length of time for ashing process to volatilize non-mineral components (Klass 1998).

Because of the minerals contained within plant matter, slagging and fouling are two major issues with burning biomass. Slagging and fouling are caused by inorganic constituents within ash. Alkali metals from combusted biomass form sticky deposits on the metal and refractory surfaces of combustion chambers. These ill effects are called slagging when “the deposition of ash on furnace walls, mainly in the radiant section, is in a highly viscous state and forms a liquid layer...” (Hare et al. 2010) Fouling is “...when the deposit is built up by condensed materials, forming a dry deposit, generally in the convective section...” (Hare et al. 2010). These deposits are found on grates and in fluidized beds of power plants (Miles et al. 1996). Clinkers are formed by the agglomeration of low viscosity molten ash particles on stoker grates (Magasiner et al.

2001). They are more readily created within stoker-fired boilers than pulverized fuel boilers. The processes inside the furnace are what determine the level of problems. According to Demirbas (2005), “slagging and fouling reduces heat transfer of combustor surfaces and causes corrosion and erosion problems which reduce the lifetime of the equipment.” Stoker-fired boilers allow the fuel more residence time and thus more time for deposits to form. Clinkers, slagging and fouling are all a result of elemental volatility and the viscosity (dependent on chemistry, oxidizing conditions and temperature) of the ash left after the transformation of the fuel being combusted (Magasiner et al. 2001). Ash is formed when a solid residue is produced by the combustion of the fuel in the air (McKendry 2002).

In addition to slagging and fouling, a third problem called sintering can also result from using biomass. Sintering occurs when loosely attached particles in fluidized bed boilers densify and compact into a hard mass (Skrifvars et al. 1998). Skrifvars et al. (1998) evaluated 10 biomass ashes to compare the sintering tendencies. They determined that silicate and alkali salts may result in formation of extensive deposits. Sintering can be calculated using a formula called “multicomponent, multiphase thermodynamic equilibrium”.

Miles et al. (1996) investigated the complex chemistry involved in formation of deposits. They created a database which includes an elemental analysis of a wide variety of biofuels and their ash. Their results also indicated that gasification may reduce alkali volatilization from biofuels. However, current coal fired facilities would need to be retrofitted for gasification.

Indices for slagging (Table 2) and fouling (Table 3) have also been determined (Magasiner et al. 2001). Slagging is determined by measuring ash deformation temperatures under reducing and oxidizing conditions. Slagging index A involves the base/acid ratio and the total sulfur content. Index B is (maximum hemisphere temperature plus four times the minimum initial deformation temperature)/5 (Magasiner et al. 2001). Both indices can portray whether slagging is unlikely, possible, or probable (Magasiner et al. 2001).

Table 2. Slagging potential as indicated by calculations of Slagging Index A and Slagging Index B (Magasiner et al. 2001).

	Slagging unlikely	Slagging possible	Slagging probable
Slagging Index A	< 0.6	0.6 to 2.6	>2.6
Slagging Index B	>1340	1340 to 1150	<1150

Fouling indices are also available as reliable indicators of the likelihood of fouling. The presence of sulfur makes determining fouling indices slightly more difficult. Coal itself is considered to be a fouling fuel. Because of this coal fired boilers are usually equipped with sootblowers (Magasiner et al. 2001). Two fouling indices have been developed. TES stands for the Thermal Energy Systems Index, and DOE stands for the Department of Energy's index. Both indices can portray whether fouling is unlikely, possible, or probable (Magasiner et al. 2001).

Table 3. Fouling potential as indicated by calculations of TES Index and DOE Index (Magasiner et al. 2001).

	Fouling unlikely	Fouling possible	Fouling probable
TES Index	<0.17	0.17 to 0.34	>0.34
DOE Index	<0.10	0.10 to 1.00	>1.00

According to Miles et al. (1995), a calculation can be done that combines slagging and fouling into one index. The equation to calculate a combined slag and foul index is as follows:

$$\frac{1 \times 10^6}{\text{HHV Btu/Lb(Dry)}} \times \text{Ash\%} \times \text{Alkali\% in Ash} = \text{Lb Alkali/MMBtu} = \text{Combined Index}$$

MMBtu stands for one million BTU, a British unit of energy. HHV stands for Higher Heating Value, a value depicting the heat produced from combustion. The values of the parameters are the same as the fouling TES Index above. The guidelines stated above and the equation in Miles et al. (1995) provides the limits for slagging used for our project.

Concentrations of alkali per heat unit within the fuel are one way the coal industry attempts to classify coal. Using the equation for the combined index, one can classify all other fuels containing these alkalis and use the resulting calculated number to determine which fuel source causes less fouling (Miles et al. 1995).

According to Magasiner et al. (2001) and Miles et al. (1995), the criteria for fouling potential are as follows: Values from 0-0.4 lb/MMBtu (0 to 0.17 kg/GJ) indicate fouling is unlikely; values from 0.4-0.8 lb/MMBtu (0.17 to 0.34 kg/GJ) indicate fouling is possible, and any value over 0.8 lb/MMBtu (0.34 kg/GJ) indicates it is probable.

The combined slagging and fouling equation provides the data necessary to determine which of the species studied will cause problems within coal-fired power plants. This equation provides a means to compare slagging and fouling potential of samples related to fall and spring harvests. To reduce slagging and fouling, the optimal time for harvest is when the mineral content of the ash is lowest. This is determined by testing the ash.

Many biomass fuels cause slagging and other forms of deposit formation during combustion. In comparison to varieties of biomass in general, coal is likely to have a lower fraction of alkali-earth metals such as calcium and magnesium (Magasiner et al. 2001). These deposits can reduce heat transfer, reduce combustion efficiency, and damage combustion chambers when large particles break off. Trace metals, silica, sulfur, potassium, sodium, chloride, phosphorus, calcium, magnesium, and iron present in plant tissue all have the capacity to cause undesirable reactions in furnaces and boilers. These minerals can lead to fouling and slagging due to ash deposits (Demirbas 2005). In some situations, these minerals “can cause corrosion, slagging, and fouling of boilers and increased emissions” (Lewandowski and Kircherer 1997).

These elements differ in terms of the magnitude of their effect on slagging and fouling. Therefore, some are greater concern than others regarding combustion as a biofuel. A brief summary of aspects of each element is provided below (Biolex 2015).

Silicon is the most common bulk ash-forming element in biomass. Silicon is present in significant concentrations in certain plants especially grass stems. SiO_2 forms the main matrix for the ash and slag during biomass combustion. The melting

temperature depends strongly on the mixture of other ash forming elements; the alkali metals potassium and sodium, in particular, lower the ash melting temperature of biomass ashes (Biolex 2015).

Sulfates formed from sulfur lower the ash melting temperature and can thus be significant contributors to slagging and fouling problems in biomass boilers. However, due to competing reactions with chloride, high sulfur to chloride ratios can in some cases be of advantage, as it can decrease chloride corrosion problems (Biolex 2015).

Potassium is a major nutrient and very important for growth of plants. High concentrations are common in rapidly growing plants. The concentration does commonly also depend on growing season of the plant (i.e. in summer and spring when the growth of the plant takes place, the concentrations are higher than in the winter when no growth occurs). Potassium may be lost as an aerosol during combustion, and consequently one of the main components of fouling in boilers using solid biomass fuels. Moreover, it reacts with other ash forming elements in the ash and in high concentrations it can significantly lower the melting temperature of ash and thereby cause slagging and fouling (Biolex 2015).

Sodium is not a plant nutrient like potassium. However, plants growing in soil high in sodium can have significant concentrations of sodium. Sodium behaves similar to potassium during combustion and therefore causes the same problems of fouling and slagging and particle emissions described for potassium (Biolex 2015).

Chloride is typically a major component in particulate emissions from biomass combustion units, mainly in the form of KCl. Chlorides have relatively low melting

temperatures and thus chloride particles can significantly contribute to fouling. Slagging is less common as typically very low concentrations of chloride remain in the bottom ash due to the relatively high volatility of chlorides compared to oxides and sulfates (Biolex 2015).

Phosphorus is an essential nutrient both as a part of several key plant structure compounds and as a catalyst in the conversion of numerous key biochemical reactions in plants. Generally phosphorus is a controlling element in ash transformation reactions during biomass combustion. The addition of calcium and magnesium tends to lower melting temperature and thus increases slagging and fouling (Biolex 2015).

Calcium is a main ash forming elements in biomass ashes. However, CaO increases the melting temperature of ash and thus is not much of a concern in slagging and fouling (Biolex 2015). Magnesium, a component of chlorophyll, is not a particular concern in slagging fouling as MgO increases the melting temperature of ash and green plants are seldom used as fuel (Biolex 2015). Iron is very common in earth minerals, however, it has low involvement in biological activities and thus does not naturally exist in high concentrations in plant material (Biolex 2015).

Research related to causes of slagging and fouling by biofuels has focused on two alkali metals, potassium and sodium, and silica. As indicated above, all three elements are common in living plants. In general, it appears that faster growing plants (or faster growing plant components) tend to have higher concentrations of alkali metal and silica (Miles et al. 1993).

Research Questions

When evaluating plant species as potential sources of biomass to burn for electrical generation, it is important to know which plants are most likely to cause slagging and fouling at the time of combustion. With the exception of switchgrass, little is known about biomass productivity and mineral content of the prairie species. Those that retain the most mass and the least amount of fouling and slagging minerals would be the best sources for burning for electrical generation.

The goal of the Prairie Power Project is to develop a mixture of prairie species for optimal production of biomass to burn for electrical generation. Consequently it is important to (1) know the level of slag inducing minerals of plants and (2) if changes occur in these minerals during dormancy. This information would provide some insight into biofuel quality.

Adler et al. (2006) determined that delaying switchgrass harvest over winter until spring appeared to improve biofuel quality due to a reduction in the slagging and fouling potential although biomass yield was reduced. However, no information is available regarding biomass productivity and slagging and fouling potential in forbs. From these limited observations one might infer that other grasses would behave similarly to switchgrass. As two of the seed mix treatments in the Prairie Power Project contain forbs, it is desirable to know the level of slag inducing minerals present in these forbs and if changes in the levels of these minerals occur after the onset of dormancy.

This study was designed to assess the mineral content of several prairie forbs to determine the concentration of slag inducing chemicals and, thus, the feasibility of

including them in biofuel mixtures for burning for electrical generation. As potassium, sodium and silicon are the most studied of slag inducing minerals, the design also included determining if changes in the concentration of these minerals occurred during dormancy.

Nine forb species from the treatment mixes of the Prairie Power Project were selected for this study. Samples of these species from five sites were analyzed for potassium, sodium and silicon and changes in content of these minerals after dormancy. Also, soils in the vicinity of each forb species were analyzed to ascertain whether there was a relationship between the mineral content of the soil and the mineral content of the forbs.

Hypotheses

The following hypotheses are tested in this study:

1. Concentrations of slag inducing minerals (potassium, sodium and silicon) in selected forbs will vary from species to species.
2. Concentrations of slag inducing minerals (potassium, sodium and silicon) present in selected forbs will decline from fall to spring.

CHAPTER 2

MATERIALS AND METHODS

Site Description

Five sites were chosen for sampling minerals in selected forbs and the soil surrounding them. One was a prairie remnant and four were prairie plantings. To ensure that the plantings were well established, the sites had to have been planted more than five years prior to the study. All were located within reasonable proximity to the university to limit the amount of winter driving.

The five sites selected were the Dunkerton Railroad Prairie, Big Woods Lake Prairie, University of Northern Iowa (UNI) Campus Prairie, University of Northern Iowa (UNI) Museum Prairie and Pheasant Ridge Golf Course Prairie. Soil types of the sites were ascertained by consulting the Soil Survey of Black Hawk County, Iowa (Natural Resources Conservation Service 2006). Site information was provided by Williams (pers. comm. 2010). All sites can be found on the image below.

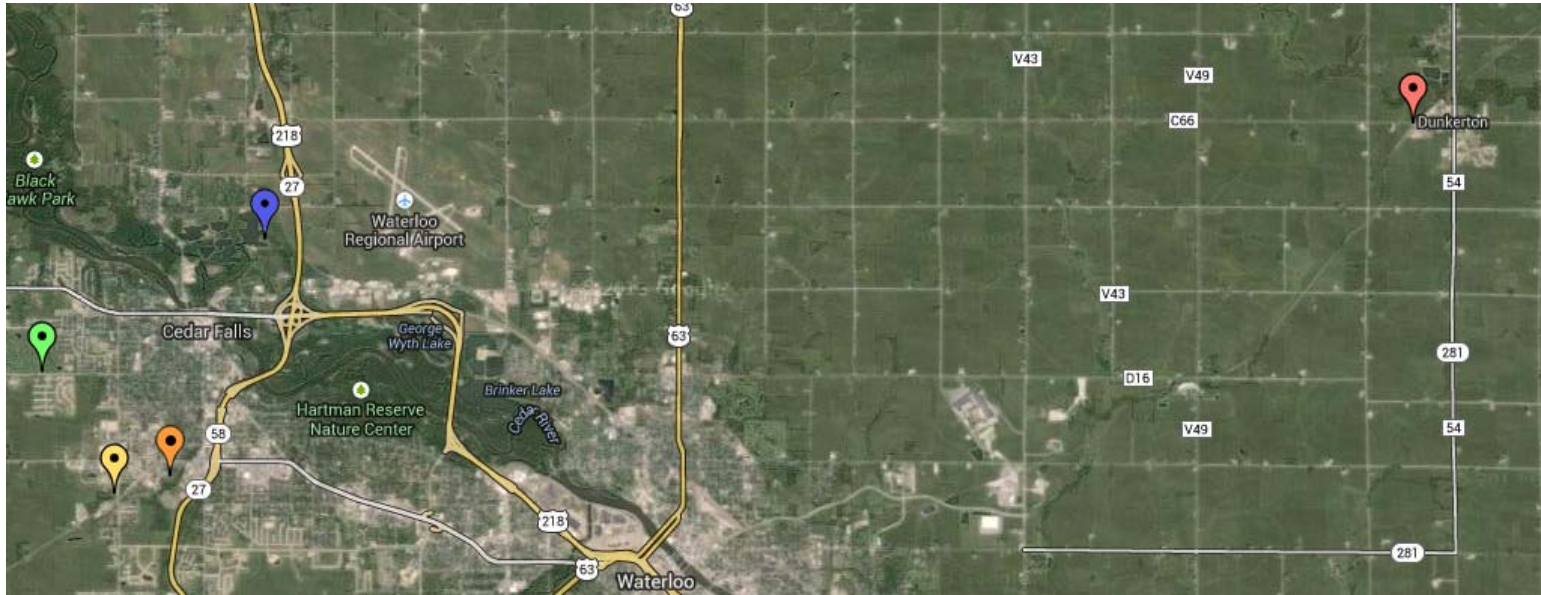


Figure 1. Map of research site locations within Black Hawk County, Iowa. Taken from MapQuest.

-  Dunkerton Railroad Prairie
-  Big Woods Lake Prairie
-  UNI Campus Prairie
-  UNI Museum Prairie
-  Pheasant Ridge Golf Course Prairie

The Dunkerton Railroad Prairie site (42.569745, -92.170378) was used as a reference site for the project because it is a prairie remnant rather than a reconstructed prairie. It can be found at the red marker on Figure 1. As a remnant, it has more diversity and is of better natural quality than the other sites. This 3 acre area (Figures 2-4) was included within the right-of-way of the Iowa Northern Railroad when it was constructed in 1885 (Smith pers. comm. 2008) and has never been cropped. Smith conjectured from site characteristics that topsoil had been removed from a portion of the right-of-way for roadbed fill during construction of the railroad. As prairie vegetation was still adjacent to the site at that time, the scraped area recovered through secondary succession to approximate the pre-settlement prairie.



Figure 2: View of Dunkerton Prairie site during fall sampling



Figure 3: The same area of Dunkerton Prairie, before the second sampling (winter) the first year.



Figure 4: Different view, standing on the train tracks, of the same area of Dunkerton Prairie site during spring sampling. Please note the crushed vegetation by the fence where the large drift was located.

The soils of the Dunkerton site are primarily Floyd loam, a somewhat poorly drained upland soil, and Marquis loam, a moderately drained upland soil (Natural Resources Conservation Service 2006). The 3 acre tract slopes upward from the north end to the south end on the west side of the right-of-way. Soil moisture ranges along the same slope from wet mesic at the north end to mesic to dry mesic at the south end. The site is usually burned on a 3 year rotation, and was burned in April, 2008 prior to the

study. Vegetation samples were taken randomly throughout the prairie remnant, but not in the far north end and where there was standing water.

The Big Woods Lake Prairie site (42.550240, -92.432770) is located on the Cedar River floodplain in Cedar City, Iowa. The site can be found on Figure 1 at the blue marker. The 10 acre site contained some native vegetation when it was overseeded with 80 native species in May 2001. Different portions of the area are burned annually. The sample sites were last burned in 2006 prior to the study (Williams pers. comm. 2010). The soil type is Finchford loamy sand, excessively drained alluvium on a stream terrace (Natural Resources Conservation Service 2006). Much of the area was disturbed by sand extraction for roadbed construction of Highway 58 and 218 in the 1990s. Some of the slurry from sand extraction was left on the site (Smith pers. comm. 2008). Sample areas are located on both sides of the bike trail east of the lake with some on the “Indian mound”. This site was flooded in June 2008 for several days (Figure 5), resulting in absent data to our study.



Figure 5. Big Woods Lake Prairie after the flood April 2008; between years 1 and 2.

The UNI Campus Prairie site, (42.510502, -92.453657) is located in the southeast portion of the UNI campus. The site can be found on Figure 1 at the orange marker. The 8 acre site (Figure 6) is managed by the Biological Preserves Committee and the Tallgrass Prairie Center. To begin the prairie reconstruction, native grasses were drill seeded in June of 1973. To increase diversity, forbs were added to the grass planting at various times from 1976-1989 (Smith pers. comm. 2008). It has been burned on a three to four year rotational basis since 1975 (Smith pers. comm. 2008, Williams pers. comm. 2010). One-half of it was burned in April of 2008 prior to the start of the project. The soil is Saude loam located on a stream terrace adjacent to a small floodplain (Natural

Resources Conservation Service 2006). Samples were collected throughout the prairie area.



Figure 6. UNI Campus Prairie, after sampling time 1, year 1.

The UNI Museum Prairie site, (42.507465, -92.466558) is located on the UNI campus in the northwest corner of the intersection of University Ave. and Hudson Rd. The site can be found on Figure 1 at the yellow marker. In June 2002, the approximately 1 acre site (Figure 7) was no-till drilled with source identified Northern Iowa Zone 1 seed (Williams pers. comm. 2010). This site was burned in April of 2007, and again in April of 2008. The soil of the Museum Prairie is Bremer-Marshan-Urban land complex located

on an alluvium terrace that is occasionally flooded (Natural Resources Conservation Service 2006). Samples were collected throughout the prairie area.



Figure 7. UNI Museum Prairie, after sampling time 1, year 1.

The Pheasant Ridge Golf Course Prairie site (42.527955, -92.488487) is located on the south edge of Pheasant Ridge Golf Course adjacent to 12th St. The site can be found on Figure 1 at the green marker. This 2 acre site (Figure 8) was broadcast seeded in November 2000. It was burned in April of 2007, and again in April of 2008 (Williams pers. comm. 2010). The upland soil is Kenyon and is moderately well drained (Natural

Resources Conservation Service 2006). Samples were collected throughout the prairie area.



Figure 8. Pheasant Ridge Prairie, after sampling time 1, year 1.

Species Sampled

Forbs rather than grasses were selected for the study because few studies have been done regarding forbs and minerals that cause fouling and slagging. Forb species that would likely be utilized in a biomass mixture were selected.

Eight criteria were used in selecting the nine forbs for this project. Forbs that would likely be included in biomass plantings were selected. The forb selection criteria were based upon years of personal experience working with the forbs (Williams pers. comm. 2010). The criteria were as follows: abundant distribution statewide; adaptability to different soil types and moisture variations; easily grown from seed; wood-like stems (greater bulk biomass); ability to fix nitrogen (legumes); standability (ability to resist being matted down by heavy snow throughout the winter); relatively long-lived; and capable of growing in close proximity to other prairie species. The species chosen are in Table 4.

Table 4. Forb species studied

Common Name	Scientific Name	Abbreviation
Showy tick-trefoil (legume)	<i>Desmodium canadense</i>	Deca
Pale purple coneflower	<i>Echinacea pallida</i>	Ecpa
Ox-eye sunflower	<i>Heliopsis helianthoides</i>	Hehe
Round-headed bush clover (legume)	<i>Lespedeza capitata</i>	Leca
Wild bergamot	<i>Monarda fistulosa</i>	Mofi
Grey-headed coneflower	<i>Ratibida pinnata</i>	Rapi
Compass plant	<i>Silphium laciniatum</i>	Sila
Canada goldenrod	<i>Solidago canadensis</i>	Soca
Stiff goldenrod	<i>Solidago rigida</i>	Sori

As knowledge of over-winter standability of the forbs is limited, I observed the standability of the species throughout the two winters of this study.

Data for all of the nine species were not collected at each of the five locations due to variations in seed mix, management, and site history. Some species were not present, and other species were not of sufficient size. One condition of collection was that each collected plant must possess a flowering ramet. Big Woods Prairie contained all the species the first year, but many were not present the second year due to extensive flooding in June. Campus Prairie was missing *Heliopsis helianthoides*, Dunkerton Prairie was missing *Desmodium canadense* and *Silphium laciniatum* the second year. Basal leaves of *Silphium laciniatum* were present, but no flowering stalks could be found. Museum Prairie was missing *Lespedeza capitata*, and Pheasant Ridge Prairie was missing *Lespedeza capitata* as well as *Solidago canadensis*.

Species identification during the dormant season was difficult. Therefore, during the early fall, sites were visited to determine whether the selected species were present and to note their location.

During testing and data analysis, several samples were thrown out due to insufficient amount of plant material, as the ISU lab required about 10 grams for vegetation testing. Also, frozen soil made it impossible to obtain some soil samples. These problems resulted in gaps in data. Furthermore, Big Woods Prairie was not included in the summer sampling for biomass and species richness because numerous species were absent or of inadequate size due to the flood of June, 2008. Several species

were not available for sampling the next year due to the flood. Within the data, this will be denoted as NA, for not available.

Mineral Sampling and Analysis

Plants and associated soil cores were sampled three times to determine mineral content during the first dormant period (2007-2008). They were sampled twice for mineral content the second dormant period (2008-2009). In addition, the vegetation was sampled once for biomass and species richness during the summer (2008).

Sampling for plant and soil mineral content was done after the first hard frost of the fall when we were certain the plants were senescent. The first year's fall sampling was done from December 4, 2007 to December 18, 2007. The second sampling period was January 22, 2008 to February 20, 2008. The spring sampling period was March 25, 2008 to April 8, 2008. In the second year, the winter sample period was dropped due to difficulties in sampling when the ground was frozen. To be consistent, data from the second sampling in year 1 was not included in the analyses. The second year's fall sampling was done November 25, 2008 to December 8, 2008 and the spring sampling was conducted March 13, 2009 to March 27, 2009.

Species in the study were sampled at each of the five locations for mineral content. When possible, nine full plants of each species were collected at each location and combined at random to create three individual plant replicates. Three individual plants collectively comprised one sample for that species at that location, so the result was three samples for each of the nine species at every site. Only plants in fruit were collected to insure the specimen was at or near maximum productivity. In addition, stems

with fruit were much easier to locate in the winter with snow on the ground. Some sites did not contain a sufficient number of plants of a particular species to harvest three entire plants in both fall and spring. In such a case, the species was not collected, or, if it had more than one ramet to the plant then only one ramet was harvested from each of nine plants of that species per sampling. These deviations were noted on the data for those samples. If the amount of sample material collected in this manner was insufficient for testing, it was not included in the material sent to ISU for analysis, but was included in the combined material tested by Hazen Research, Inc.

When sampling plants, the maximum height of the plant was measured and the number of fruiting ramets counted. There were two exceptions to the counting of the ramets: (1) if only one fruiting ramet (of large, multi-ramet species) was collected due to an insufficient number of plants and (2) if the plants were colonial or highly rhizomatous with numerous ramets making distinguishing of individual plants impossible. In these cases we did not count the fruiting ramets, and only measured the height of the one collected.

The plants were clipped off with scissors as close to ground level as possible, placed in paper bags, and taken to the TPC to be dried. After the samples were dried they were prepared to be sent to the Iowa State University Soil and Plant Analysis Laboratory for analysis.

All samples were prepared according to directions provided by the Iowa State University Soil and Plant Analysis Lab. The plant material was dried in large paper bags for three days in drying ovens (Quincy Lab, Inc. Model 21-250) at 60 degrees Celsius.

After being dried, the plant material was ground using a Wiley Grinder with a size 20 mesh screen. Up to 10 grams of material of each sample (a composite of 3 clipped plants) was placed in individual plastic bags for analysis of mineral content of potassium, sodium and silicon. The samples were sent to the ISU Soil and Plant Analysis Lab (Skrifvars et al. 1998) to be tested for silicon and the alkali metals sodium and potassium.

To determine if soil mineral content influenced the mineral content of the plants, we compared the minerals in soil samples with the minerals in adjacent sampled plants. Soil core samples of 2 cm x 15 cm were taken near the base of each plant collected using a soil core sampler.

The soil samples were returned to the TPC where they were oven dried at 30 degrees Celsius for three days. They were then crushed with a hammer and placed in plastic bags. The soil samples were combined to produce composite soil samples in exactly the same combinations as the vegetation samples. For each vegetation sample (composite of three plants) there was a soil sample (a composite of the three soil samples taken next to those three plants). After this preparation of the soil material, 100 grams were measured out according to test lab requirements, and were sent to the ISU Soil and Plant Analysis Lab. They determined plant available potassium, sodium and silica within the soil samples. ISU results will be referred to as individual site data.

Vegetation samples and soil samples were also sent to Hazen Research, Inc. for a more general, overall mineral analysis. Before being submitted to Hazen for analysis, the original vegetation samples of each species from the five sites were combined and mixed further. For each fall and spring sampling, samples of individual species from each site

were combined with samples of the same species from other sites. This formed a composite vegetation sample of each species for each sample period (four samples of each species-one each for fall 2007, spring 2008, fall 2008 and spring 2009).

An associated composite soil sample was created from the soil cores collected next to the vegetation samples. As with the vegetation samples, one composite soil sample per species for fall and spring of both sample years was created. The soil samples were tested for total plant available sodium, potassium and silica.

Hazen provided ash analysis, gross energy, and ultimate and proximate analysis of the vegetation samples. These samples were analyzed after the combustion process took place, so they depict an accurate account of the residue of material that would be left as a byproduct in a power plant. These composite samples provided an overall value of the species mineral content per sample time, and will be referred to as composite site data.

Vegetation sampling in the vicinity of the nine research species was sampled at the four sites during August 2008 to determine species composition and richness and biomass productivity. Big Woods Prairie was excluded due to severe June flooding. From within the population of each species, three random sample areas containing at least one plant of the species were selected. A circular hoop of 0.25 meter squared area was centered on one plant of the target species in the three areas. All species within the circular area were identified to ascertain species composition and calculate species richness. To determine biomass within the vicinity of the target species, all vegetation within the circular area was clipped. The clippings were separated into three categories

and bagged. The three categories were target species, grasses, and other forbs. Both native and non-native species were included in each category. The plant material was dried in drying ovens at the Tallgrass Prairie Center (TPC) and the dry weight recorded.

Weather Component

Because mineral movement after dormancy can possibly be affected greatly by the temperature and precipitation any given year, some attention must be paid to the climate of each sample year. Table 5 shows the monthly mean temperatures and total precipitation. Tables 6, a and b contain the mean temperature and precipitation totals for the weeks within the two sample years. The mean temperature and total precipitation were recorded at the Waterloo Municipal Airport.

Table 5. Temperature and precipitation at the Waterloo Municipal Airport 2007-2009

Month	Mean Temp (F)	Total Precipitation (inches)
January-07	20.26	0.72
February-07	14.11	1.23
March-07	40.32	1.59
April-07	45.97	4.24
May-07	64.77	4.67
June-07	70.03	5.11
July-07	73.23	4.65
August-07	73.42	10.32
September-07	64.73	4.18
October-07	54.94	3.76
November-07	35.90	0.14
December-07	19.19	2.51
January-08	14.68	0.75
February-08	15.79	2.41
March-08	30.29	1.68
April-08	45.50	10.79
May-08	57.00	6.25
June-08	69.80	8.77
July-08	74.13	5.51
August-08	70.13	1.61
September-08	63.77	2.6
October-08	50.65	1.53
November-08	36.93	1.97
December-08	15.00	1.65
January-09	11.19	0.62
February-09	25.14	0.56
March-09	36.94	3.08
April-09	47.00	4.63
May-09	59.87	4.07
June-09	69.13	3.58
July-09	67.87	5.52
August-09	68.68	5.36
September-09	63.13	2.09
October-09	44.55	5.86
November-09	42.73	0.61
December-09	19.23	2.34

Table 6 a. Year 1: Temperature and precipitation weekly in sample time at the Waterloo Municipal Airport

Start Day	End Day	Mean Temp (F)	Total Precipitation (inches)
11/1/2007	11/7/2007	39.71	0
11/8/2007	11/14/2007	40.86	0
11/15/2007	11/21/2007	38.57	0.13
11/22/2007	11/28/2007	28.43	0.01
11/29/2007	12/5/2007	21.43	1.27
12/6/2007	12/12/2007	15.43	0.68
12/13/2007	12/19/2007	16.71	0
12/20/2007	12/26/2007	24.71	0.18
12/27/2007	1/2/2008	14.86	0.1
1/3/2008	1/9/2008	28.29	0.1
1/10/2008	1/16/2008	21.00	0.11
1/17/2008	1/23/2008	1.00	0.5
1/24/2008	1/30/2008	11.14	0.04
1/31/2008	2/6/2008	23.57	0.53
2/7/2008	2/13/2008	9.57	0.16
2/14/2008	2/20/2008	10.29	0.84
2/21/2008	2/27/2008	17.00	0.65
2/28/2008	3/5/2008	24.00	0.57
3/6/2008	3/12/2008	19.43	0
3/13/2008	3/19/2008	36.57	0.12
3/20/2008	3/26/2008	35.43	0.28
3/27/2008	4/2/2008	35.43	0.94
4/3/2008	4/9/2008	42.43	0.39
4/10/2008	4/16/2008	43.71	1.56
4/17/2008	4/23/2008	53.29	3.89
4/24/2008	4/30/2008	45.57	4.95

Table 6 b. Year 2: Temperature and precipitation weekly in sample time at the Waterloo Municipal Airport.

Start Day	End Day	Mean Temp (F)	Total Precipitation (inches)
11/1/2008	11/7/2008	55.57	0.79
11/8/2008	11/14/2008	36.57	0.75
11/15/2008	11/21/2008	26.71	0.01
11/22/2008	11/28/2008	31.14	0.01
11/29/2008	12/5/2008	20.57	0.42
12/6/2008	12/12/2008	14.71	0.23
12/13/2008	12/19/2008	12.14	0.7
12/20/2008	12/26/2008	11.43	0.37
12/27/2008	1/2/2009	22.14	0.34
1/3/2009	1/9/2009	16.86	0.3
1/10/2009	1/16/2009	0.00	0.3
1/17/2009	1/23/2009	15.43	0.00
1/24/2009	1/30/2009	6.57	0.02
1/31/2009	2/6/2009	18.86	0.00
2/7/2009	2/13/2009	35.29	0.05
2/14/2009	2/20/2009	22.71	0.19
2/21/2009	2/27/2009	25.14	0.32
2/28/2009	3/6/2009	29.29	0.00
3/7/2009	3/13/2009	27.71	2.46
3/14/2009	3/20/2009	43.86	0.00
3/21/2009	3/27/2009	44.43	0.57
3/28/2009	4/3/2009	38.14	0.05
4/4/2009	4/10/2009	39.43	0.28
4/11/2009	4/17/2009	46.86	0.14
4/18/2009	4/24/2009	53.57	0.09
4/25/2009	5/1/2009	52.29	3.86

Analysis Methods of External Laboratories

The ISU Soil and Plant Analysis Lab tested the independent sample materials. They conducted a microwave assisted acid digestion of the plant biomass to determine total potassium and sodium using Method 3051A as provided by the EPA (Environmental Protection Agency 2007a).

A representative sample is extracted and/or dissolved in concentrated nitric acid, or alternatively, concentrated nitric acid and concentrated hydrochloric acid using microwave heating with a suitable laboratory microwave unit. The sample and acid(s) are placed in a fluorocarbon polymer (PFA or TFM) or quartz microwave vessel or vessel liner. The vessel is sealed and heated in the microwave unit for a specified period of time. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate determinative method. (21)

The method used to test silica is classified as 3015A as provided by the EPA, but the procedure was the same as above for testing potassium and sodium (Environmental Protection Agency 2007b).

As indicated, Hazen Research, Inc. analyzed the composite samples. Based upon suggestions in papers by Florine et al. (2006), and Demirbas (2005), I requested proximate (ASTM D 3172) and ultimate (ASTM D 3176) analyses, ash (ASTM D 2795) analysis and gross energy (ASTM D 5865). Hazen Research, Inc. used test methods prescribed by the Annual Book of ASTM Standards Volume 05.06 2002 and 2008.

The proximate analysis (ASTM D 3172) is found in ASTM Standards Volume 05.06 2008 on page 224. This test determines the amounts of moisture, volatile matter, ash and circulation of fixed carbon of the samples provided. The test results are useful to compare prairie forbs as fuels to fuels like coal. The results can be used to calculate ratios of combustible to incombustible components.

The ultimate analysis (ASTM D 3176) is located in ASTM Standards Volume 05.06 2008 on page 235. This tests the sample's composition of hydrogen, carbon, sulfur, nitrogen and oxygen, including "...the determination of carbon and hydrogen in the material, as found in the gaseous products of its complete combustion, the determination of sulfur, nitrogen and ash in the material as a whole, and the calculation of oxygen by difference."

Ash analysis (ASTM D 2795) is useful for an estimate of total fuel quality and ash composition. The method for ASTM D 2795 is on page 197 of Volume 05.06 2002 and is as follows:

3.1 The coal or coke to be analyzed is ashed under standard conditions and ignited to constant weight. Two solutions are prepared from the ash. Solution A is obtained by fusing the ash with sodium hydroxide (NaOH) followed by a final dissolution of the melt in dilute hydrochloric acid (HCL). Solution B is prepared by decomposition of the ash with sulfuric (H_2SO_4), hydrofluoric (HF), and nitric (HNO_3) acids. Solution A is used for the analysis of SiO_2 and Al_2O_3 , and Solution B for the remaining elements.

3.2 The two solutions are analyzed by a combination of methods: (1) spectrophotometric procedures are used for SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , and P_2O_5 ; (2) chelatometric titration for CaO and MgO; and (3) flame photometry for Na₂O and K₂O.

The standard test method for gross calorific value (ASTM D 5865) of coal and coke is used to determine the total calorific content of the fuel. The method for ASTM D 5865 is in Volume 05.06 on page 571 and is as follows:

4.1 The heat capacity of the calorimeter is determined by burning a specified mass of benzoic acid in oxygen. A comparable amount of the analysis sample is burned under the same conditions in the calorimeter. The calorific value of the analysis sample is computed by multiplying the corrected temperature rise, adjusted for extraneous heat effects, by the heat capacity and dividing by the mass of the sample.

The soil samples were tested for plant-available sodium and potassium.

Potassium testing required 2 grams of soil, 20 mL of extracting solution and 5 minutes of shaking. The resulting solutions were then filtered and analyzed with an atomic adsorption/emission spectrometer (Warncke and Brown 1998). The sodium procedure consisted of adding water to the soil sample, mixing, filtering and applying a vacuum. Then they used the conductivity to assay the mineral content (Warncke and Brown 1998).

To analyze for the plant available soil silica, the ISU laboratory used a method from Bair (1966). It involves 10 grams of soil, 50 mL of .5 M NH_4OAc (pH 4.8), and 30 minutes of shaking. The silica is soluble and can be assayed within the solution by atomic absorption spectrometry or colorimetric techniques (Savant et al. 1999). The ISU soil lab used a process called Inductively Coupled Plasma (ICP) Optical Emission System (OES) ICP-OES manufactured by Spectro. This process gives similar results to atomic absorption, but is more accurate (Culp 2011).

Statistical Analysis

The data were analyzed using SPSS. The statistical analyses were done using the means of collected samples: dry weight for biomass, and combusted and analyzed means for the minerals. Numerous comparisons can be made on the data collected for this project. It should be noted that our analyses contain numerous missing samples and inconsistent samplings due to temperature and snow. We have compared what was possible with the available data.

Most of our analyses consist of one way ANOVAs and running the Tukey's B analysis, comparing potassium, sodium and silicon in vegetation and soil samples from

one species to another, within each species from fall to spring, and also comparing them by species from fall to spring. One way ANOVAs were also used to compare the sizes of the samples in terms of their biomass, or what they would contribute in terms of bulk. We also compared the soil samples to the vegetation samples with a correlation analysis.

After the tests were run, the data was transformed (square-root) to check if the violates of equality of variance and normality were important. Big Woods Prairie could not be included in the comparison due to small sample sizes as a result of incomplete data sets due to flooding.

CHAPTER 3

RESULTS

Biomass and Species Richness

The five study sites included a prairie remnant, and four prairie reconstructions of varying ages. Biomass and species richness provide a means to compare the vegetation at the sites (Tables 7 and 8). Biomass varied significantly among species, and was sampled in the summer to determine how different the sites were. Biomass at the Dunkerton site was 2-3 times less than all other sites tested (Table 7). Biomass of vegetation of the compass plant, *Silphium laciniatum*, was significantly higher than the vegetation adjacent to other species (Table 7).

Dunkerton Prairie has the highest levels of species richness as compared to the other sites (Table 8), but the differences were not significant.

Table 7. Mean biomass of vegetation adjacent to selected forb species sampled, August 2008. NA-no data available

Mean Biomass (g/0.25m ²)											
Site / Species	Deca	Ecpa	Hehe	Leca	Mofi	Rapi	Sila	Soca	Sori	Total Mean	Standard Dev.
Dunkerton	NA	80.1	119.6	41.3	NA	102.7	NA	72.2	73.1	81.5 ^{xz}	27.11
Campus	1331.9	139.5	NA	218.1	95.1	121.3	424.0	151.2	115.8	324.6 ^x	420.5
Museum	NA	NA	157.4	NA	197.7	130.1	362.4	348.4	388.6	264.1 ^{xy}	114.90
Pheasant Ridge	284.3	131.4	95.4	NA	94.8	133.2	350.3	104.5	132.7	165.8 ^{xyz}	96.5
Species Mean	208.1 ^b	117.0 ^b	124.3 ^b	129.7 ^b	129.2 ^b	121.8 ^b	378.9 ^a	169.1 ^b	177.6 ^b	172.9 ^{xyz}	83.35

Table 8. Mean species richness of vegetation sampled adjacent to selected species sampled in August, 2008. A one way ANOVA was used to determine significant mean differences between species richness of sites. The sample size was 0.25 m². NA-no data available.

Mean Species Richness											
Site / Species	Deca	Ecpa	Hehe	Leca	Mofi	Rapi	Sila	Soca	Sori	Total Mean	Standard Dev.
Dunkerton	NA	10.6	7.3	11.6	NA	10.0	NA	10.6	12.3	8.9 ^x	1.73
Campus	7.3	7.6	NA	9.6	8.6	7.6	4.6	5.0	6.3	7.1 ^x	1.70
Museum	NA	NA	7.6	NA	7.0	8.0	7.0	6.0	9.3	7.5 ^x	1.12
Pheasant Ridge	8.3	7.6	8.0	NA	7.0	10.0	6.0	NA	9.3	8.0 ^x	1.35
Species Mean	7.8 ^{bc}	8.6 ^{abc}	7.6 ^{bc}	10.6 ^a	7.5 ^{bc}	8.9 ^{abc}	5.9 ^c	7.2 ^{bc}	9.3 ^{ab}	8.2 ^x	1.36

Dormant Biomass

Silphium laciniatum flower stalk biomass was significantly different from the other species in each sample time (Table 9). All other species in this study had similar flower stalk biomass throughout the samplings (Table 9).

Table 9. Mean flowering stalk biomass (g) and standard error of selected forbs sampled in 2007-08 and 2008-09. Means were derived from combining three randomly selected flower stalks, replicated a minimum of three times. Means of each species were independently analyzed with an ANOVA Repeated Measures to test for significances over time. A Tukey's Test was used to determine significance differences among means. NA-No data available.

Mean Biomass (g)

Species	Fall 2007			Spring 2008			Difference	Fall 2008			Spring 2009			Difference
	Mean	std	N	Mean	std	N		Mean	std	N	Mean	std	N	
Deca	38.4	7.74	18	17.6	4.36	18	-20.8	29.5	4.36	18	47.3	10.72	18	17.8
Ecpa	9.7	1.75	45	8.2	1.27	45	-1.5	6.5	0.87	36	8.4	1.08	36	1.9
Hehe	12.2	3.56	18	7.8	1.47	9	-4.4	5.3	1.15	18	8.6	1.57	9	3.3
Leca	40.0	7.89	27	36.4	7.85	27	-3.6	16.0	3.27	27	28.3	7.12	27	12.3
Mofi	9.5	2.19	45	9.3	2.63	45	-0.2	8.1	2.38	36	10.9	2.90	36	2.8
Rapi	32.0	7.09	45	30.3	8.28	45	-1.7	23.0	9.18	36	33.0	10.67	36	10
Sila	120.1	14.65	45	143.6	16.15	45	23.5	95.7	7.20	27	97.3	12.27	27	1.6
Soca	NA			NA			NA	NA			NA			NA
Sori	51.3	12.28	45	43.0	11.25	45	-8.3	31.4	9.22	36	NA			NA
p-value	<.001			<.001				<.001			<.001			

Potassium

Table 10 and Figures 9 and 10 are a compilation and illustration of the concentrations of potassium in the nine prairie plants in the fall and spring of years 1 (fall 2007 and spring 2008) and 2 (fall 2008 and spring 2009). It is apparent there is a wide range of potassium concentrations with a high of 10,732 ppm for *Solidago canadensis* for spring 2008 and a low of 862 ppm for *Desmodium canadense* for fall of 2007. In fall 2007, the concentration of potassium in *Solidago canadensis* and *Solidago rigida* was significantly higher than the other species. *Silphium laciniatum* was significantly higher than the remainder, while *Desmodium canadense* and *Echinacea pallida* concentrations were significantly lower. *Ratibida pinnata* was significantly lower than the rest. In spring 2007, the concentration in *Solidago canadensis* was significantly higher than all but *Silphium laciniatum*, while the concentrations of the remaining species were somewhat similar. In fall 2008, *Solidago canadensis* was once again significantly higher than the others, and only *Echinacea pallida* was significantly lower than the others. In spring 2009, concentrations in both *Solidago canadensis* and *Silphium laciniatum* were significantly higher than the others while there was little difference in the concentrations of the others.

Table 10. Mean concentration (ppm) of potassium in selected forbs sampled during dormancy in fall 2007, spring 2008, fall 2008 and spring 2009. The means of each species were independently analyzed with a one-way ANOVA to test significance between species. A Tukey's Test was used to determine differences among means.

Mean concentration (ppm) of K								
Species	N	F1(2007)	N	S1 (2008)	N	F2 (2008)	N	S2 (2009)
Deca	12	1737.0 (232.37) ^f	12	9047.3 (466.42) ^{bc}	6	3223.0 (939.20) ^{bc}	6	862.0 (264.82) ^h
Ecpa	9	1812.9 (125.99) ^f	12	8180.5 (547.91) ^{bc}	12	2774.2 (356.17) ^c	12	1514.6 (174.04) ^g
Hehe	6	2664.0 (293.61) ^p	9	8082.2 (973.19) ^{bc}	12	4582.2 (565.48) ^b	12	2016.6 (444.78) ^{fg}
Leca	6	3451.3 (336.26) ^o	9	7630.4 (972.78) ^c	9	4008.2 (603.88) ^b	9	1667.3 (251.93) ^g
Mofi	9	3757.1 (165.80) ^o	10	7760.8 (694.90) ^c	12	4097.0 (368.25) ^b	12	2344.0 (370.44) ^f
Rapi	15	2154.9 (122.59) ^q	12	7440.8 (720.46) ^c	12	2140.2 (162.61) ^d	12	1195.2 (169.77) ^{gh}
Sila	15	5139.6 (468.69) ⁿ	15	10239.9 (643.39) ^{ab}	9	4769.8 (683.10) ^b	9	3445.3 (542.68) ^e
Soca	12	6997.7 (557.90) ^m	9	10731.8 (674.06) ^a	12	5990.2 (473.43) ^a	12	4110.3 (471.55) ^e
Sori	12	6455.0 (312.47) ^m	15	9148.4 (505.46) ^b	12	4619.2 (262.82) ^b	9	1756.3 (187.98) ^g
p-value		<.001		.006		<.001		<.001

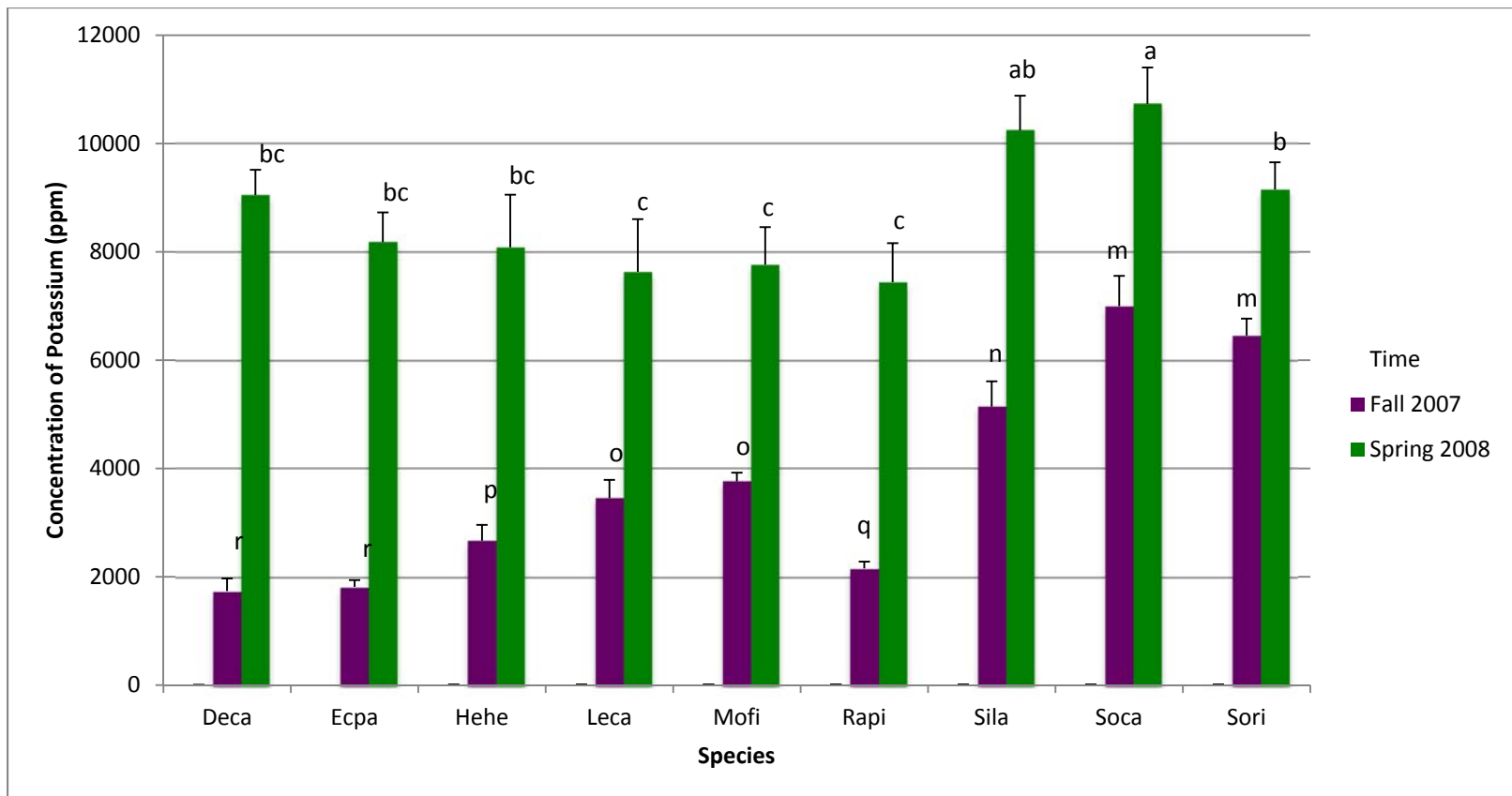


Figure 9. Mean concentration (ppm) of potassium of selected forbs sampled fall 2007 and spring 2008. The means of each species were independently analyzed with a one-way ANOVA to test significances between means. A Tukey's Test was used to determine differences among means.

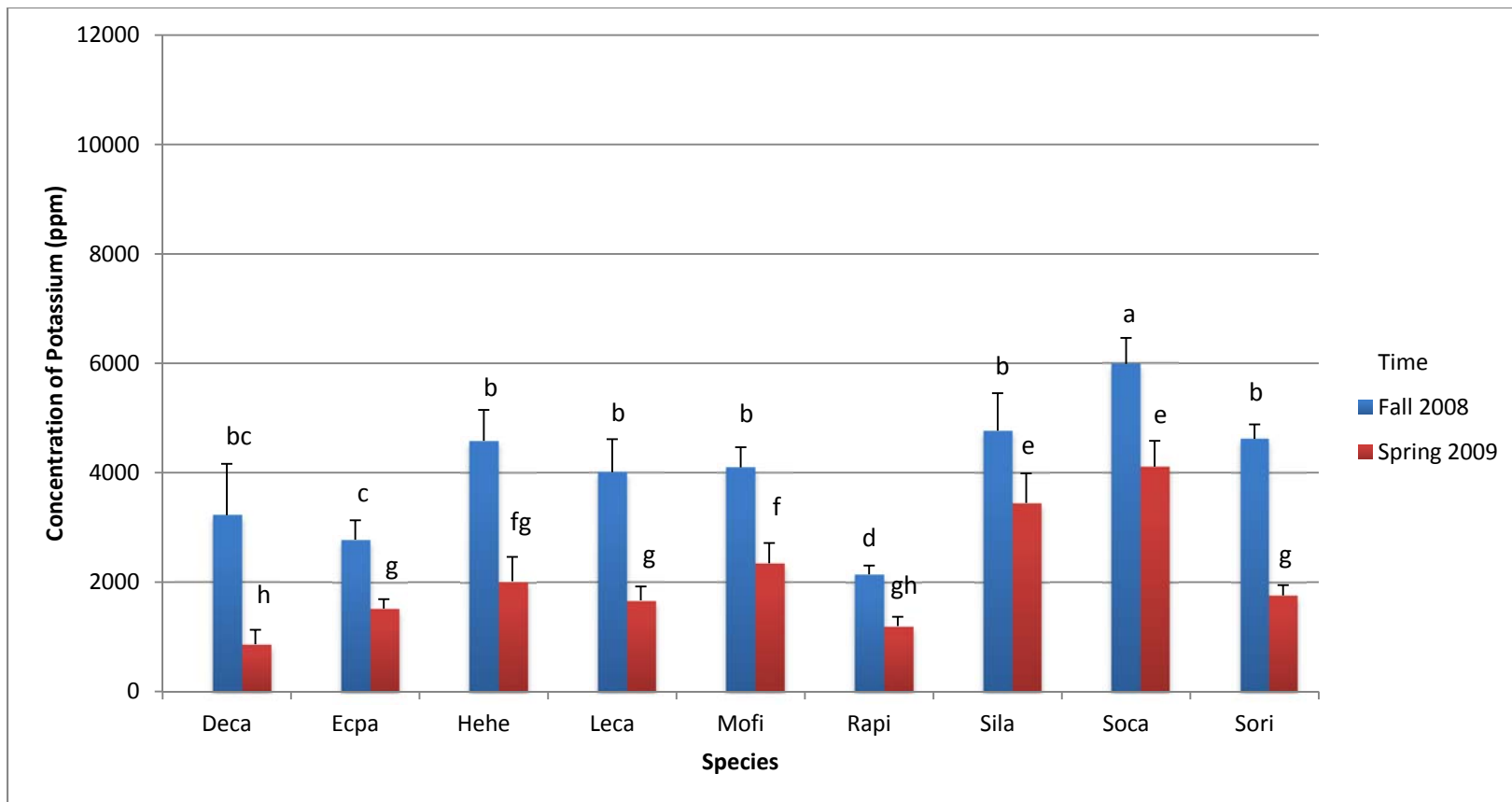


Figure 10. Mean concentration (ppm) of potassium of selected forbs sampled fall 2008 and spring 2009. The means of each species were independently analyzed with ANOVA repeated measures to test significance between means. A Tukey's Test was used to determine differences among means.

Sodium

Table 11 and Figures 11 and 12 represent the concentrations of sodium in the nine prairie plants in the fall and spring of year 1 (fall 2007 and spring 2008) and year 2 (fall 2008 and spring 2009). Unlike the potassium, the sodium concentrations are lower and show a much more limited range of concentrations with a maximum of 260.33 ppm in *Ratibida pinnata* in fall 2008, and a minimum of 30.96 ppm in *Desmodium canadense* in spring 1. In fall 2007, *Desmodium canadense*, *Heliopsis helianthoides*, *Ratibida pinnata*, and *Solidago rigida* have significantly higher concentrations than *Lespedeza capitata* and *Solidago canadensis* while the concentration of *Echinacea pallida* is intermediate. All species concentrations are within 50 ppm of the others. In the spring of year 1, the concentrations of sodium were much less than those of potassium. *Solidago canadensis* is significantly higher in sodium concentration than *Desmodium canadense*, *Echinacea pallida*, *Heliopsis helianthoides*, *Monarda fistulosa*, *Ratibida pinnata*, and *Silphium laciniatum*, but similar to *Lespedeza capitata* and *Solidago rigida*. Interestingly, *Solidago canadensis* and *Lespedeza capitata* both increased in concentration from fall to spring and *Solidago rigida* stayed about the same. All others with the exception of *Monarda fistulosa* declined considerably in sodium concentration from fall to spring.

Concentrations of sodium in fall 2008 were higher than the previous year.

Desmodium canadense, *Lespedeza capitata* and *Silphium laciniatum* had a significantly lower sodium concentration than the other six species. *Ratibida pinnata* was significantly higher in concentration of sodium than *Echinacea pallida* and *Solidago canadensis*. Spring 2009 concentration levels between species did not vary significantly.

Table 11. Mean concentration (ppm) of sodium in selected forbs sampled fall 2007, spring 2008, fall 2008, and spring 2009. The means of each species were independently analyzed with a one-way ANOVA to test significance between species. A Tukey’s Test was used to determine differences among means.

Mean concentration (ppm)/std. error of Na/sample time								
<u>Species</u>	<u>N</u>	<u>F1(2007)</u>	<u>N</u>	<u>S1 (2008)</u>	<u>N</u>	<u>F2 (2008)</u>	<u>N</u>	<u>S2 (2009)</u>
Deca	12	80.8 (10.09)	12	31.0 (3.62)	6	82.0 (15.83)	6	130.7 (36.11)
Ecpa	9	74.7 (9.44)	12	47.5 (7.93)	12	128.5 (28.46)	12	138.7 (35.05)
Hehe	6	92.3 (14.09)	9	56.6 (9.87)	12	232.2 (66.66)	12	120.2 (11.40)
Leca	6	64.9 (3.45)	9	114.9 (27.14)	9	29.3 (99.33)	9	113.8 (15.40)
Mofi	9	80.4 (5.68)	9	75.1 (10.66)	12	181.3 (31.35)	12	134.8 (16.78)
Rapi	15	101.6 (17.47)	12	58.1 (11.92)	12	260.3 (63.88)	12	93.7 (16.74)
Sila	15	75.8 (10.08)	15	49.6 (6.31)	9	84.7 (11.74)	9	119.6 (44.47)
Soca	12	75.3 (4.31)	9	152.2 (32.76)	12	160.2 (28.14)	12	141.0 (17.46)
Sori	12	93.1 (15.18)	15	91.6 (14.67)	12	179.3 (25.97)	12	130.3 (23.69)
p-value		.584		<.001		.039		.922

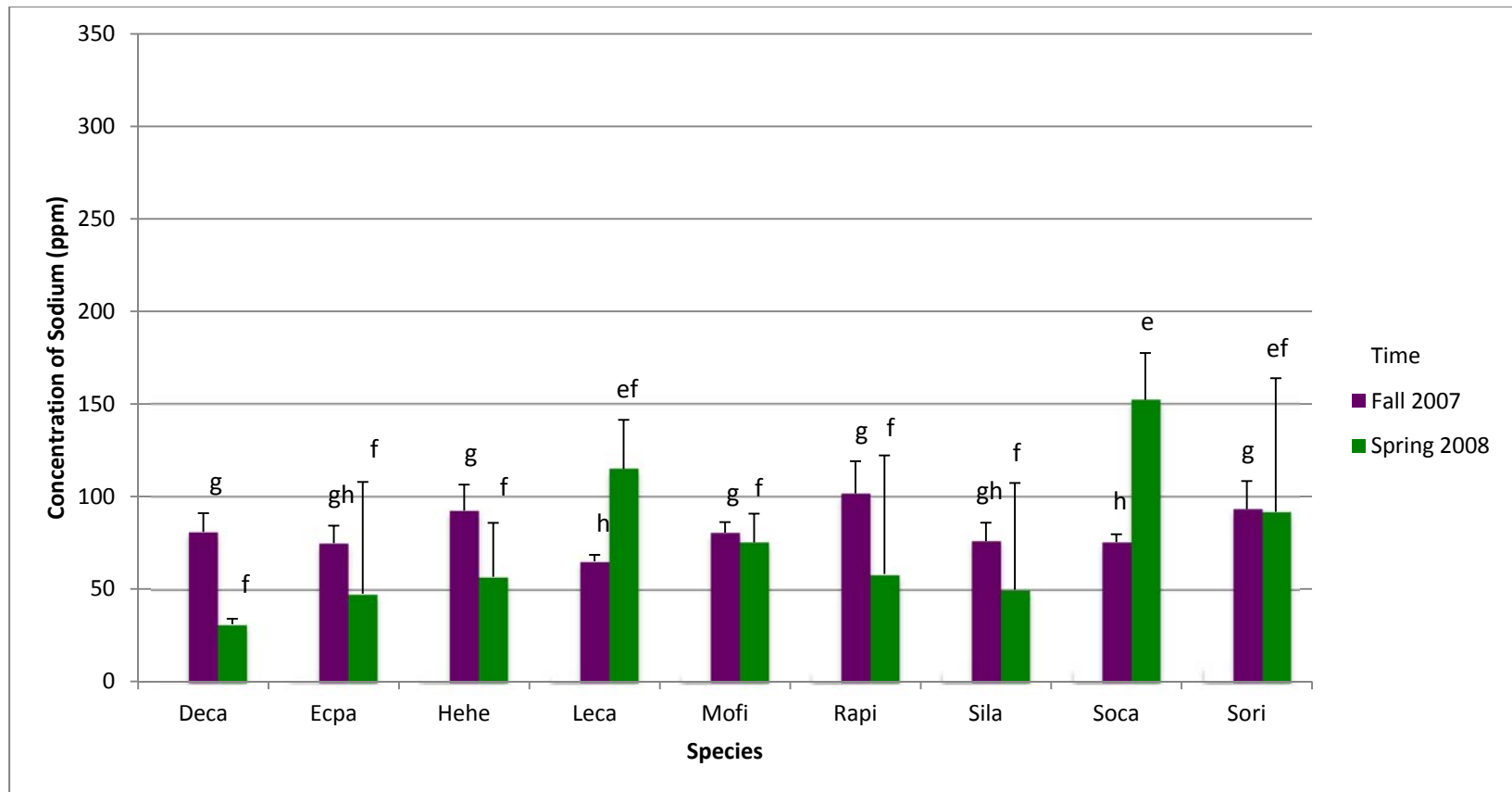


Figure 11. Mean concentration (ppm) of sodium of selected forbs sampled in fall 2007 and spring 2008. The means of each species were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

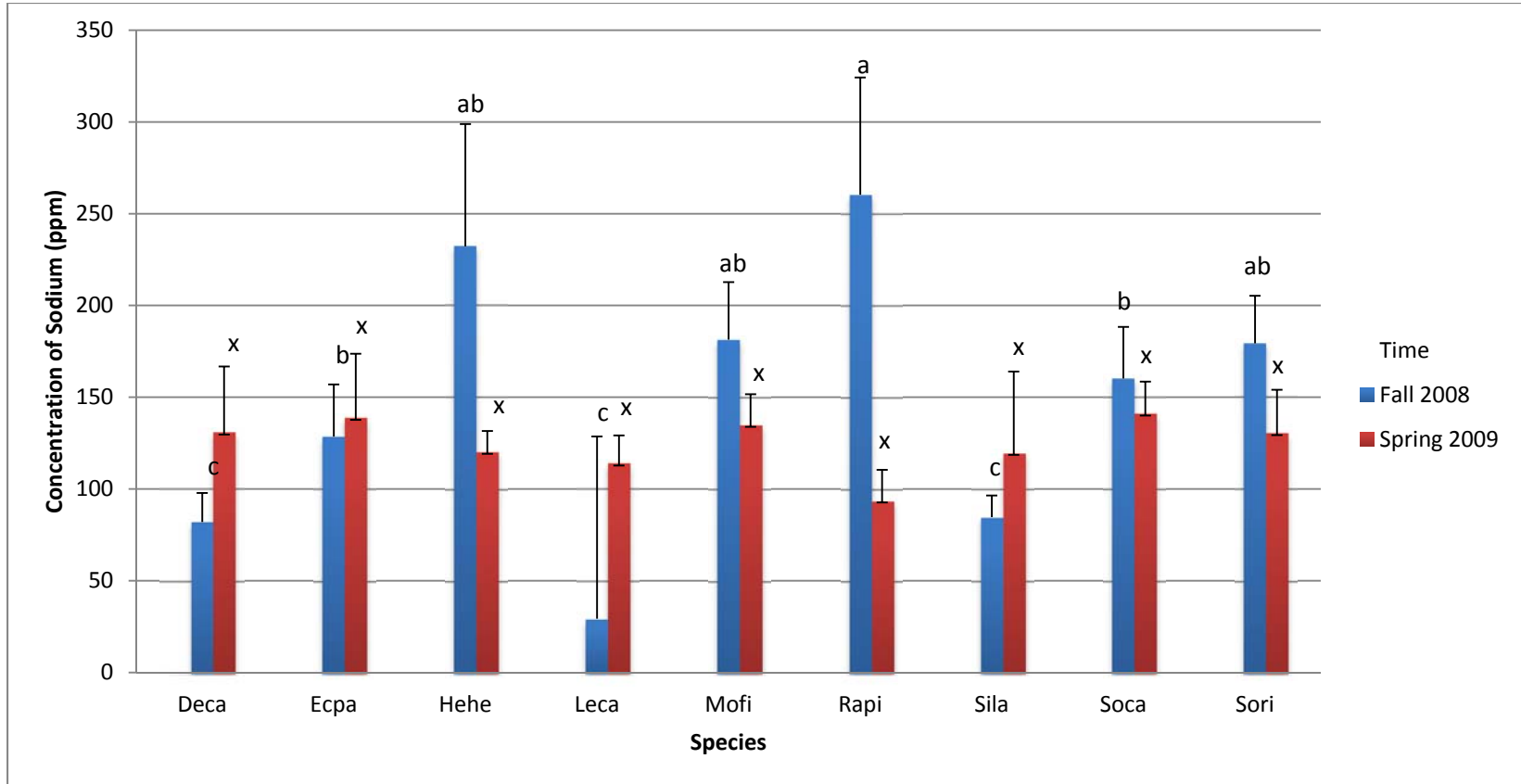


Figure 12. Mean concentration (ppm) of sodium of selected forbs sampled fall 2008 and spring 2009. The means of each species were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

Silicon

Table 12 and Figures 13 and 14 depict concentrations of silicon in the nine prairie plants in the fall and spring of years 1 (fall 2007 and spring 2008) and 2 (fall 2008 and spring 2009). Like the potassium concentrations, there is a wide variation of concentrations ranging from a minimum of 52.14 ppm in *Monarda fistulosa* in spring 2, to a maximum for *Solidago rigida* in fall 1 at 1272.47 ppm. Also like potassium, the concentrations tended to be higher in year 1 than year 2. In the fall of year 1, *Heliopsis helianthoides*, *Ratibida pinnata*, *Solidago rigida*, and *Silphium laciniatum* were not statistically different from each other. The first three species were significantly higher in concentration than *Desmodium canadense*, *Echinacea pallida*, *Lespedeza capitata*, *Monarda fistulosa* and *Solidago canadensis*. *Desmodium canadense*, *Lespedeza capitata* and *Monarda fistulosa* were significantly lower than the other six species. In spring of year 1, the concentrations of silicon in *Ratibida pinnata*, *Silphium laciniatum*, and *Solidago rigida* were significantly higher than the others while *Desmodium canadense* and *Monarda fistulosa* were significantly lower than the others. *Echinacea pallida*, *Lespedeza capitata* and *Solidago canadensis* had a significantly higher concentration of silicon than *Desmodium canadense* and *Monarda fistulosa* but were significantly lower in concentration than the other forbs. *Heliopsis helianthoides* stands alone being significantly higher than the lower five species, and significantly lower than the top three.

The concentrations of silicon in fall year 2 were less varied. The concentrations of *Heliopsis helianthoides*, *Lespedeza capitata*, and *Solidago canadensis* were

significantly higher than *Echinacea pallida* and *Monarda fistulosa*, but the rest were similar.

The concentrations of silicon were low in spring year 2. *Solidago rigida* showed significantly higher concentrations while *Monarda fistulosa* was significantly lower than the others. *Desmodium canadense*, *Echinacea pallida*, and *Silphium laciniatum* were similar and significantly lower than all but *Monarda fistulosa*. *Heliopsis helianthoides*, *Lespedeza capitata*, *Ratibida pinnata*, and *Solidago canadensis* were all similar at an intermediate level of concentration.

Table 12. Mean concentration (ppm) of silicon in selected forbs sampled fall 2007, spring 2008, fall 2008, and spring 2009. The means of each species were independently analyzed with a one-way ANOVA to test significance between species. A Tukey’s Test was used to determine differences among means.

Mean concentration (ppm)/std. error of Si/sample time								
<u>Species</u>	<u>N</u>	<u>F1(2007)</u>	<u>N</u>	<u>S1 (2008)</u>	<u>N</u>	<u>F2 (2008)</u>	<u>N</u>	<u>S2 (2009)</u>
Deca	12	189.2 (16.08)	12	63.2 (2.96)	6	375.8 (138.13)	6	85.3 (14.47)
Ecpa	9	729.8 (175.93)	12	158.2 (60.37)	12	240.7 (50.49)	12	83.7 (20.13)
Hehe	6	1076.3 (177.81)	9	303.4 (29.13)	12	410.3 (87.59)	12	145.9 (27.72)
Leca	6	360.1 (66.31)	9	151.9 (26.51)	9	421.2 (52.57)	9	142.6 (23.21)
Mofi	9	128.2 (11.74)	9	76.0 (15.57)	12	153.0 (43.72)	12	52.1 (5.20)
Rapi	15	1172.0 (133.79)	12	465.1 (64.07)	12	337.0 (94.11)	12	139.7 (5.67)
Sila	15	951.7 (153.67)	15	496.2 (57.71)	9	370.8 (124.80)	9	102.7 (8.58)
Soca	12	578.3 (86.63)	9	152.1 (25.29)	12	430.8 (100.53)	12	120.1 (7.16)
Sori	12	1272.5 (170.08)	15	598.3 (72.26)	12	339.3 (76.83)	12	210.2 (21.31)
p-value		<.001		<.001		.287		<.001

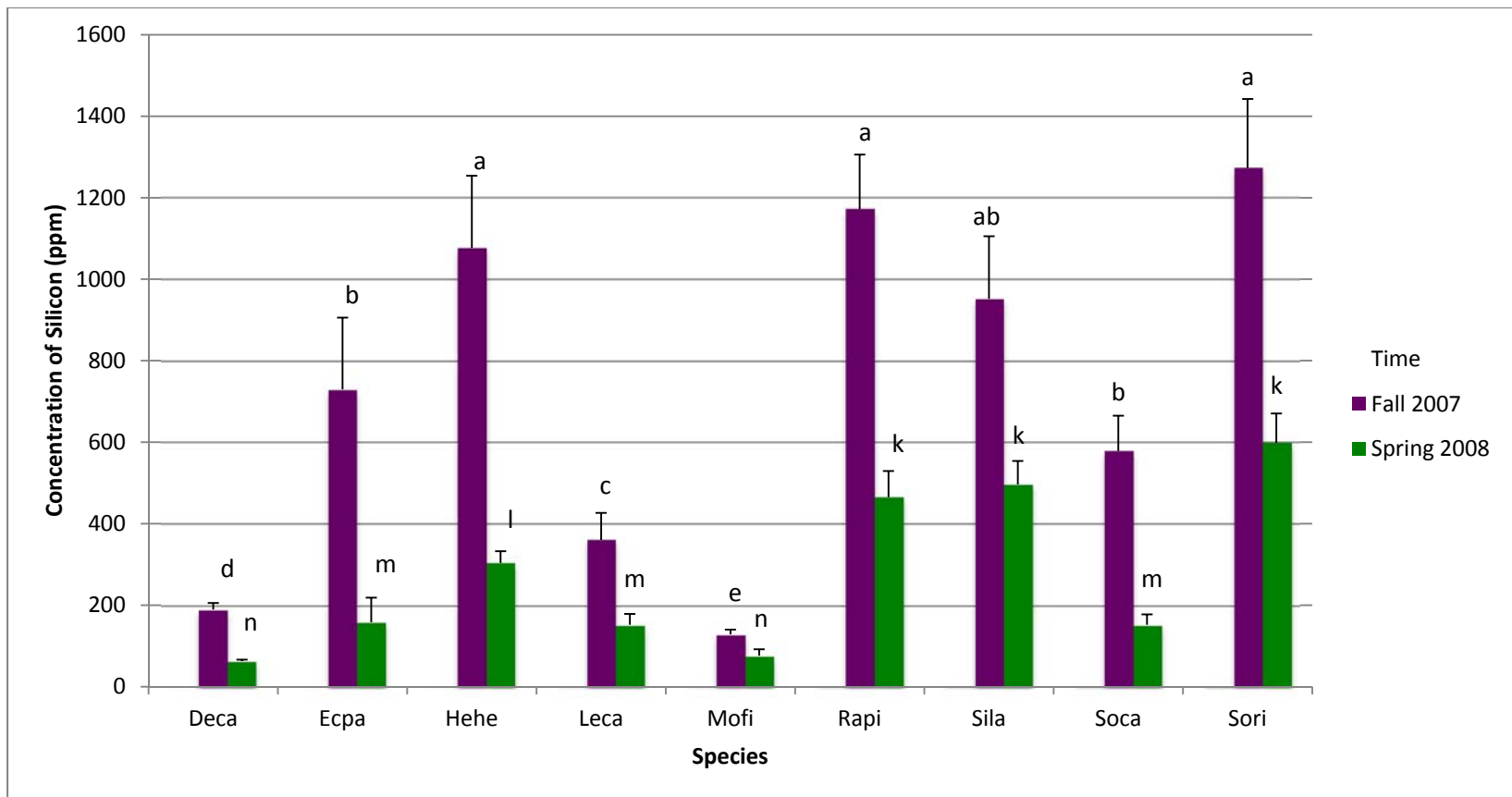


Figure 13. Mean concentration (ppm) of silicon of selected forbs sampled fall 2007 and spring 2008. The means of each species were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

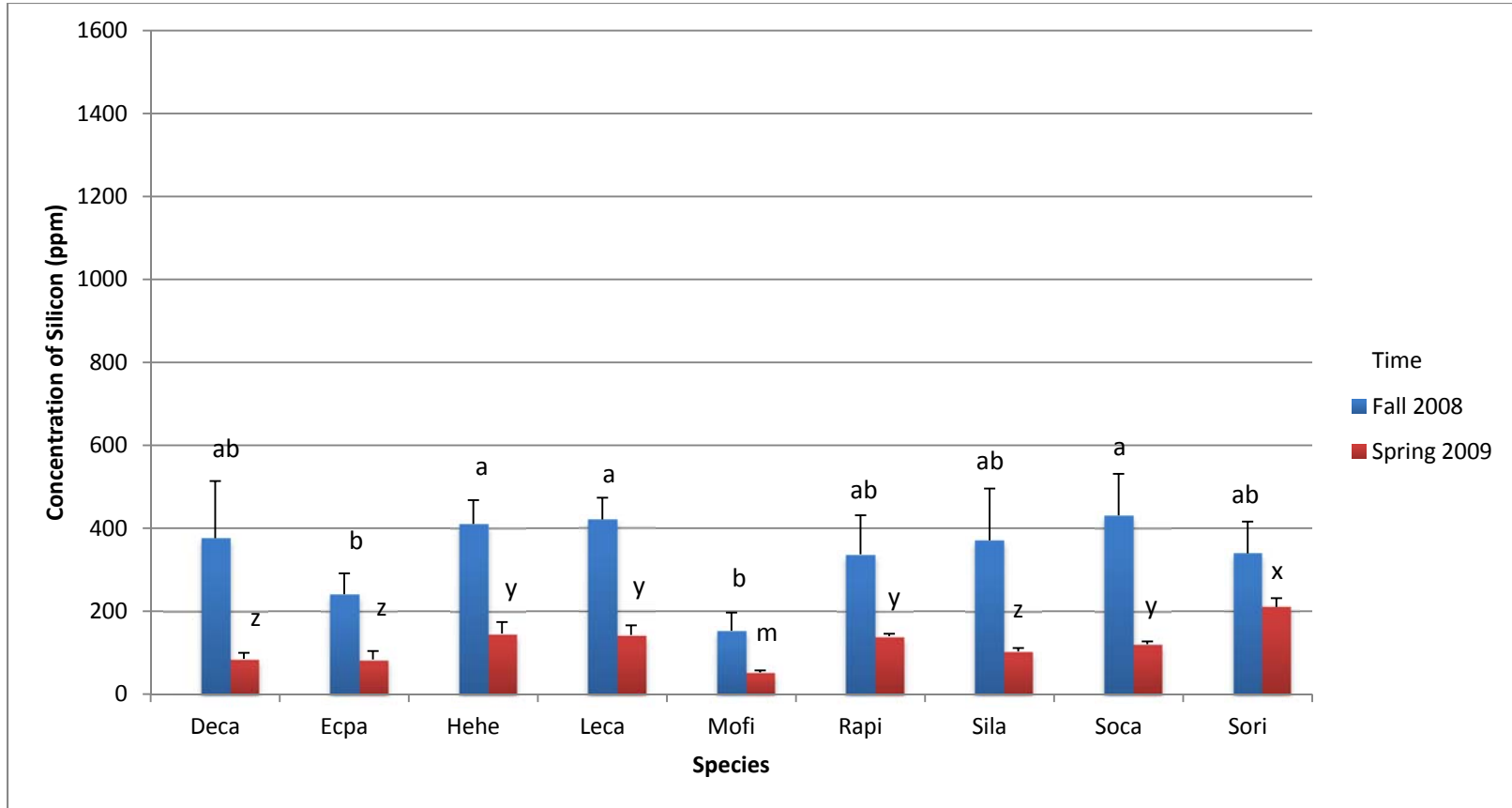


Figure 14. Mean concentration (ppm) of silicon of selected forbs sampled fall 2008 and spring 2009. The means of each species were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

Energy and Slagging

Table 13 shows that the mineral levels of the ash deposits of combusted composite samples of a species across all sites. In the first year both spring and fall potassium levels were the lowest in *Echinacea pallida* and *Solidago canadensis*. However in the second year, again both spring and fall, concentrations were lowest in *Desmodium canadense* and *Solidago canadensis*. Sodium levels in species were much less variable. *Silphium laciniatum* had the lowest amount for all four sample periods whereas *Solidago canadensis* was highest in the fall sample and *Lespedeza capitata* was highest for spring samples. The amount of variability between species for silicon was more similar to that of potassium. *Monarda fistulosa* had the lowest mineral concentration for the fall samples and *Desmodium canadense* was the lowest of the spring species. *Solidago rigida* contained the highest mineral concentration for all four sample periods.

Table 13. Percentage mineral levels of ash of combusted composite samples

Percent of Ash												
Species	K ₂ O				Na ₂ O				SiO ₂			
	F ₁	S ₁	F ₂	S ₂	F ₁	S ₁	F ₂	S ₂	F ₁	S ₁	F ₂	S ₂
<i>Desmodium canadense</i>	3.72	1.48	4.08	2.01	0.57	0.35	0.30	0.60	6.09	7.88	4.98	4.38
<i>Echinacea pallida</i>	2.45	1.44	9.95	4.20	0.20	0.27	0.59	0.72	15.44	15.14	9.96	10.92
<i>Heliopsis helianthoides</i>	9.88	3.45	10.80	3.86	0.42	0.22	0.53	0.44	18.54	23.96	17.27	12.09
<i>Lespedeza capitata</i>	9.76	3.86	13.40	7.60	0.42	1.18	0.71	1.01	17.33	17.35	10.67	12.01
<i>Monarda fistulosa</i>	9.01	5.18	10.30	5.26	0.37	0.49	1.23	0.91	3.83	11.99	4.61	6.44
<i>Ratibida pinnata</i>	4.87	2.32	5.00	3.14	0.36	0.21	0.86	0.41	15.27	17.34	16.36	21.32
<i>Silphium laciniatum</i>	7.15	3.49	6.55	6.30	0.13	0.21	0.19	0.17	16.22	22.23	9.27	10.96
<i>Solidago canadensis</i>	20.80	10.70	16.40	11.9	0.76	0.76	0.76	0.98	17.99	19.86	15.57	11.82
<i>Solidago rigida</i>	11.30	5.55	9.18	5.80	0.41	0.43	0.61	0.73	22.08	31.60	20.75	23.81

Table 14 shows the percent of dry ash and energy production from combustion of each species per sample time. There doesn't seem to be a relationship between the number of BTUs per pound of material and the percent of dry ash left behind. There is no drastic change in energy output from the fall samples to the spring samples, although generally it appears that there is less ash after the combustion of the spring samples than of the fall samples. *Silphium laciniatum* did have the highest percent of dry ash and tended to be lowest in energy production.

Table 14. Percent dry ash and energy output of composite samples of species per sample time.

Species	% of Dry Ash					BTU/lb (HHV)				
	F ₁	S ₁	F ₂	S ₂	Mean	F ₁	S ₁	F ₂	S ₂	Mean
<i>Desmodium canadense</i>	2.77	2.44	2.81	3.79	2.95	8096	8319	8105	8138	8165
<i>Echinacea pallida</i>	3.63	2.98	3.52	2.9	3.26	8039	8202	8028	7907	8044
<i>Heliopsis helianthoides</i>	4.20	3.52	4.45	2.72	3.72	8016	8164	8181	8177	8135
<i>Lespedeza capitata</i>	2.22	2.41	2.71	1.96	2.33	8697	8398	8261	8487	8461
<i>Monarda fistulosa</i>	2.80	2.32	2.96	2.33	2.6	8279	8203	8178	8067	8182
<i>Ratibida pinnata</i>	4.16	2.61	2.76	2.87	3.1	8225	8472	8210	8105	8253
<i>Silphium laciniatum</i>	8.28	5.42	5.53	5.19	6.11	7853	8016	7904	7992	7941
<i>Solidago canadensis</i>	4.68	2.57	2.99	2.32	3.14	8571	8705	8330	8241	8462
<i>Solidago rigida</i>	5.48	4.75	4.07	4.11	4.6	8017	8090	8051	8109	8067
Mean	4.25	3.22	3.53	3.13	3.53	8199	8285	8139	8136	8190

There was little variation between species in terms of energy production per unit mass. As indicated above, *Silphium laciniatum* was least, but only three percent less than the man energy production. *Lespedeza capitata* and *Solidago canadensis* showed the most energy production per unit mass, but only slightly more than 3 percent above the man energy production.

Tables 15 a and b illustrate the data of the sequence of calculating slagging potential of the species using the equation developed by Miles et al. (1995), and applies the data provided in Table 11 to calculate the slag index, the likelihood that slag will be deposited during combustion of the material. To use the equation, the percent ash and percent alkali must first be converted to decimal form.

$$\frac{1 \times 10^6}{\text{HHV Btu/Lb(Dry)}} \times \text{Ash\%} \times \text{Alkali\% in Ash=Lb Alkali/MMBtu} = \text{Combined Index}$$

Miles et al.'s equation provides a numerical value which can be used to assess the likelihood of slagging. Table 15 a shows the values used as a first step of the calculation of the slagging potential. Figure 15 b illustrates the slag index indicating the slag potential of the different species for each sample period.

Table 15 a. The potassium and sodium concentrations of composite samples of species per sample time.

Species	Na ₂ O (% of ash)				K ₂ O (% of ash)			
	F ₁	S ₁	F ₂	S ₂	F ₁	S ₁	F ₂	S ₂
<i>Desmodium canadense</i>	0.57	0.35	0.30	0.60	3.72	1.48	4.08	2.01
<i>Echinacea pallida</i>	0.20	0.27	0.59	0.72	2.45	1.44	9.95	4.20
<i>Heliopsis helianthoides</i>	0.42	0.22	0.53	0.44	9.88	3.45	10.80	3.86
<i>Lespedeza capitata</i>	0.42	1.18	0.71	1.01	9.76	3.86	13.40	7.60
<i>Monarda fistulosa</i>	0.37	0.49	1.23	0.91	9.01	5.18	10.30	5.26
<i>Ratibida pinnata</i>	0.36	0.21	0.86	0.41	4.87	2.32	5.00	3.14
<i>Silphium laciniatum</i>	0.13	0.21	0.19	0.17	7.15	3.49	6.55	6.30
<i>Solidago canadensis</i>	0.76	0.76	0.76	0.98	20.80	10.70	16.40	11.90
<i>Solidago rigida</i>	0.41	0.43	0.61	0.73	11.30	5.55	9.18	5.80

Table 15 b. Slagging potential value of selected species calculated from potassium and sodium ash concentrations using Miles et al. (1995)

Slagging Potential Calculated								
Species	Total (Na ₂ O%+K ₂ O%)/100				Slag Index (lb./MMBtu)			
	F ₁	S ₁	F ₂	S ₂	F ₁	S ₁	F ₂	S ₂
<i>Desmodium canadense</i>	0.043	0.018	0.044	0.026	0.147	0.054	0.152	0.122
<i>Echinacea pallida</i>	0.027	0.017	0.106	0.049	0.120	0.062	0.462	0.18
<i>Heliopsis helianthoides</i>	0.103	0.037	0.113	0.043	0.540	0.158	0.616	0.143
<i>Lespedeza capitata</i>	0.102	0.051	0.141	0.086	0.260	0.145	0.463	0.199
<i>Monarda fistulosa</i>	0.094	0.057	0.115	0.062	0.317	0.16	0.417	0.178
<i>Ratibida pinnata</i>	0.052	0.025	0.059	0.036	0.265	0.078	0.197	0.126
<i>Silphium laciniatum</i>	0.073	0.037	0.067	0.065	0.768	0.25	0.472	0.42
<i>Solidago canadensis</i>	0.216	0.115	0.172	0.129	1.177	0.338	0.616	0.363
<i>Solidago rigida</i>	0.117	0.060	0.098	0.065	0.800	0.351	0.495	0.331

The red lines in Figure 15 indicate the dividing lines between the degrees of slagging potential. From 0 to 0.4 lb./MMBtu, slagging and fouling is unlikely. Between 0.4 lb./MMBtu and 0.8 lb./MMBtu, slagging and fouling is possible. Values above 0.8 lb./MMBtu indicate that slagging and fouling is certain.

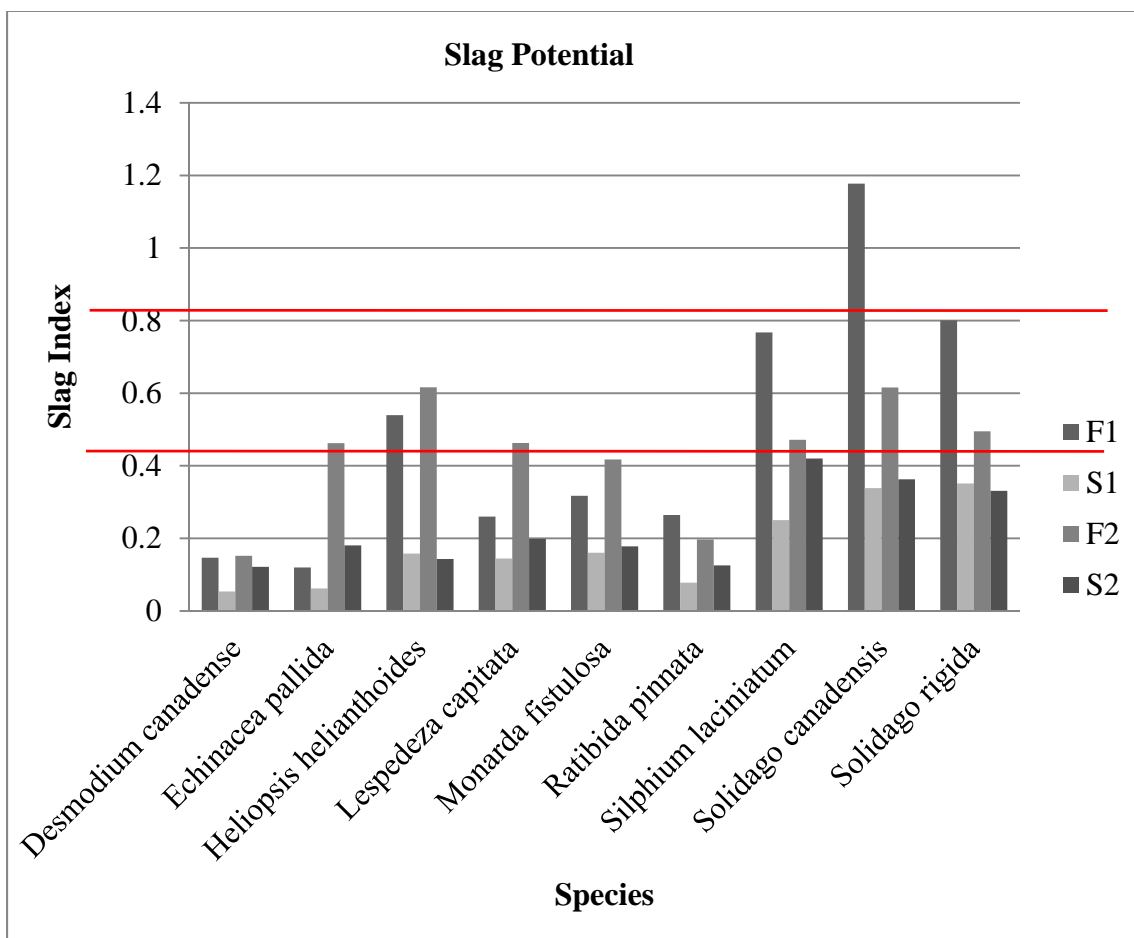


Figure 15. Potential for slagging of selected species as indicated by slag index.

Solidago canadensis was the only species to be above the 0.8 level, and certain to slag in the first fall sampling. *Solidago rigida* was right at 0.8. According to Miles et al. (1995), field experience and boiler operating conditions may determine whether this species will certainly slag, although it is very likely. *Echinacea pallida*, *Heliopsis helianthoides*, *Lespedeza capitata*, *Monarda fistulosa*, *Silphium laciniatum* and of course the two *Solidago* species all fall at one time or another within various samplings between 0.4 lb./MMBtu and 0.8 lb./MMBtu. Each species slagging potential drops from a fall to spring harvest.

The slagging index for all species in both sample periods declined from fall to spring, and a slagging index greater than 0.4 lb/MMBtu was only observed once in the spring (*Silphium laciniatum* in spring 2 with a value of 0.42 lb/MMBtu). Figure 16 shows slagging changes within each species from fall to spring. The more negative numbers indicate that a greater decline has occurred. In some instances the decline from fall to spring was considerable (e.g. *Silphium laciniatum*, *Solidago canadensis*, and *Solidago rigida*), more so during the first year. In other instances, the decline was greater in the second year (e.g. *Echinacea pallida*, *Heliopsis helianthoides*, *Monarda fistulosa*).

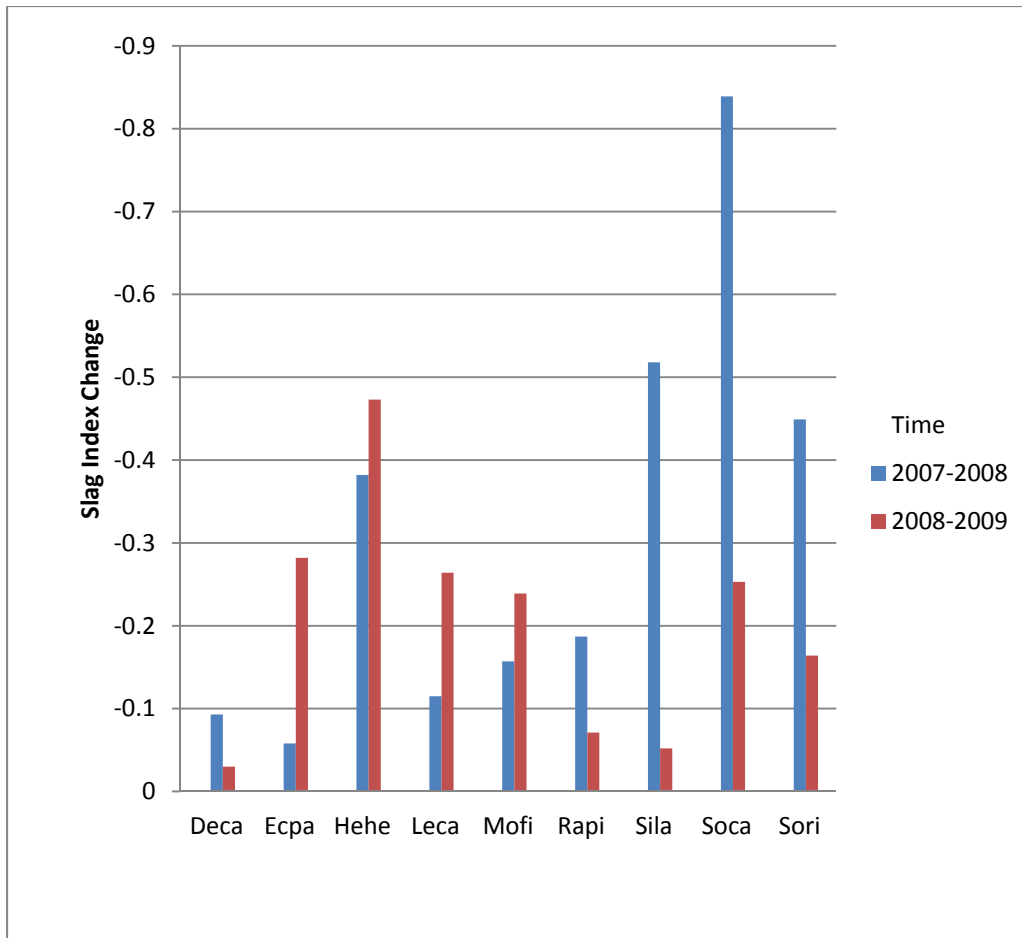


Figure 16. Change in slag index value of sampled forbs from fall to spring in 2007-08 and 2008-09

CHAPTER 4

INTERPRETATION AND DISCUSSION

The sampling of the vegetation of the five sites for species richness and biomass was a means of characterizing the experimental sites and providing insight into these factors in prairie reconstructions of varying ages. The Dunkerton Prairie, a secondary-succession prairie remnant with longevity of more than a century, provided a reference for comparison with the reconstructed sites. I assumed it would have greater diversity as (1) the area likely had ample time to re-establish after undergoing secondary succession from proximal seed sources following disturbance by rail construction in the 1880s, and (2) a limited number of species were planted in the reconstructions. That assumption proved to be valid as it had greater species richness.

Biomass and Species Richness

The relationship of biomass productivity and species richness was not as expected. Tilman et al. (2006) reported that prairie reconstructions with greater species richness produced greater biomass. As a remnant with greater species richness, I assumed that the Dunkerton Prairie would therefore have the greater biomass production. This did not prove to be true. In fact, while fairly diverse, individual plants appeared to be smaller and the site had the least biomass productivity. There are two plausible explanations for this apparent deviation from the findings of Tilman et al. (2006). One explanation is the lack of flowering *Silphium laciniatum* at the time of my study. This was unusual in that the Dunkerton Prairie often has a large number of this species present. *Silphium laciniatum* comprised a large portion of the biomass of the other sites.

If similar amounts had been included in the Dunkerton sample, the biomass productivity would have been considerably higher. A second explanation is a possible limitation in the work of Tilman et al. (2006). The maximum number of species in their research plots was 16, less than one-half the number (34), found in our limited sample at Dunkerton Prairie and well below that of a robust native prairie remnant. It is conceivable that in adapting over many years to maximize niche utilization through higher species richness in a low nitrogen environment, biomass production has been curtailed. If so, less species in a newer prairie reconstruction would have more space available, both above and below ground, and could develop more robustly.

Plants can vary in size from season to season and site to site, but more notably from species to species. For example, the leaves and stalks of *Silphium laciniatum* provide much more biomass than other species in the study. In terms of biomass production for electrical production, larger, more robust plants provide more material for combustion. However, size is not the only consideration. First of all, energy yield per unit is important. Secondly, plants containing a high content of minerals that contribute to slagging are not desirable as they can increase frequency of shutdown to clean slag from the furnace.

Most of the biomass values for each species were similar over the two year period. With one exception, *Desmodium canadensis* fall 2007 vs. spring 2008, there were no differences in dry-weight mass between plants harvested in the spring or fall or between plants harvested in different years. However, for some species, flower stem biomass varied significantly over time. For example, *Desmodium canadense* biomass

was considerably lower in spring 2008 samples than in spring 2009 samples. In contrast, *Lespedeza capitata* biomass was much higher in fall 2007 than in fall 2008 (Table 7).

Biomass changes from fall to spring were inconclusive. The first dormant season all species declined slightly, but not significantly, except *Silphium laciniatum* which increased significantly. Conversely in year 2, flower stem biomass increased slightly in all except *Lespedeza capitata* which increased significantly. The small sample size and the sampling method of locating plants could have influenced the results. Also, in the spring some of the vegetation was flattened by snow and larger stems were easier to locate.

Energy does not vary much between fall and spring of either year (Table 14). The variation in energy appears from species to species and not from fall to spring.

Variability of Minerals between Species

Like most research related to causes of slagging and fouling by biofuels, this study focused on three elements common in plants, two alkali metals, potassium and sodium, and silicon.

I hypothesized that the concentrations of the three minerals would vary from species to species. The mineral concentrations of the nine species did differ, but the differences were not consistent for the four sample times in the two-year study. The concentrations ranged as follows: potassium 862-10,732 ppm, sodium 31-260 ppm and silicon 52-1172 ppm.

Potassium is an essential plant nutrient and is required in large amounts. Consequently it is absorbed by plants in larger amounts than any other mineral element

except nitrogen. For optimal growth potassium levels in plants should be between 2 and 3 percent of the dry weight (Patterson 2015). I observed concentrations of 0.1 to 1 percent remaining in the standing dead stem tissue of the nine species.

Although the concentrations of potassium did vary from species to species as hypothesized, with a few exceptions, the differences were not significant. The concentrations of potassium for all species seemed to be unusually high in spring 2008. *Solidago canadensis* had the highest concentration of potassium at all four sample times. Its potassium level was significantly higher than all species in fall 2008 and at the other three sample times the level was significantly higher than all except that of either *Silphium laciniatum* or *Solidago rigida*. Although the values were not always significant, *Desmodium canadensis*, *Echinacea pallida* and *Ratibida pinnata* tended to have lower concentrations of potassium than the others.

Sodium levels in plants tend to be much lower than potassium levels. I found them to be lower by a factor of ten or more. Sherrell (1978) harvested agronomic species when they were still vegetative and undergoing rapid growth. He observed a wide difference in sodium concentrations ranging from 0.01 to 0.3 percent of dry matter. In my study, sodium levels varied from species to species, as hypothesized, however, the range of variation was not as great as potassium, probably in part because the concentrations were lower. All species had similar concentrations of sodium in spring 2009. In spring 2008 eight of the nine species were similar to one another although *Solidago canadensis* was significantly higher than six of the species. There did not

appear to be a trend where any one species was higher or lower over the four sample times so they essentially did not vary from species to species as hypothesized.

Silicon is readily absorbed so that terrestrial plants contain it in appreciable concentrations, but usually less than potassium. Plants easily absorb silicon in the form of H_4SiO_4 and all plants growing in soil contain it as an appreciable fraction of the dry matter (Raven 1983). The concentration of silicon in plants usually ranges from 0.1 to 10 percent although some may contain more than that. I observed much lower silicon concentrations of 0.001 to 0.012 percent in my samples. Apparently the species studied are not silicon accumulators. Although my values are somewhat lower, they correspond to values in the review of Jones and Handreck (1967). They noted that the percentage/dry weight of silicon in dicotyledons was approximately 0.1 percent and about 1 percent in dryland grasses.

Even at the low levels in the plants I studied, there was variation in silicon concentration between species. More variation was apparent in the first year, especially in fall 2007, than in the second year. Three species, *Heliopsis helianthoides*, *Ratibida pinnata* and *Solidago rigida* were significantly higher than all the others except *Silphium laciniatum*. However, those higher concentrations were only for one sample time and did not recur in the other three. The concentration of silicon in *Monarda fistulosa* was consistently very low at all four sample times, in fact, it was significantly lower than all others at three of the four sample times. As hypothesized, there was variation between species; however, in most cases the variations were not consistent from sample time to sample time.

Changes in Mineral Concentrations during Dormancy

The debate continues regarding the best harvest time for optimal fuel quality to minimize slagging in burning plant biomass for energy. Both the total amount of ash as well as specific inorganic constituents in herbaceous biomass can be manipulated by the timing of harvesting. Fuels harvested in the summer are too green and contain large quantities of minerals acquired during growth. Extending harvest dates later in the season generally leads to lower ash content. The delay allows time for more retranslocation of minerals into the roots (Ogden et al. 2010) and leaching by rain, mist or dew. After a killing frost, minerals can still be leached from the standing dead stems. In addition, any remaining leaves are usually shed over winter. Consequently, the general recommendation has been to delay harvesting until the following spring for more mineral reduction and thus lower potential for slagging.

Based upon that background information regarding spring harvesting of biomass, I hypothesized that the concentration of the minerals in the plants would be less in the spring than in the fall. However, the changes in concentrations of the three minerals from fall to spring in plant samples from each site were variable, inconsistent and not as predicted.

The concentrations of potassium increased significantly from fall to spring in all the samples of individual species in year 1. This was unexpected and contrary to what I hypothesized and, also, contrary to the data of the composite of plant material from all sites. On the other hand, the potassium concentrations in all samples of individual species dropped significantly from fall to spring in year 2 as hypothesized. In all the

plant samples of the composite material, the level of potassium declined from fall to spring as expected.

Potassium is a major nutrient and very important for growth of plants; high concentrations are common in rapidly growing plants. The concentration does commonly depend on growing season of the plant, e.g. in summer and spring when the growth of the plant takes place, the concentrations are higher than in the winter when no growth occurs. Much of the potassium for the initial rapid spring growth comes from storage in the roots than by concurrent absorption. My late winter samples were of standing dead stems prior to initiation of growth; it is unlikely there would be any increase in potassium in those tissues. In the fall, potassium is translocated from senescing leaves into fruits, supports root growth and contributes to potassium storage. Potassium ions are highly water-soluble and can be lost from tissue by leaching. Some grasses have been shown to be highly susceptible to leaching during frost (Hinnant and Kothmann 1982).

Potassium in the dead stems declined in both the second year of the independent samples and in both years of the composite samples. As indicated above, potassium concentration would be expected to be higher in the fall than in the spring. It is likely that any changes in potassium concentration in the dead stems during the winter dormant period is due to leaching. Due to high solubility in water, potassium loss would be more likely in wet winters than in dry winters and in those winters with more days above freezing when melting occurs. In year 2 there were six more days at 32° F or above than year 1. However, I am hard pressed to explain the increase in potassium in the independent sample data of year 1.

The changes in sodium concentration from fall to spring in the independent samples are quite similar, although of lesser magnitude, to those of potassium. The concentrations of sodium in the independent samples decreased in 8 of the 9 species from fall 2007 to spring 2008; in 6 species the decrease was significant. In the composite samples 7 of 9 decreased. These changes were consistent with my hypothesis. In year 2, all 8 species of the independent samples increased in concentration and the increase was significant in 5 species. In the composite samples, 5 of 9 species had a decrease in concentration. The independent samples were opposite what I hypothesized although the results of the composite samples were mixed.

Sodium is a functional plant nutrient rather than an essential one like potassium (Subbarao et al. 2003). Sodium occurs in plant roots and the shoot including leaves. Deposits occur in epidermal, strengthening, storage and vascular tissues during the growth and development of the shoot.

Kronzucker and Britto (2011) note that the complexity of sodium transport in plants appears, in some ways, to exceed that of most other ions, resulting in models of influx, efflux, sequestration, long-distance transport and recirculation whose complexity seems disproportionate to the extremely limited value of sodium as a provisional plant nutrient.

The entry of sodium ions into plant cells is essentially a passive process due to electrical potential difference at the plasma membrane and low sodium concentrations in the cells. In contrast, sodium extrusion from cells is an indirect active process. With the death of plants after a killing frost any changes in sodium content with the plants would

be the result of passive movement like leaching. Sodium and potassium are sufficiently soluble to leach out of the dead stems during the winter months which would explain the decrease in sodium concentration from fall to spring in year 1. However, like the changes in potassium, it is difficult to conceive an explanation as to why it increased from fall to spring in year 2.

The species data of the composite samples and the independent samples from all sites were not consistent for silicon. Silicon in the independent samples from all sites declined in all species both years as hypothesized. However, the changes in concentration of silicon data of the composite samples were contrary to that as most species in year 1 increased (8) as did 6 in year 2. Little is known regarding what happens to silicon after the plant matures, becomes dormant and is killed by freezing.

Silicon is readily absorbed so that plants contain it in appreciable concentrations. It is generally thought that silica in solution as monosilicic acid is carried passively in the transpiration stream and is deposited in larger quantities in parts of the plant from which water is lost in greatest quantities. Soluble silicon in soil solution at a pH range from 2 to 9 is mainly present as orthosilicate. In this form silicon is an uncharged compound and sensitive to leaching. Again leaching of silicon from the plant tissue is the likely explanation for decreases from fall to spring.

Slagging Potential

To address concern raised regarding slag production from trace metals and other minerals in plants during the combustion process of burning prairie biomass for electrical generation, I tested the experimental species for concentrations of potassium, sodium and silicon to determine their potential for slagging. The inorganic elements contribute directly to the quantity of ash left behind in combustion testing.

Plant materials were sent to both the Iowa State University Soil and Plant Analysis Lab and to Hazen Research, Inc. As discussed in Materials and Methods, I sent samples of each species from each site to the ISU Lab, but only combined plant material from all sites for each species to Hazen. Although the ISU results provided more data for statistical analysis, the more consistent results from Hazen were more useful in calculating slagging index and comparing slagging potential of different species.

Miles et al. (1995) developed a calculation using concentrations of alkaline metals, potassium and sodium, that combined slagging and fouling potential into one index. The scale of this index can be used as a guide to assess the potential of plant material for both slagging and fouling. On the combined index a value below 0.4 lb/MM Btu is considered a fairly low slagging risk. Values between 0.4 and 0.8 lb/MM Btu indicate the probability of increasing certainty of slagging as 0.8 lb/MM Btu is approached. Above 0.8 lb/MM Btu, the fuel is virtually certain to slag and foul.

Data from the combined plant materials of the five sites applied to this scale indicates that fall-harvested, plant material from *Solidago canadensis*, *Solidago rigida*, or *Silphium laciniatum* is almost certain to slag. Their slagging probability would not make

them good candidates for burning as biomass although they do drop to the low end of slagging probability in the spring. On the other hand, *Desmodium canadensis* would be a good candidate and *Echinacea pallida* and *Ratibida pinnata* are possibilities. The candidacy of *Lespedeza capitata*, *Monarda fistulosa* or *Heliopsis helianthoides* might depend on harvest time. For spring harvesting, only *Silphium laciniatum* reached a level of possible potential for slagging and that was just in the second spring. The two *Solidago* species did approach the minimum value for potential slagging in both spring samples.

While silicon concentrations are not used in calculations to predict slagging, it is a major mineral constituent of plants and has been found to be a contributor to slagging (Demirbas 2005). Therefore, its concentration levels should be a consideration when selecting species in a mix for biomass that will be burned. As there is a fairly consistent pattern of decline in silicon concentration from fall to spring in all species, it appears that silicon content may not be a fouling or slagging problem if harvest is delayed until spring.

Summary

A primary concern about the burning prairie biomass for electrical generation is the production of slag during the combustion process from trace metals and other minerals within plants. The slagging potential of herbaceous plants could be high because they contain potassium and silicon as their principal ash-forming constituents. This concern is based almost exclusively on experience gained from the use of graminoids as biofuels.

This study was initiated to ascertain if forbs in prairie biomass mixtures should be the subject of such concern. If so, then the next question is whether all forbs have potential for slagging. Concentrations of potassium, sodium and silicon in nine species, *Desmodium canadense*, *Echinacea pallida*, *Heliopsis helianthoides*, *Monarda fistulosa*, *Lespedeza capitata*, *Ratibida pinnata*, *Silphium laciniatum*, *Solidago canadensis* and *Solidago rigida*, were examined to gain insight into their potential for slagging.

Energy yields per unit weight upon combustion of the eight species were similar. However, the concentrations of the alkaline minerals in plant tissues indicate that *Solidago canadensis*, *Solidago rigida*, and *Silphium laciniatum* have high potential for slagging and should be avoided as biofuels. Although the results of the independent samples were somewhat inconsistent, those coupled with the composite samples suggest *Desmodium canadensis* would be a good candidate for a biomass mix and *Echinacea pallida* and *Ratibida pinnata* are possibilities. The use of *Lespedeza capitata*, *Monarda fistulosa* or *Heliopsis helianthoides* might depend on harvest time as their concentrations declined from fall to spring.

Solidago rigida, *Silphium laciniatum*, *Heliopsis helianthoides*, and *Ratibida pinnata* concentrations of silicon tended to be somewhat high in the fall, but declined in the spring. The concentration in *Monarda fistulosa* was consistently low.

For a utility company planting to produce biomass for electrical generation, serious consideration should be given to a spring harvest.

Conclusion

- Concentrations of slag inducing minerals, potassium, sodium and silicon present in the forb species studied vary from species to species.
- *Solidago canadensis*, *Solidago rigida*, and *Silphium laciniatum* have a high potential for slagging and should be avoided as biofuels.
- *Desmodium canadensis* has a low potential for slagging and would be a good candidate for a biomass mix. The slagging potentials of *Echinacea pallida* and *Ratibida pinnata* are sufficiently low enough for them to also be considered for a biomass mix.
- Concentrations of slag inducing minerals, potassium, sodium and silicon, present in certain forbs usually decline from fall to spring. In that case, *Lespedeza capitata*, *Monarda fistulosa* and *Heliopsis helianthoides* could be considered for biomass production.

LITERATURE CITED

- Adler PR, Sanderson MA, Boateng AA, Weimer PJ, Jung HG. 2006. Biomass yield and biofuel quality of switchgrass harvested in the fall or spring. *Agron. J.* 98:1518-1525. Doi: 10.2134/agronj2005.0351. Retrieved 2008 Jan 21 from <https://www.soils.org/publications/aj/articles/98/6/1515>.
- ASTM Standard D 2795. 1995. Standard test methods for analysis of coal and coke ash. ASTM International, West Conshohocken, PA, 2002, DOI: 10.1520/D2795-95, Retrieved from: www.astm.org. Book Volume 05.06.
- ASTM Standard D 3172. 1997. Standard Practice for Proximate Analysis of Coal and Coke. ASTM International, West Conshohocken, PA, 2008, DOI:10.1520/D3172-07A, Retrieved from: www.astm.org. Book Volume 05.06.
- ASTM Standard D 3176. 1997. Standard Practice for Ultimate Analysis of Coal and Coke. ASTM International, West Conshohocken, PA, 2008, DOI:10.1520/D3176-09, Retrieved from: www.astm.org. Book Volume 05.06.
- ASTM Standard D 5865. 2007. Standard test methods for Gross Calorific Value of Coal and Coke. ASTM International, West Conshohocken, PA, 2008, DOI: 10.1520/D5865-7A, Retrieved from: www.astm.org. Book Volume 05.06.
- Auclair AN. 1977. Factors affecting tissue nutrient concentrations in a *Carex* meadow. *Oecologia.* 28:233-246.
- Bair RA. 1966. Leaf silicon in sugarcane, field corn and St. Augustine grass grown on some Florida Soils. *Soil Crop Sci. Soc. Fla.* 26:63-70.
- Bakker RR, Elbersen HW. 2005. Managing ash content and quality in herbaceous biomass: an analysis from plant to product. Pages 17-21. *In* 14th European Biomass Conference and Exhibition.
- Bevill K. 2011. The Core of Advancement. *Ethanol Producer Magazine*, Retrieved 2011 Feb 15 from: <http://www.ethanolproducer.com/articles/7484/the-core-of-advancement>.

- Biolex. 2015. Main ash forming elements. Information bulletin. Biolex Therapeutics. Retrieved 2015, Jan 29th from: <http://biolex.dk-teknik.dk/cms/site.aspx?p=4732>.
- Burvall J. 1997. Influence of harvest time and soil type on fuel quality in reed canary grass (*Phalaris Arundinacea* L.). *Biomass and Bioenergy* 12: 149-154.
- Casler MD, Vogel KP, Taliaferro CM, Wynia RL. 2004. Latitudinal adaptation of switchgrass populations. *Crop Sci.* 44: 293-303.
- Clayworth J. 2007. Iowa Power Fund, Governor signs bills fostering renewable energy. Des Moines Register Online. Retrieved 2008 Jan 15 from: <http://pqasb.pqarchiver.com/desmoinesregister/access/1729356001.html?did=1729356001:1729356001&FMT=ABS&FMTS=ABS:FT&type=current&date=May+24%2C+2007&author=Clayworth+Jason&pub=Des+Moines+Register&edition=&startpage=B.1&desc=Governor+signs+bills+fostering+renewable+energy>.
- Culp K. 2011. Iowa State Soil and Plant Analysis Lab. Personal Communication.
- Demirbas A. 2005. Potential applications of renewable energy sources, biomass combustion problems in boiler powered systems and combustion related environmental issues. *Progress in Energy and Combustion Science* 31: 171-192.
- Energy Information Administration. 2008. Retrieved 2009 Jan 15 from: <http://www.eia.gov/state/state-energy-profiles.cfm?sid=IA>.
- Environmental Protection Agency. 2007a. Method 3015A: Microwave assisted acid digestion of aqueous samples and extracts. Revision 1.
- Environmental Protection Agency. 2007b. Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils and oils. Revision 1.

- Florine SE, Moore KJ, Fales SL, White TA, Burras CL. 2006. Yield and composition of herbaceous biomass harvested from naturalized grassland in southern Iowa. *Biomass and Bioenergy*, 30(6). Retrieved 2008 Jan 15 from: http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6V22-4J4HK84-2&_user=10&_coverDate=06%2F30%2F2006&_alid=1152010434&_rdoc=1&_fmt=high&_orig=search&_cdi=5690&_sort=r&_docanchor=&view=c&_ct=1&_acct=C000050221&_version=1&_urlVersion=0&_userid=10&md5=5d3b6ab671732b1a0d5f667ad8beb76a.
- Hare N, Rasul MG, Moazzem S. 2010. A review on boiler deposition/fouling prevention and removal techniques for power plant. In Proceedings of the 5th IASME/WSEAS International Conference on Energy and Environment2: 23-25.
- Hinnant RT, Kothmann MM. 1982. Potassium content of three grass species during winter. *Journal of Range Management* 35: 211-3.
- Iowa Renewable Fuels Association. 2012. Iowa ethanol output held steady at 3.7 billion gallons in 2012. Retrieved from: <http://ethanolproducer.com/articles/9414/iowa-ethanol-output-held-steady-at-3-7-billion-gallons-in-2012>.
- Jones LH, Handreck KA. 1967. Silica in soils, plants, and animals. *Advances in Agronomy* 19: 107-149.
- Klaas DL. 1998. Biomass for renewable energy, fuels and chemicals. Pages 74, 202-224. Academic Press, San Diego, CA.
- Kronzucker HJ, Britto DT. 2011. Sodium transport in plants: A critical review. *New Phytologist* 189: 54-81.
- Lawton K, Cook RL. 1954. Potassium in plant nutrition. *Advan. Agron.* 6: 253-306
- Lewandowski I, Kicherer A. 1997. Combustion quality of biomass: Practical relevance and experiments to modify the biomass quality of *Miscanthus x giganteus*. *European Journal of Agronomy* 6: 163-177.

- Lewandowski I, Scurlock JM, Lindvall E, Christou M. 2003. The development and current status of perennial rhizomatous grasses as energy crops in the US and Europe. *Biomass and Bioenergy* 25: 335-361.
- Magasiner N, van Alphen C, Inkson, MB, Misplon BJ. 2001. Characterising fuels for biomass – coal fired cogeneration. Retrieved 2008 Jan 30 from: <http://www.tesboilers.com/sasta.html>.
- McKendry P. 2002. Energy production from biomass (part 1): Overview of biomass. *Bioresource Technology* 83: 37-46.
- Miles TR, Miles TR Jr, Baxter LL, Bryers RW, Jenkins BM, Oden LL. 1995. Alkali Deposits, Summary Report, National Renewable Energy Laboratory, Golden, CO. 83.
- Miles TR, Miles TR Jr, Baxter LL, Bryers RW, Jenkins BM, Oden LL. 1996. Boiler Deposits from firing biomass fuels. *Biomass and Bioenergy* 10: 125-138.
- Miles TR, Miles TR Jr, Baxter LL, Jenkins BM, Oden LL. 1993. Alkali Slagging Problems with Biomass Fuels. First Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry 1.
- Natural Resources Conservation Service 2006. Soil Survey of Black Hawk County, Iowa. National Cooperative Soil Survey Washington.
- Ogden CA, Ileleji KE, Johnson KD, Wang Q. 2010. In-field direct combustion fuel property changes of switchgrass harvested from summer to fall. *Fuel Processing Technology* 91: 266-271.
- Patterson G. 2015. Potassium nutrition in plants. A & L Canada Laboratories, London. Retrieved 2015 March 1 from: <http://www.ccaontario.com/FCKEditor/File/Potassium%20in%20soils.pdf>.
- Picasso VD, Brummer EC, Liebman M, Dixon PM, Wilsey BJ. 2008. Crop species diversity affects productivity and weed suppression in perennial polycultures under two management strategies. *Crop Sci.* 48: 331-342.

- Price A. 2009. UT scientists weed out switch grass for biofuel potential. Austin American –Statesman, Texas. Retrieved 2010 July 13 from: <http://www.allbusiness.com/science-technology/earth-atmospheric-science/13476327-1.html>.
- Raven JA. 1983. The transport and function of silicon in plants. *Biol. Rev.* 58: 179-207.
- Renewable Fuels Association. 2013. Statistics: Historic U.S. fuel ethanol production. Retrieved from: <http://www.ethanolrfa.org/pages/statistics>.
- Rinehart L. 2006. Switchgrass as a bioenergy crop. ATTRA Publication #IP302. Retrieved 2008 Jan 18 from: <http://attra.ncat.org/attra-pub/switchgrass.html>.
- Sami M, Annamalai K, Wooldridge M. 2001. Co-firing of coal and biomass fuel blends. *Progress in Energy and Combustion Science* 27: 171-214.
- Samson R, Mehdi B. 1998. Strategies to reduce the ash content in perennial grasses. *Proc. BioEnergy '98: Expanding BioEnergy Partnerships, Madison, WI.*: 4-8.
- Sanderson MA, Wolf DD. 1995. Switchgrass biomass composition during morphological development in diverse environments. *Crop Science Society of America* 35: 1432-1438.
- Savant NK, Korndorfer GH, Datnoff LE, Snyder GH. 1999. Silicon nutrition and sugarcane production: A review. *Journal of Plant Nutrition* 22: 1853-1903.
- Sherrell CB. 1978. A note on Sodium concentrations in New Zealand pasture species. *New Zealand Journal of Experimental Agriculture* 6: 189-90.
- Skrifvars BJ, Backman R, Hupa M. 1998. Characterization of the sintering tendency of ten biomass ashes in FBC conditions by a laboratory test and by phase equilibrium calculations. *Fuel Processing Technology* 56: 55-67.
- Smith D. 2008. Personal Communication.

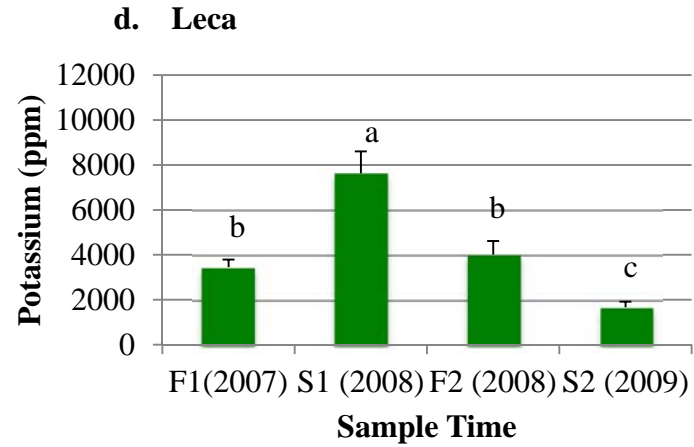
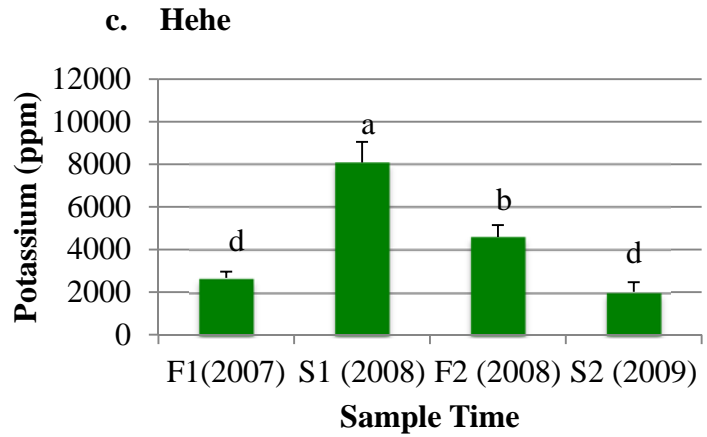
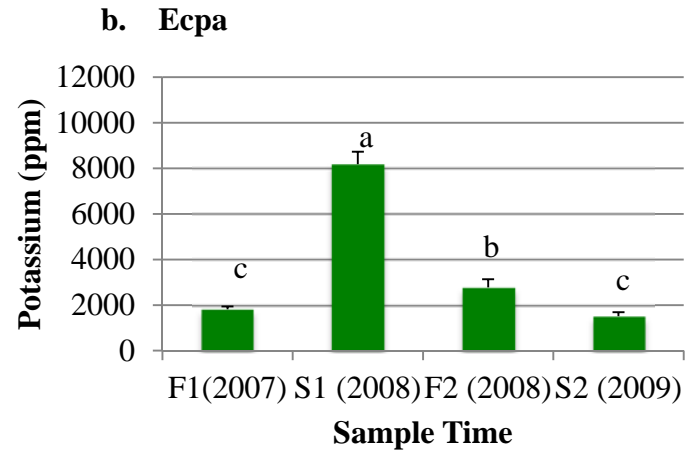
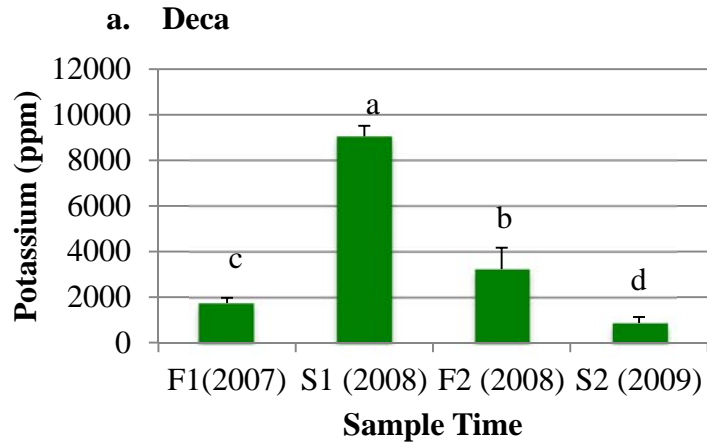
- Smith D. 2008 a. Determining maximum sustainable production of biomass with mixture of prairie species. Pre-application proposal for Iowa Power Fund to State of Iowa - Office of Energy Independence. Feb. 1, 2008.
- Smith D. 2008b. Determining maximum sustainable production of biomass with mixture of prairie species. Proposal for Iowa Power Fund to State of Iowa - Office of Energy Independence. March 22, 2008.
- Subbarao GV, Ito O, Berry WL, Wheeler RM. 2003. Sodium-a functional plant nutrient. *Critical Reviews in Plant Species* 22: 391-416.
- Tillman DA, Prinzing DE. 1995. Fundamental biofuel characteristics impacting coal-biomass cofiring.
- Tilman D, Hill J, Lehman C. 2006. Carbon-negative biofuels from low-input high-diversity grassland biomass. *Science* 314: 1598-1600.
- Tilman D, Wedin D, Knops J. 1996. Productivity and sustainability influenced by biodiversity in grassland ecosystems. *Nature* 379: 718-720.
- Warncke D, Brown JR. 1998. Chapter 7. Missouri Agricultural Experiment Station SB 1001. North Central Regional Research Publication No. 221 (Revised) Recommended Chemical Soil Test Procedures for the North Central Region.
- Williams D. 2010. Personal Communication.
- Wilsey B, Blong A. 2007 Native Cover Crops: Effects on Weed Invasion and Prairie Establishment. Retrieved from:
<http://www.ag.iastate.edu/farms/06reports/w/NativeCoverCrops.pdf>.
- World Coal Association. Online 2015. Coal use and the environment. Retrieved from:
http://www.worldcoal.org/coal-the-environment/coal-use-the-environment/#cookie_accept.

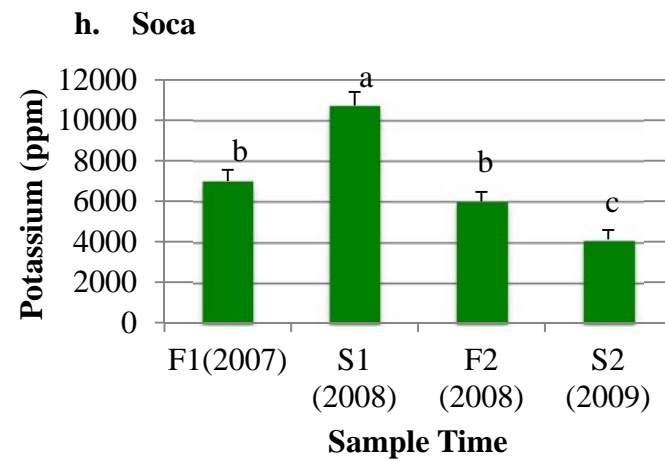
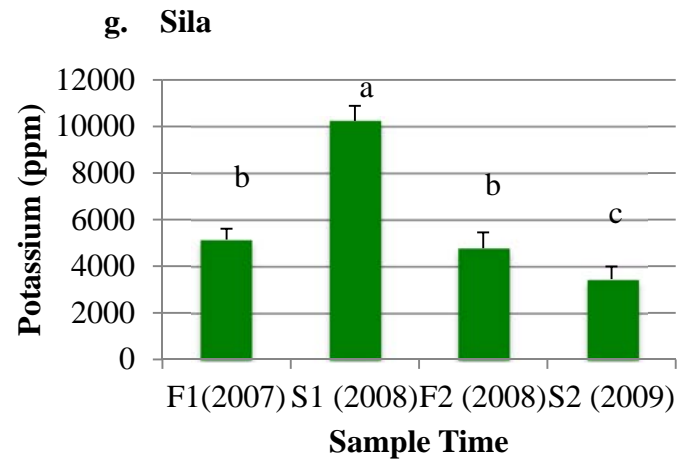
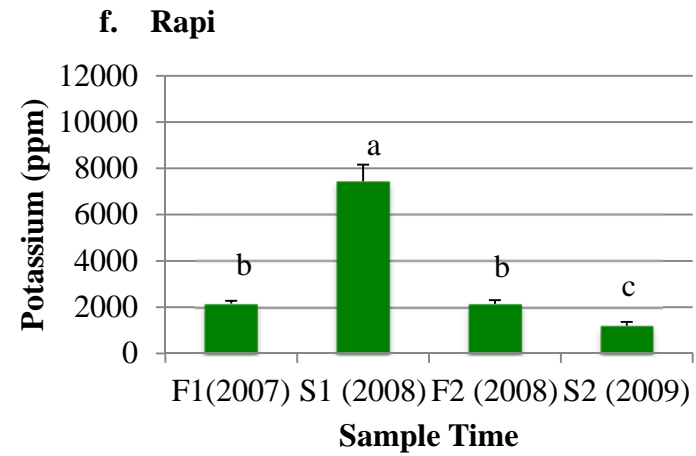
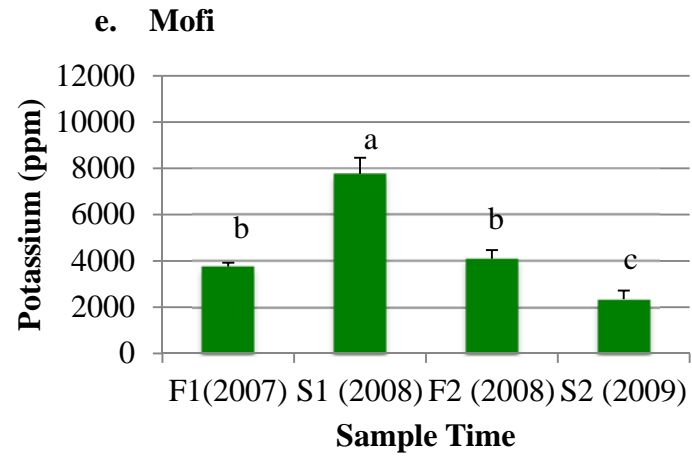
APPENDIX A
COMPARISON OF MINERAL CONCENTRATIONS OF INDIVIDUAL SPECIES
DURING TWO WINTER DORMANCY PERIODS

In year 1, the spring concentration of potassium in each of the species was significantly higher than the fall concentration. That was contrary to my hypothesis. However, in year 2, the concentration of potassium was significantly lower in the spring than in the fall. The data for this year are consistent with the hypothesis. It is difficult to explain such opposite results. One is tempted to suggest that the lab got the samples for the seasons reversed, but the samples for one sampling period were sent in before the second sampling was done. While issues did arise with ISU setting incorrect limits for the boundaries of the data, we ended with nice numbers to use.

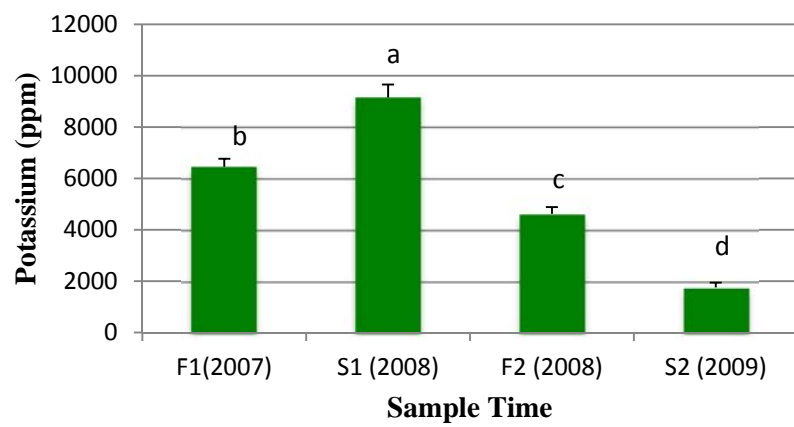
It appears that the greatest anomaly in the potassium results is the data for spring of year 1 (spring 2008). While there are significant differences (higher or lower) between the two fall readings for four of the nine species, *Desmodium canadense*, *Heliopsis helianthoides*, *Echinacea pallida*, and *Solidago rigida*, the values are much more similar than the differences between the two spring readings that are quite significantly higher. The potassium concentrations may have been affected by variations in weather patterns. The summer following this spring sample time was very wet. Figure A1 a-i shows the changes in concentration of potassium at each sample time.

Figure A1, a-i. Changes in concentration of potassium in nine species in fall 2007, spring 2008, fall 2008 and spring 2009.



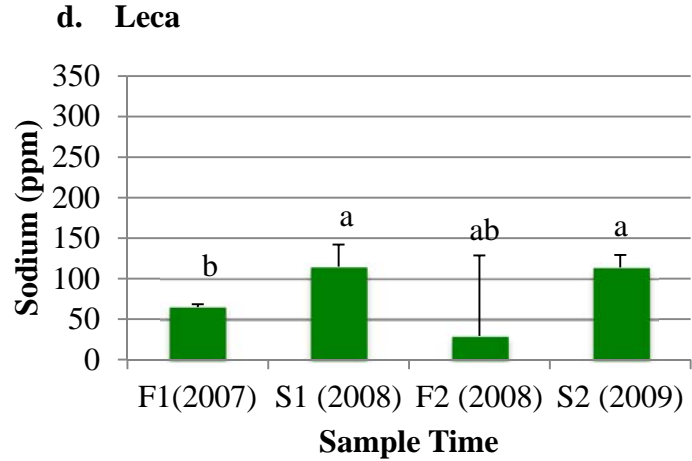
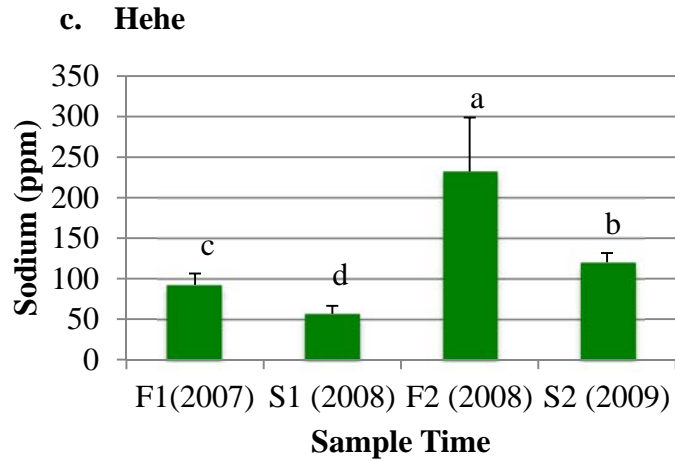
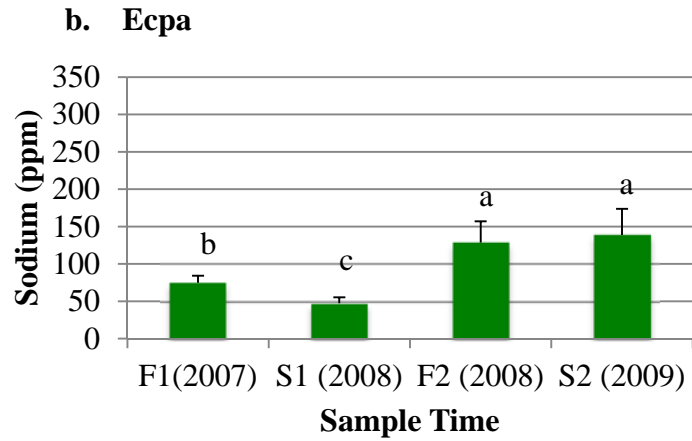
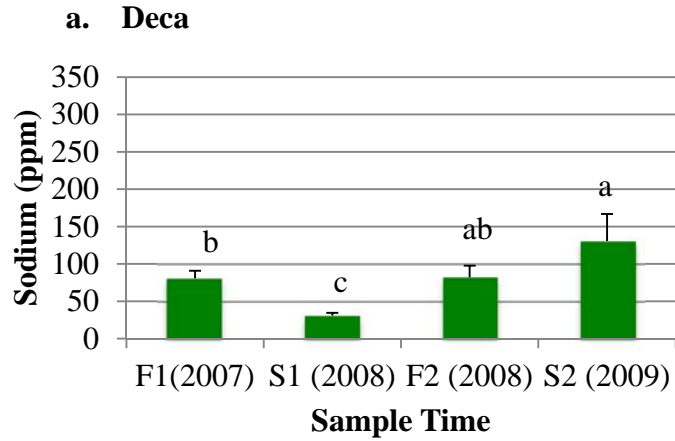


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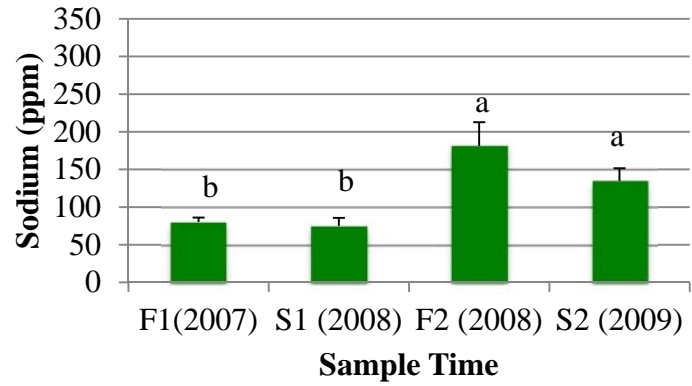


Generally speaking the concentration of sodium decreased in year 1 from fall 2007 to spring 2008, whereas in year 2 seven of the nine species did not change significantly from fall to spring. While *Heliopsis helianthoides* and *Ratibida pinnata* decreased significantly. In year 1 *Desmodium canadense*, *Echinacea pallida*, *Ratibida pinnata*, *Silphium laciniatum* decreased significantly, *Monarda fistulosa* and *Solidago rigida* did not change significantly and only *Lespedeza capitata* and *Solidago canadensis* increased significantly. The results of changes in sodium concentration during dormancy were much more consistent than those for potassium. Overall only *Lespedeza capitata* and *Solidago canadensis* showed concentration changes that were significantly different than hypothesized. If the decision of which species to put in the mix was determined by sodium alone, all of these species would be appropriate to include. Figure A2 a-i shows the changes in concentration of sodium at each sample time, and figure A3 a-i shows the changes in concentration of potassium at each sample time.

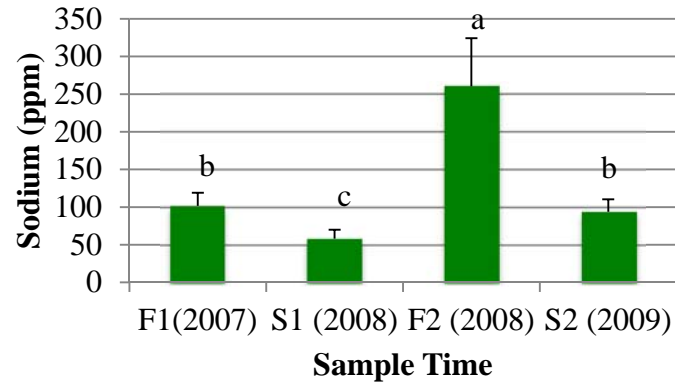
Figure A2, a-i: Concentration of sodium in nine species in fall 2007, spring 2008, fall 2008, and spring 2009.



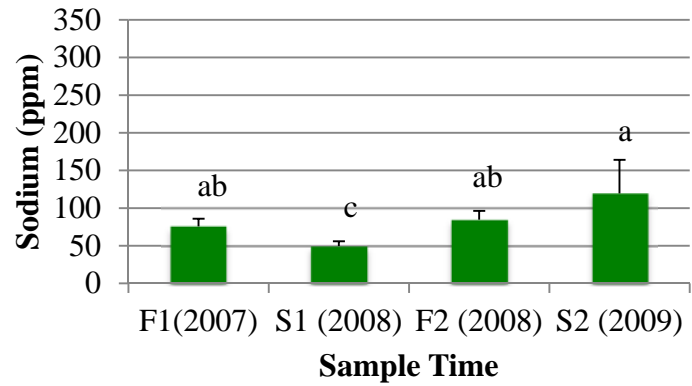
e. Mofi



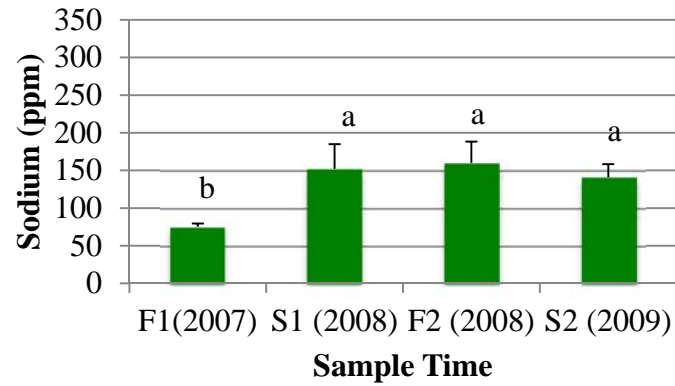
f. Rapi



g. Sila



h. Soca



i. Sori

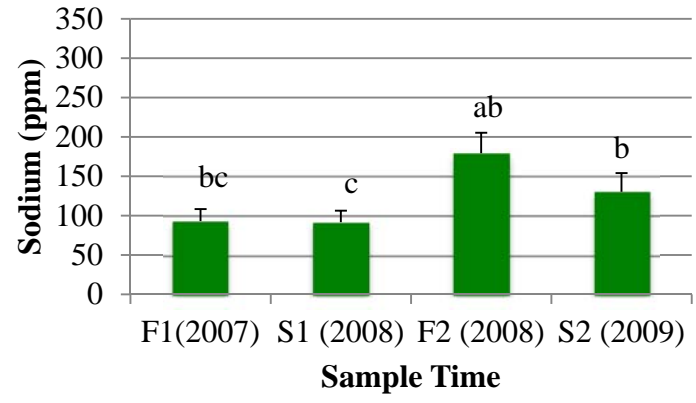
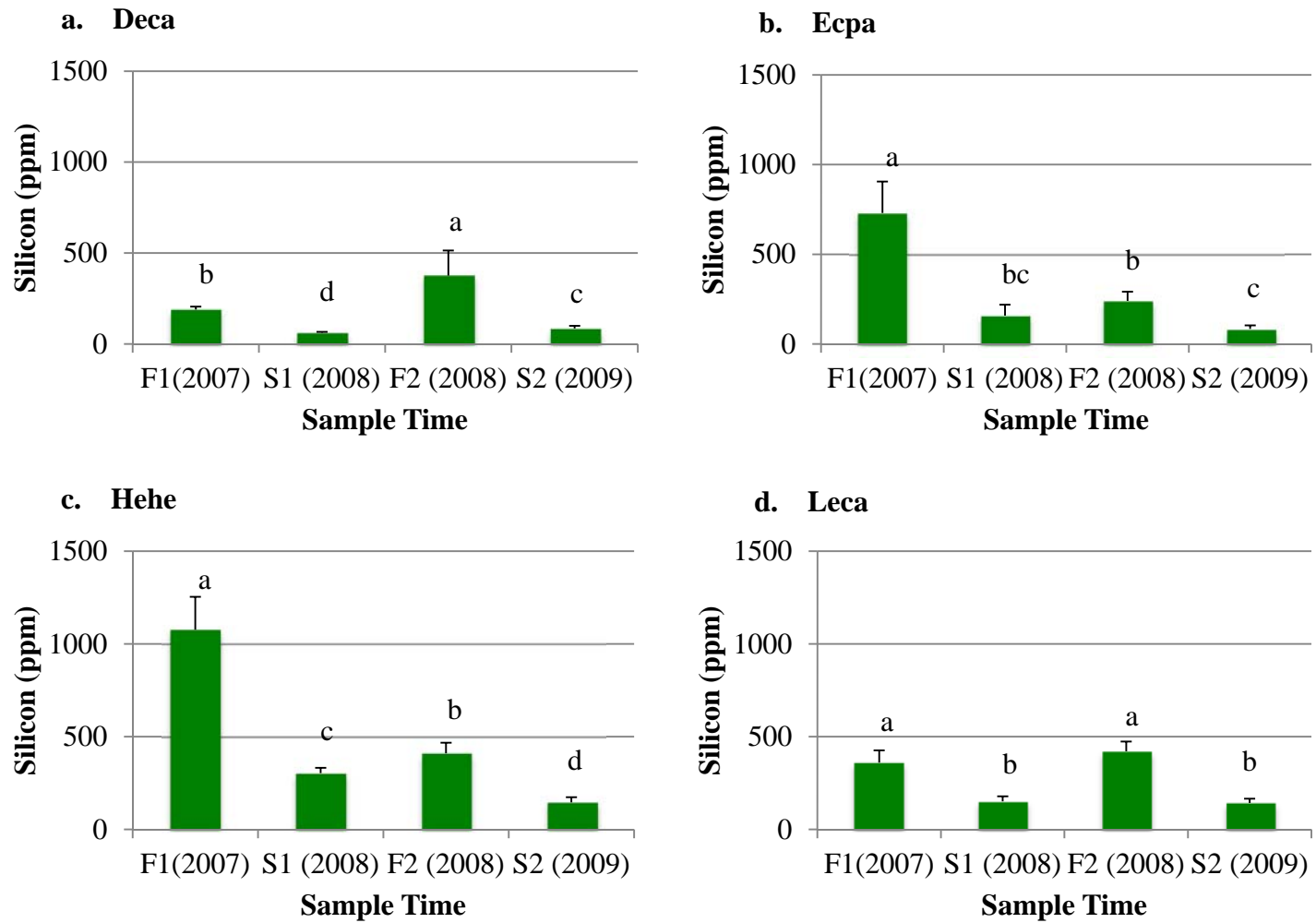
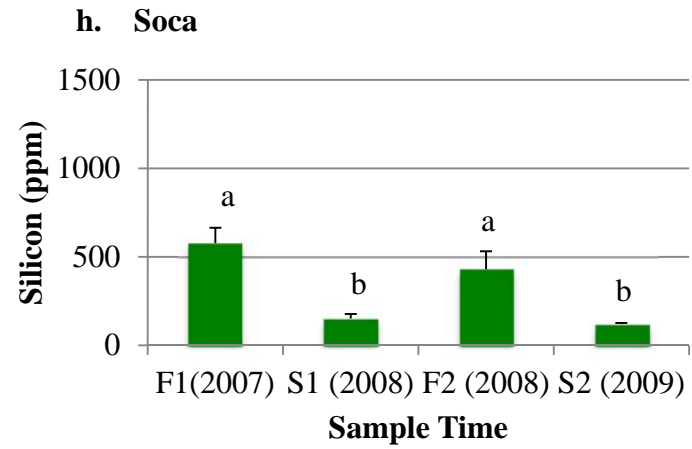
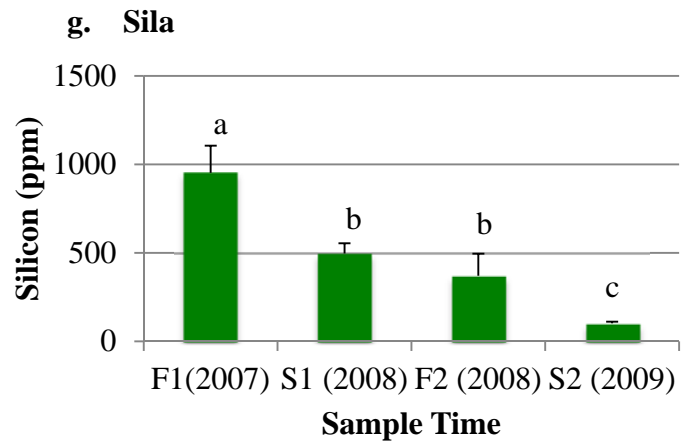
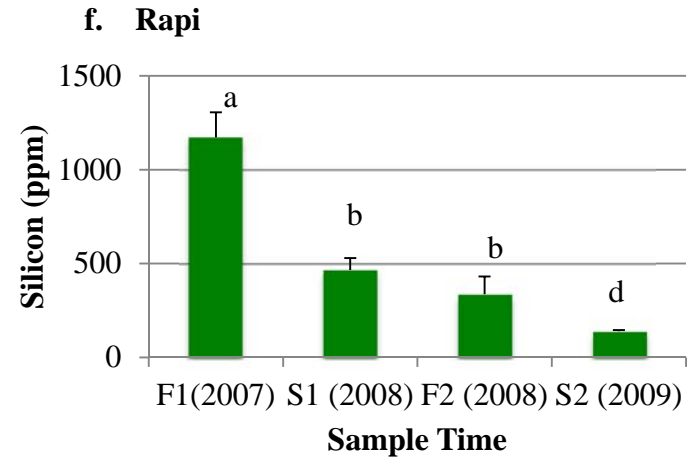
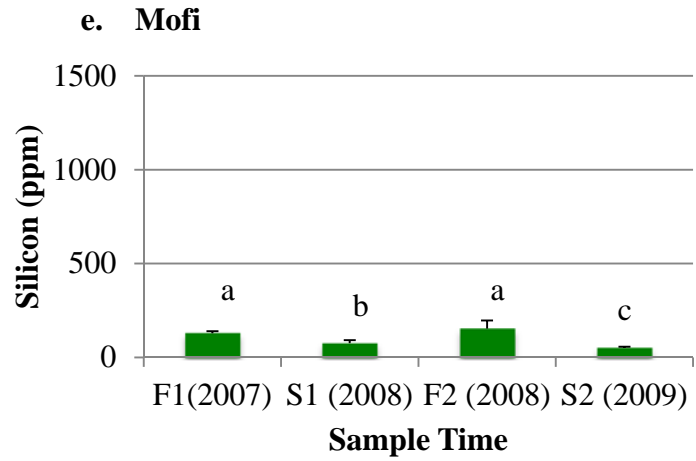
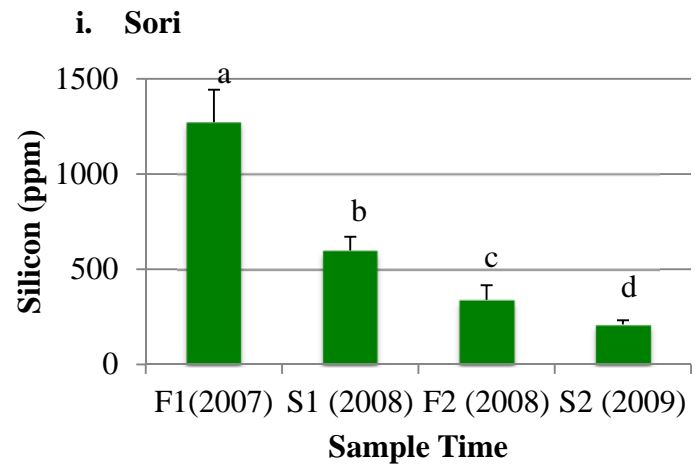


Figure A3, a-i: Concentration of silicon in nine species in fall 2007, spring 2008, fall 2008, and spring 2009.

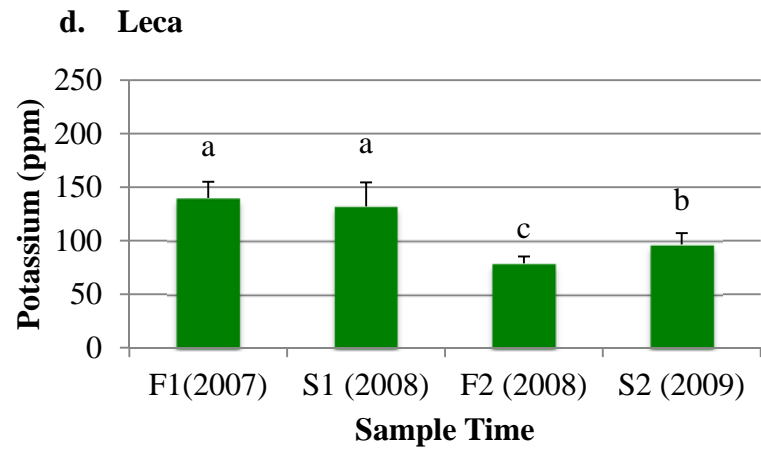
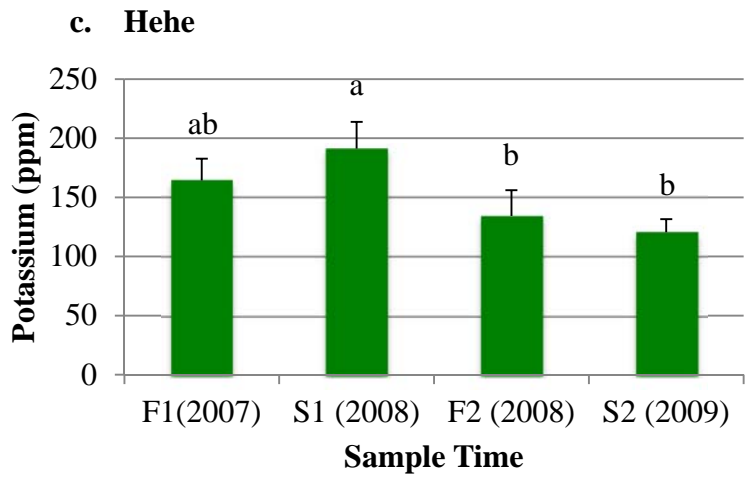
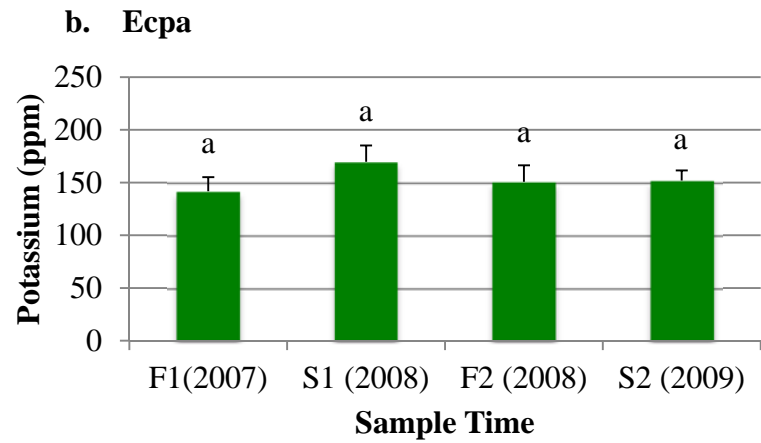
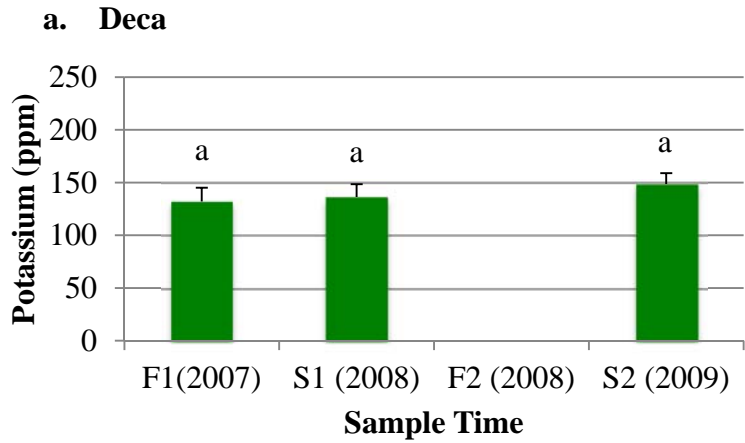


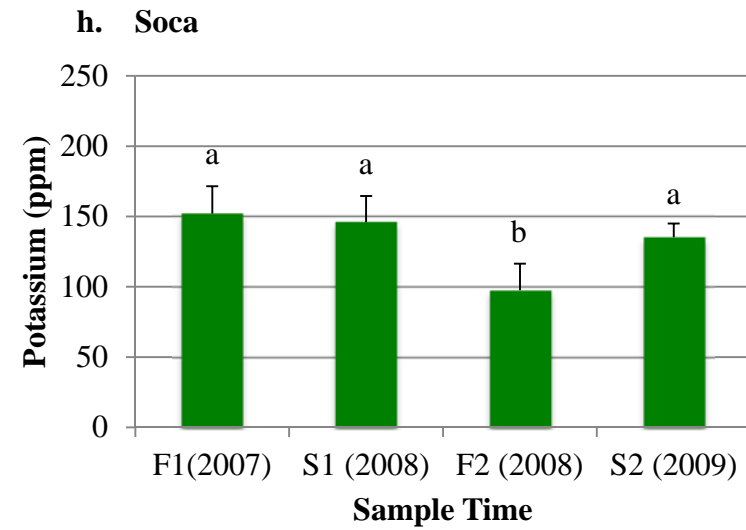
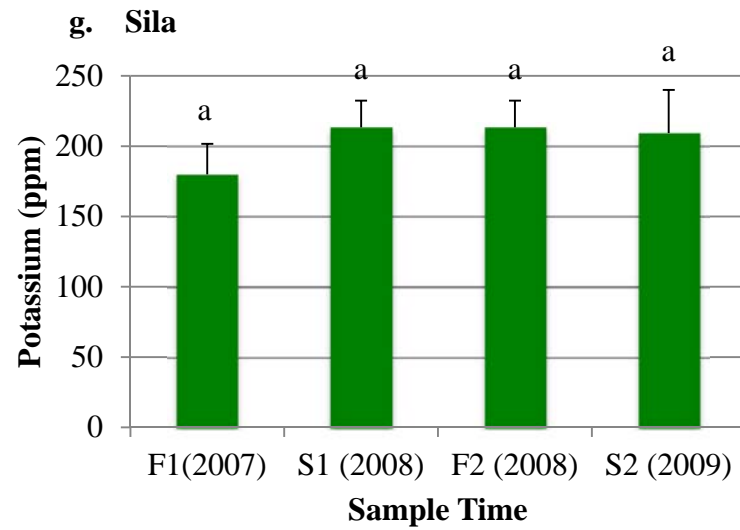
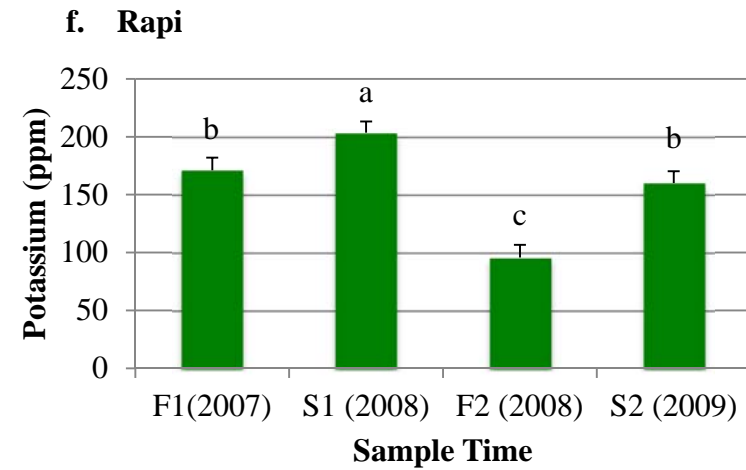
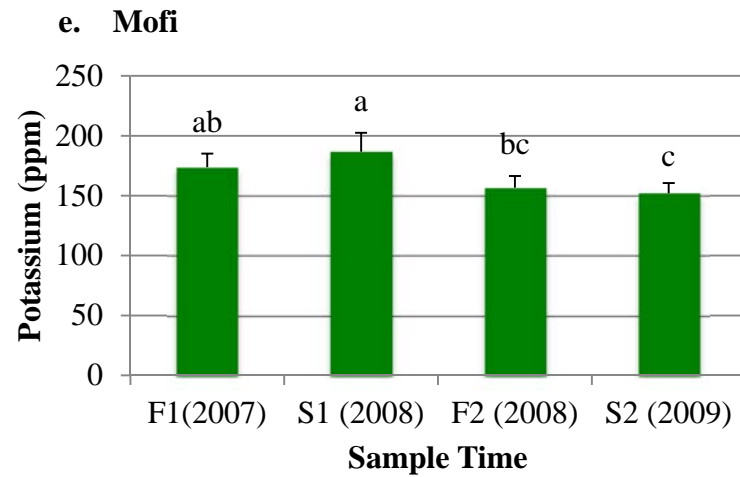


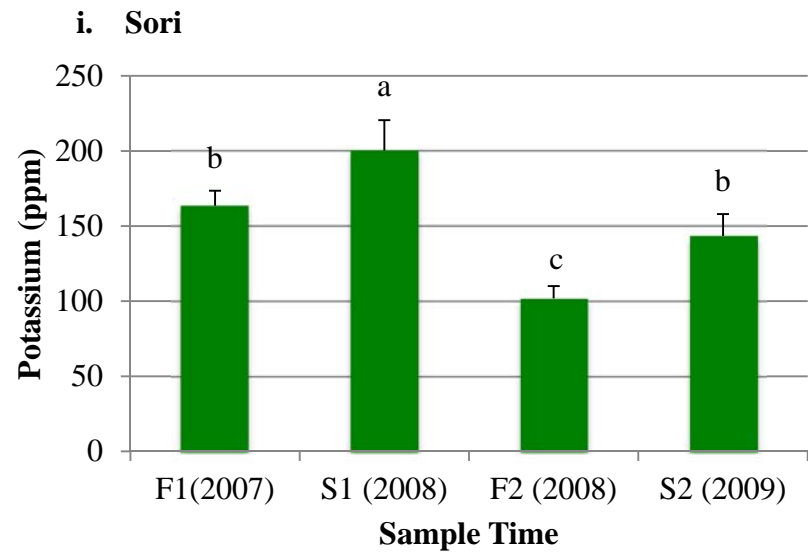


The following graphs (Figures A4 a-i) compare the concentration of plant available potassium in the soil at all the sites between the four main sample times. The soil associated with *Desmodium canadense* and *Echinacea pallida* were statistically similar from fall to spring over both sample years. Soil associated with *Heliopsis helianthoides* had a significantly different concentration from the first year to the second, but the concentrations were relatively similar. *Lespedeza capitata* is statistically similar year one, but significantly different from year two with a significant change from fall to spring year 2. Soil near *Monarda fistulosa* is significantly different between the spring concentrations, but the two fall concentrations have elements of similarity. *Ratibida pinnata* soil potassium concentrations increase from fall to spring. The first spring and the second fall are significantly different, while the first fall and second spring are the same. The concentrations the second fall are much lower than the first fall. *Silphium laciniatum* concentrations are similar across all sample times. *Solidago canadensis* has consistent concentrations across year 1, but year 2 is significantly different from fall to spring, with the low concentration being in the fall. Spring concentrations are back to the level of year 1. *Solidago rigida* soil concentration levels increase from fall to spring, with year 2 levels being significantly less than year 1. Fall 2 and spring 2 levels are similar. Many of these graphs indicate that from fall to spring, plant available potassium actually increases in the soil.

Figure A4, a-i: Concentration of plant available potassium in soil surrounding nine species in fall 2007, spring 2008, fall 2008, and spring 2009.





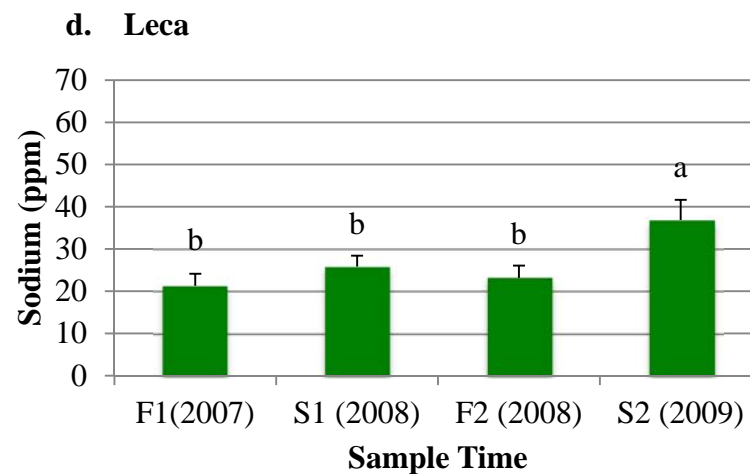
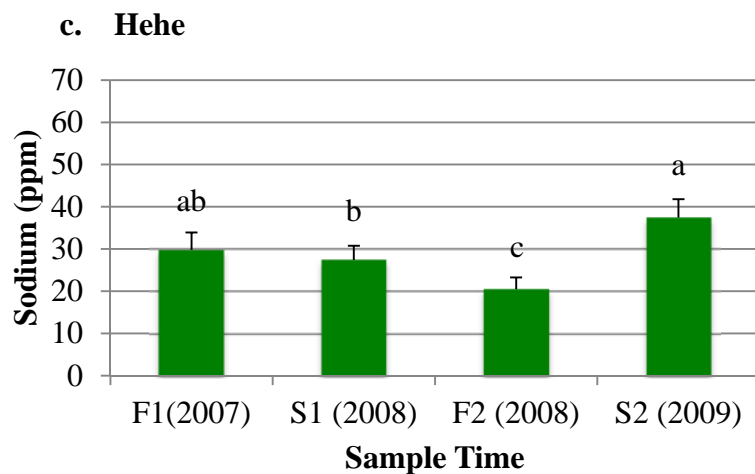
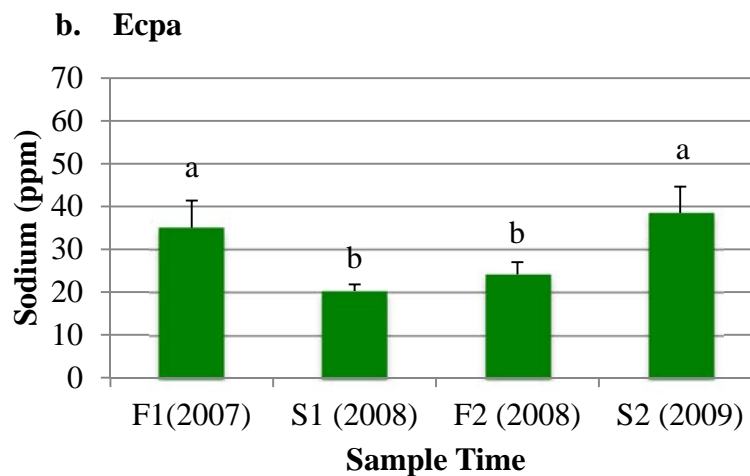
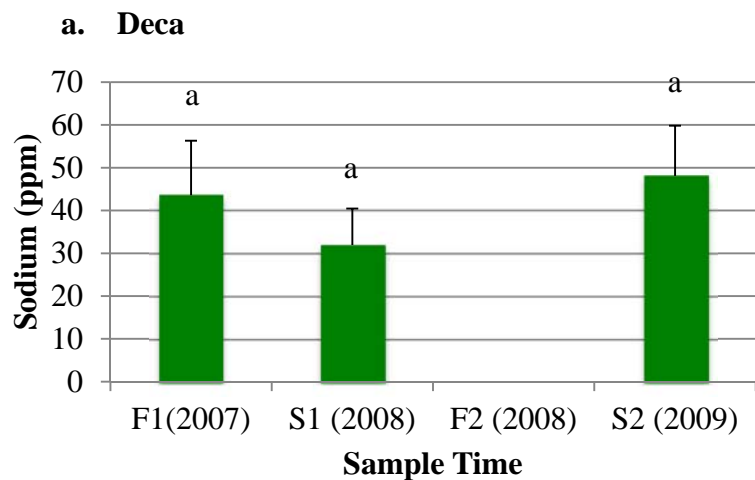


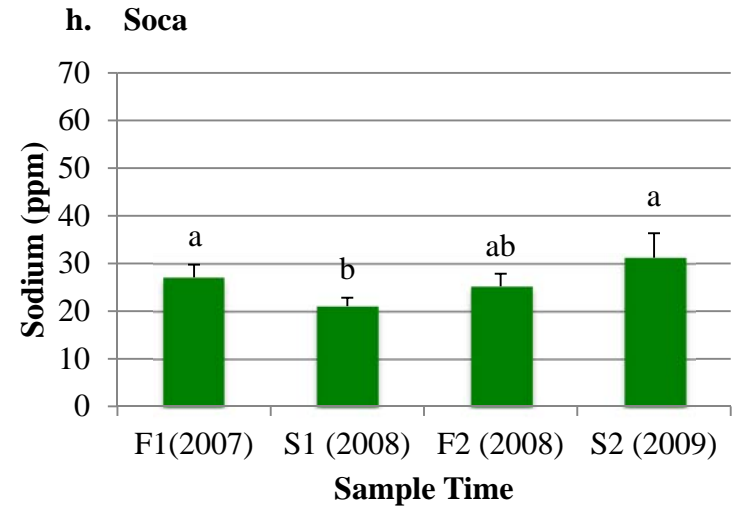
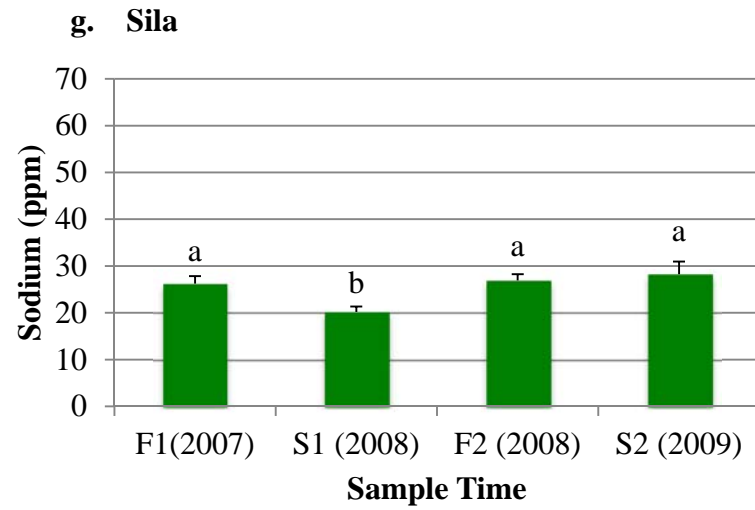
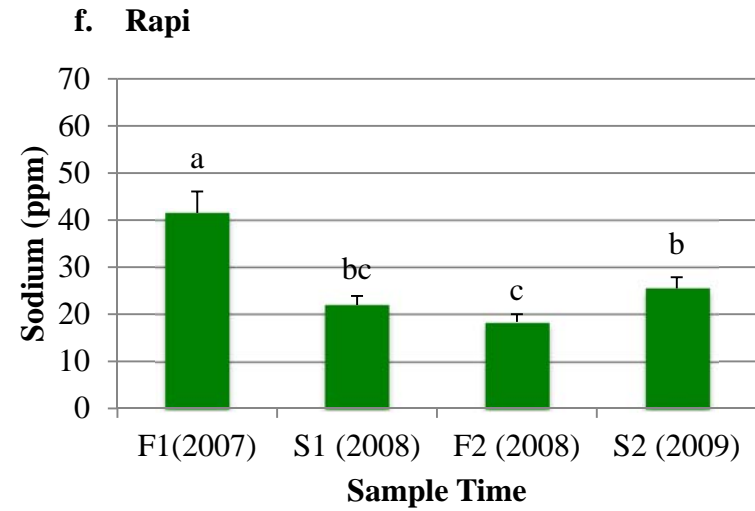
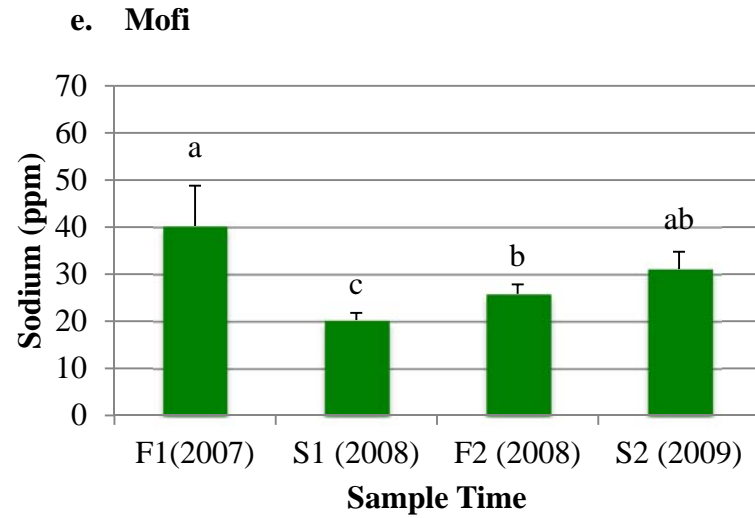
The following graphs (A5 a-i) compare the concentration of plant available sodium in the soil at all the sites between the four main sample times. While each soil profile around a species is different, the overall theme with the plant available sodium seems to be a decrease from fall to spring the first year, and an increase from fall to spring the second year. This is different than the potassium.

The soil around *Desmodium canadense* stays significantly similar across all the sample times. *Echinacea pallida* is similar from fall 1 to spring 2, and significantly similar from spring 1 to 2, but these two groups are not significantly similar. *Heliopsis helianthoides* plant available sodium soil concentrations in year 1 are statistically similar. Fall 2 is significantly less than the rest, and the concentration increases to spring 2. *Lespedeza capitata* has a significantly similar concentration across all times excluding spring 2, which has a significantly higher value. *Monarda fistulosa* concentrations are all significantly different, except spring of year 2 which is similar to fall 2007 and fall 2008. *Ratibida pinnata* has a significantly high first year fall concentration, and a significantly low second fall concentration. The spring values are in between, slightly similar but with their own significant value. *Silphium laciniatum* concentrations are mostly similar across all the times, but Spring 2 is significantly less than the others. *Solidago canadensis* soil concentrations for fall 1 and spring 2 are similar, spring 1 and fall 2 are also similar, but fall 2 is also similar to fall 1 and spring 2. *Solidago rigida* has a concentration that is significantly different from each time to the next, but is a perfect representation of the concentrations decreasing over the first year and increasing over the second.

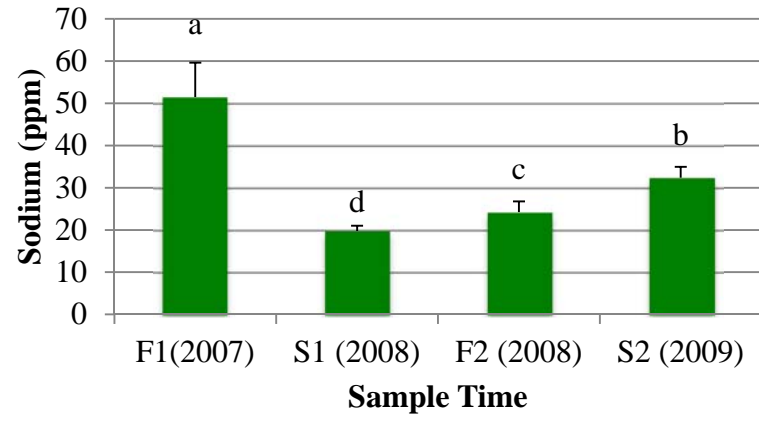
All plant available sodium in the soil decreased in concentration except for *Lespedeza capitata*, which increased slightly and was the only soil which was significantly similar to all other 8 soil groups.

Figure A5, a-i. Concentration of plant available sodium in soil surrounding nine species in fall 2007, spring 2008, fall 2008, and spring 2009.





i. Sori

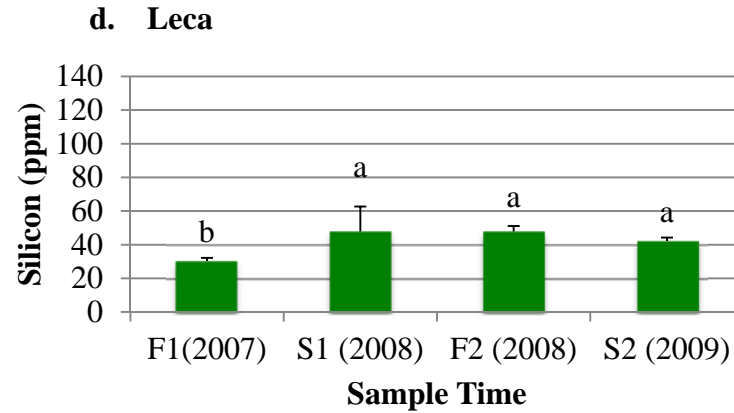
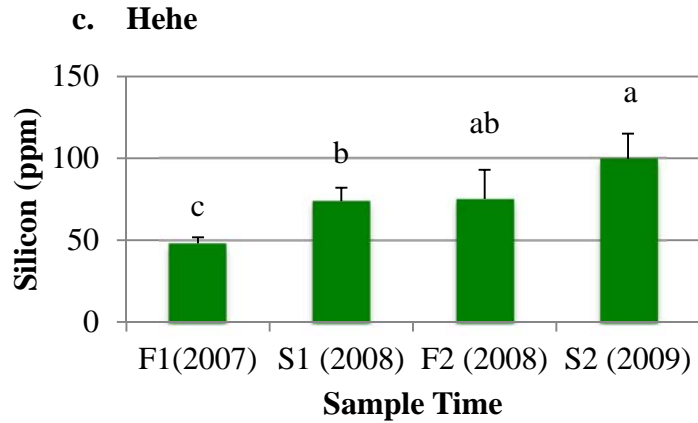
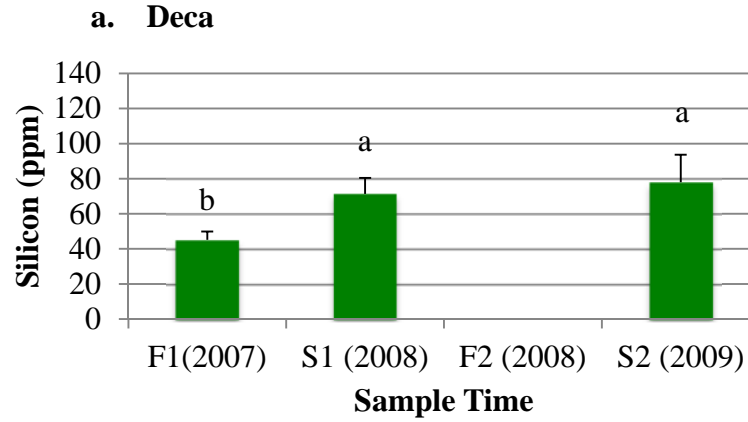
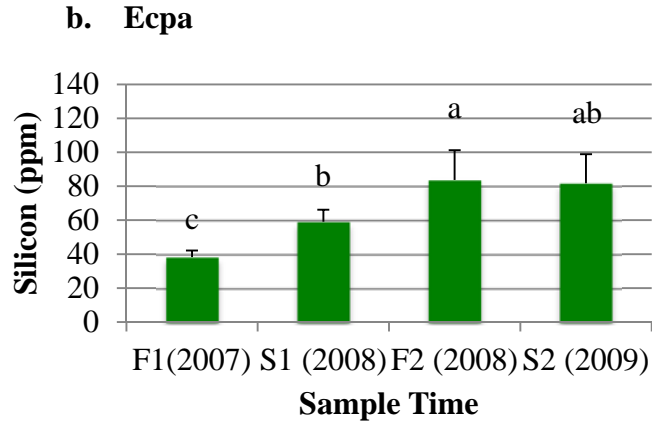


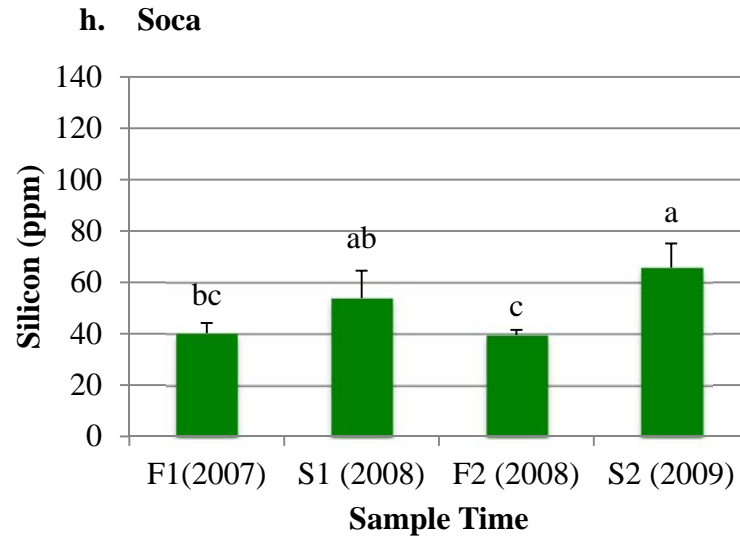
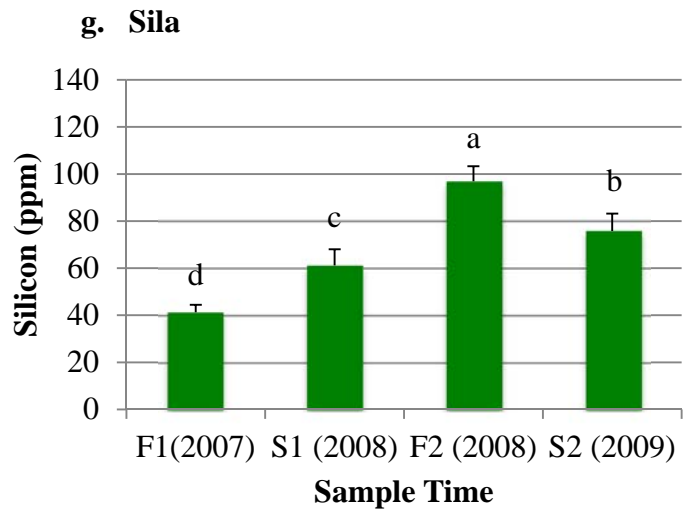
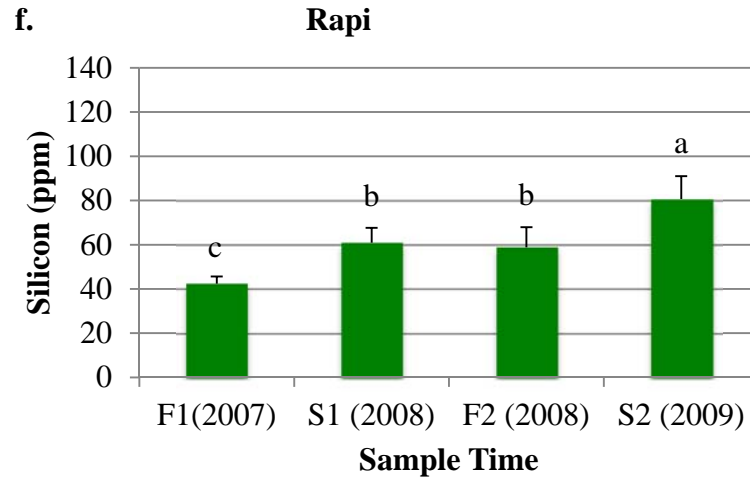
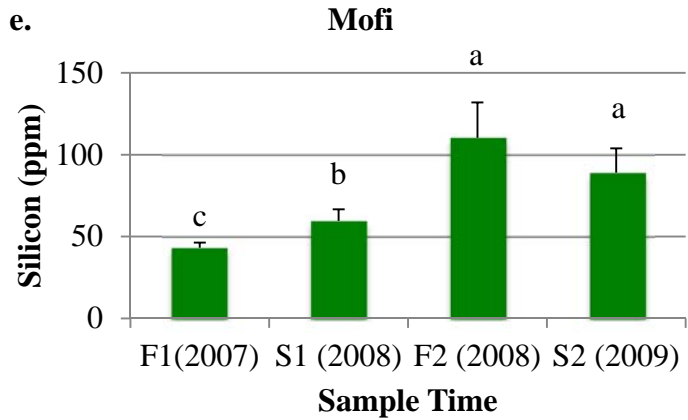
The following graphs (A6 a-i) compare the concentration of plant available silicon in the soil at all the sites between the four main sample times. There is not as clear of a pattern present in these graphs, all though most of them increase from fall to spring both years, or decrease the second year only slightly.

Desmodium canadense plant available silicon soil concentration in the fall of year 1 is significantly lower than the rest. Spring of year 1 and year 2 are statistically similar. *Echinacea pallida* again sees the lowest concentration in the fall of year 1. Spring 1 and 2 are similar, fall 2 and spring 2 are similar, but spring 1 and fall 2 are significantly different. *Heliopsis helianthoides* sees an increase from fall 1 to spring 2, with each sample time being statistically different from the last except for fall 2 which is similar to the two spring concentrations. *Lespedeza capitata* concentrations are much less than all the others. Fall 1 is the only significantly different value on the graph. *Monarda fistulosa* sees concentrations significantly higher in year 2 than year one. Year 2 the fall and spring values are similar, but in year 1 the fall is significantly less than spring concentrations. *Ratibida pinnata* soil plant available silicon levels are the lowest in the fall once again. Spring 1 and fall 2 are similar, and spring 2 is significantly higher than all the rest. *Silphium laciniatum* are all significantly different from each other, with the first year increasing, and the second year decreasing in value. *Solidago canadensis* increases from fall to spring both years. The fall values are statistically similar, as are the spring values, but they are significantly different from each other. *Solidago rigida* sees fall 1 to have the lowest values and spring 2 to have the highest values. The

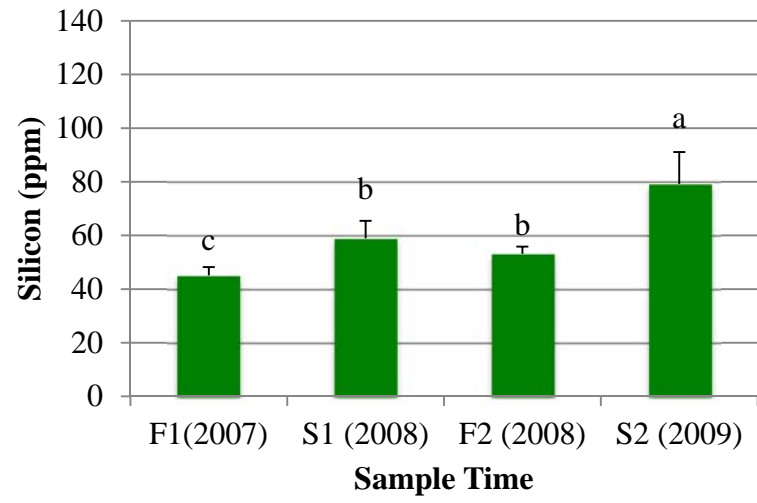
concentrations increase from fall to spring both years, and spring 1 and fall 2 have statistically similar values.

Figure A6, a-i: Concentration of plant available silicon in soil surrounding nine species in fall 2007, spring 2008, fall 2008, and spring 2009.





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APPENDIX B

CORRELATION BETWEEN VEGETATION AND SOIL MINERAL CONTENT

Table B1 and Figures B1 and B2 show the mean concentrations of plant available potassium in soil samples collected adjacent to the forbs in the study in fall 2007, spring 2008, fall 2008 and spring 2009. In fall 2007, the mean concentration of potassium was significantly higher in soils adjacent to *Monarda fistulosa*, *Ratibida pinnata*, and *Silphium laciniatum* than in soils adjacent to *Desmodium canadense*, *Echinacea pallida*, and *Lespedeza capitata*. The concentration in soils adjacent to *Heliopsis helianthoides*, *Solidago canadensis*, and *Solidago rigida* were between those of the other two groups.

There was some shifting of concentration in mean plant available potassium values of soils in spring 2008. Soil near *Desmodium canadense* contained the least amount of potassium, and was significantly lower in concentration than all but *Lespedeza capitata* and *Solidago canadensis*. Soils adjacent to *Ratibida pinnata* and *Silphium laciniatum* had the highest mean potassium concentration, and were significantly higher than those near *Desmodium canadense*, *Lespedeza capitata*, *Solidago canadensis* and *Echinacea pallida*. They were similar to those near *Heliopsis helianthoides*, *Monarda fistulosa*, and *Solidago canadensis*.

Soil Potassium

Table B1. Mean concentration (ppm) of plant available potassium in soil surrounding selected forbs sampled during dormancy in fall 2007, spring 2008 and fall 2008 and spring 2009. The means of each soil sample were independently analyzed with a one-way ANOVA to test significance between samples. A Tukey's Test was used to determine differences among means.

<u>Mean concentration (ppm) of K</u>								
<u>Species</u>	<u>N</u>	<u>F1(2007)</u>	<u>N</u>	<u>S1 (2008)</u>	<u>N</u>	<u>F2 (2008)</u>	<u>N</u>	<u>S2 (2009)</u>
Deca	12	132.1 (13.02)	12	136.3 (12.20)		na	6	148.5 (10.43)
Ecpa	15	141.7 (13.45)	15	169.7 (15.39)	6	150.7 (15.67)	12	151.8 (9.64)
Hehe	12	164.3(18.38)	12	191.2 (22.69)	6	134.2 (21.83)	12	120.4 (11.11)
Leca	9	139.9 (15.12)	9	132.0 (22.48)	6	78.9 (6.35)	9	96.4 (10.66)
Mofi	15	173.8 (11.31)	15	186.7 (15.79)	6	156.7 (9.74)	12	152.0 (8.51)
Rapi	15	171.1 (10.80)	15	203.5 (9.79)	3	95.8 (10.97)	12	160.0 (10.25)
Sila	15	179.9 (21.73)	15	213.4 (18.92)	9	213.4 (18.92)	9	209.3 (30.77)
Soca	12	152.1 (19.39)	12	145.9 (18.59)	6	97.537 (18.91)	12	135.3 (9.80)
Sori	15	163.5 (9.98)	15	200.3 (20.25)	3	101.9 (8.21)	12	143.4 (14.57)
p-value		.302		.007		<.001		<.001

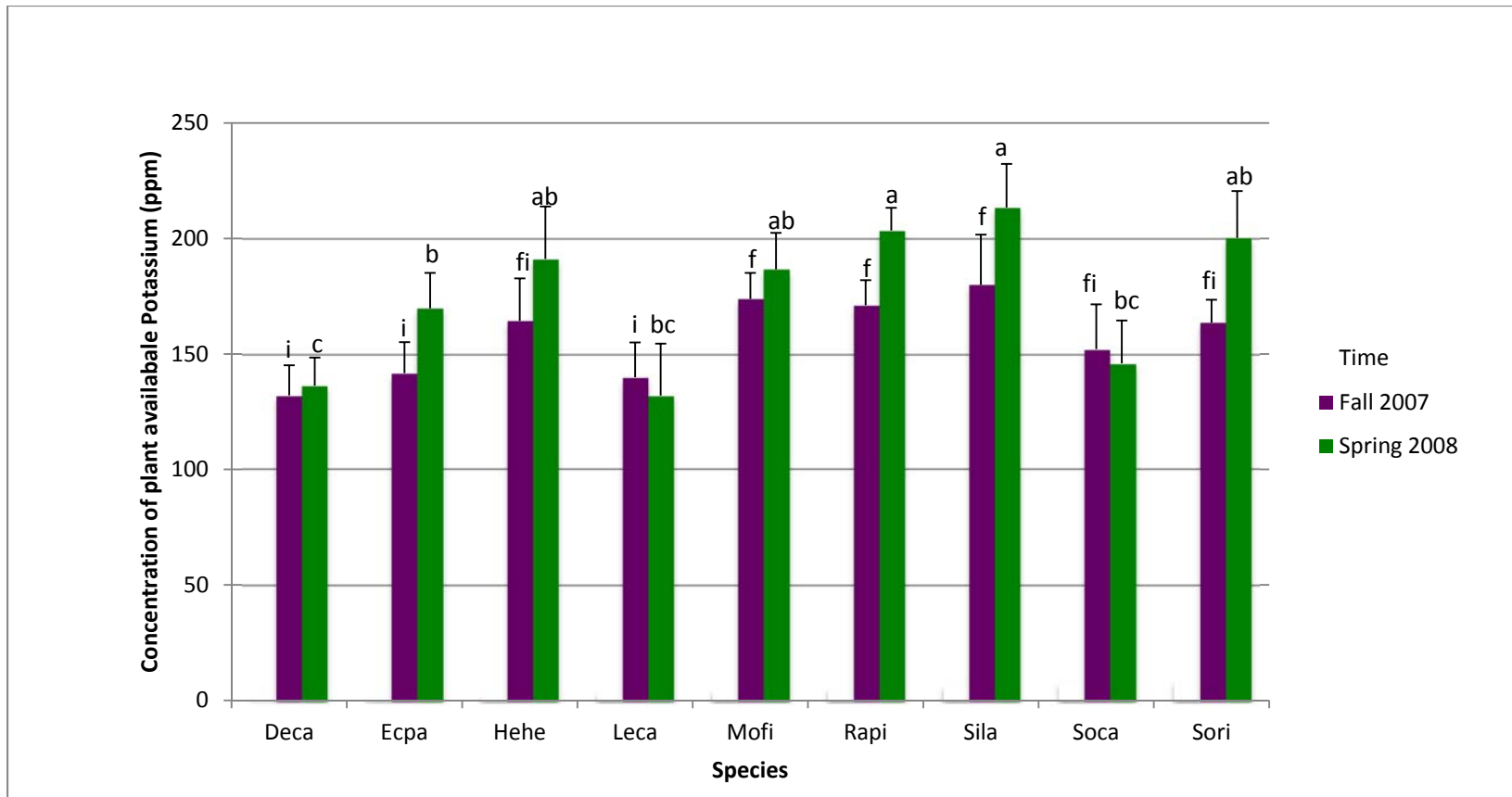


Figure B1. Mean concentration (ppm) of plant available potassium of selected soil samples near forbs sampled fall 2007 and spring 2008. The means of each sample were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

Figure B2 shows the results of mean concentration of potassium in soils near the forbs in the fall and spring of the second year. In fall 2008, the mean concentration of plant available potassium in soils adjacent to *Lespedeza capitata*, *Ratibida pinnata*, *Solidago canadensis*, and *Solidago rigida* was the lowest. The concentration in soils near these forbs was significantly less than that near *Echinacea pallida*, *Monarda fistulosa* and *Silphium laciniatum*. The concentration of plant available potassium in the soil around *Silphium laciniatum* was significantly higher than all other species.

Spring year 2, 2009, the plant available potassium in the soil around *Silphium laciniatum* was at the highest level of concentration significantly greater than the other forbs. The potassium concentration in the soil associated with *Lespedeza capitata* was significantly lower than the other forbs.

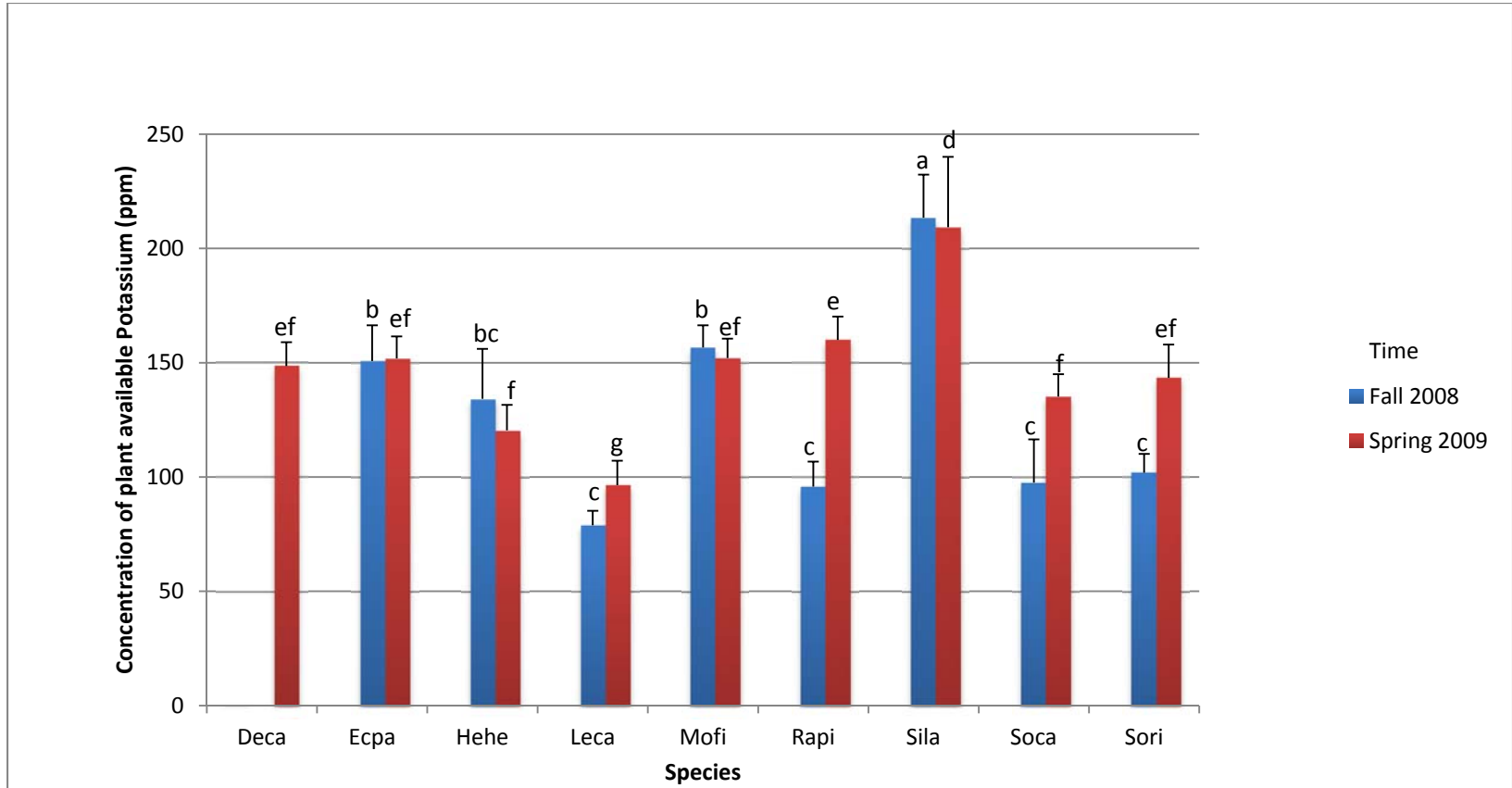


Figure B2. Mean concentration (ppm) of plant available potassium of selected soil samples near forbs sampled fall 2008 and spring 2009. The means of each sample were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

Soil Sodium

Table B2 and Figures B3 and B4 show the results of mean concentration of plant available sodium content in the soils around the nine studied prairie forbs. In the fall, the plant available sodium concentration in the soil around *Solidago rigida* is significantly higher than that around the other forbs except for *Desmodium canadense*, *Monarda fistulosa*, and *Ratibida pinnata*. The concentration of sodium in the soil around *Lespedeza capitata* is significantly lower than that around all other species.

In spring 2008, concentrations of plant available sodium in the soils near the forbs are more similar to each other than those in the fall. The soil around *Desmodium canadense* and *Heliopsis helianthoides* has significantly higher mean plant available sodium concentration than *Echinacea pallida*, *Monarda fistulosa*, *Ratibida pinnata*, *Silphium laciniatum*, *Solidago canadensis*, and *Solidago rigida*, but is similar to that in the vicinity of *Lespedeza capitata*.

Table B2. Mean concentration (ppm) of plant available sodium in soil surrounding selected forbs sampled during dormancy in fall 2007, spring 2008 and fall 2008 and spring 2009. The means of each soil sample were independently analyzed with a one-way ANOVA to test significance between samples. A Tukey’s Test was used to determine differences among means. NA represents data not available.

Mean concentration (ppm)/std. error of Na/sample time								
<u>Species</u>	<u>N</u>	<u>F1(2007)</u>	<u>N</u>	<u>S1 (2008)</u>	<u>N</u>	<u>F2 (2008)</u>	<u>N</u>	<u>S2 (2009)</u>
Deca	12	43.5 (12.76)	12	31.9 (8.54)		NA	6	48.1 (11.74)
Ecpa	15	35.0 (6.35)	15	20.2 (1.58)	6	24.1 (2.87)	12	38.5 (6.16)
Hehe	12	29.8 (4.10)	12	27.4 (3.36)	6	20.5 (2.79)	12	37.4 (4.38)
Leca	9	21.3 (2.85)	9	25.8 (2.57)	6	23.2 (2.92)	9	36.9 (4.79)
Mofi	15	40.2 (8.58)	15	20.3 (1.52)	6	25.8 (1.99)	12	31.1 (3.67)
Rapi	15	41.5 (4.56)	15	21.9 (1.94)	3	18.4 (1.65)	12	25.5 (2.40)
Sila	15	26.2 (1.60)	15	20.2 (1.18)	9	26.9 (1.32)	9	28.2 (2.70)
Soca	12	27.1 (2.67)	12	21.0 (1.77)	6	25.2 (2.64)	12	31.2 (5.16)
Sori	15	51.5 (8.14)	15	19.8 (1.23)	3	24.2 (2.55)	12	32.4 (2.58)
p-value		.052		.093		.334		.141

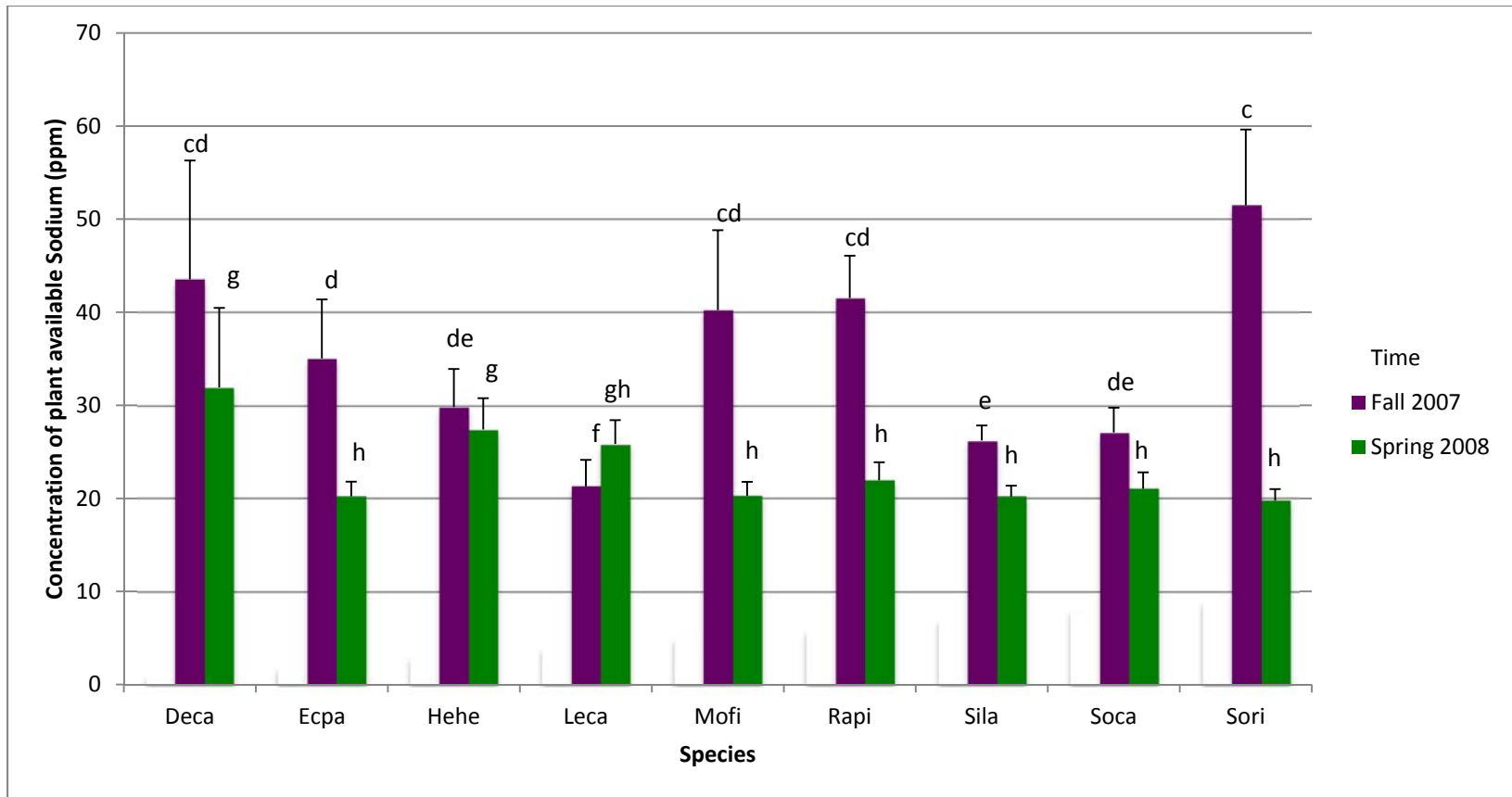


Figure B3. Mean concentration (ppm) of plant available sodium of selected soil samples near forbs sampled fall 2007 and spring 2008. The means of each sample were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

In fall 2008, there were two different concentrations of plant available sodium in the soils around the sampled forbs. The sodium in the soils around *Monarda fistulosa* and *Silphium laciniatum* had the highest concentration, but only differed significantly from *Heliopsis helianthoides* and *Ratibida pinnata*. Sodium concentration in other soils tested fell in the middle.

In the spring of year 2, 2009, sodium concentration in the soil around *Desmodium canadense* was the highest of all, significantly higher than *Ratibida pinnata*, *Monarda fistulosa*, *Silphium laciniatum* and *Solidago rigida*. *Echinacea pallida*, *Heliopsis helianthoides*, *Lespedeza capitata* and *Solidago canadensis* fall between, and are similar to both levels.

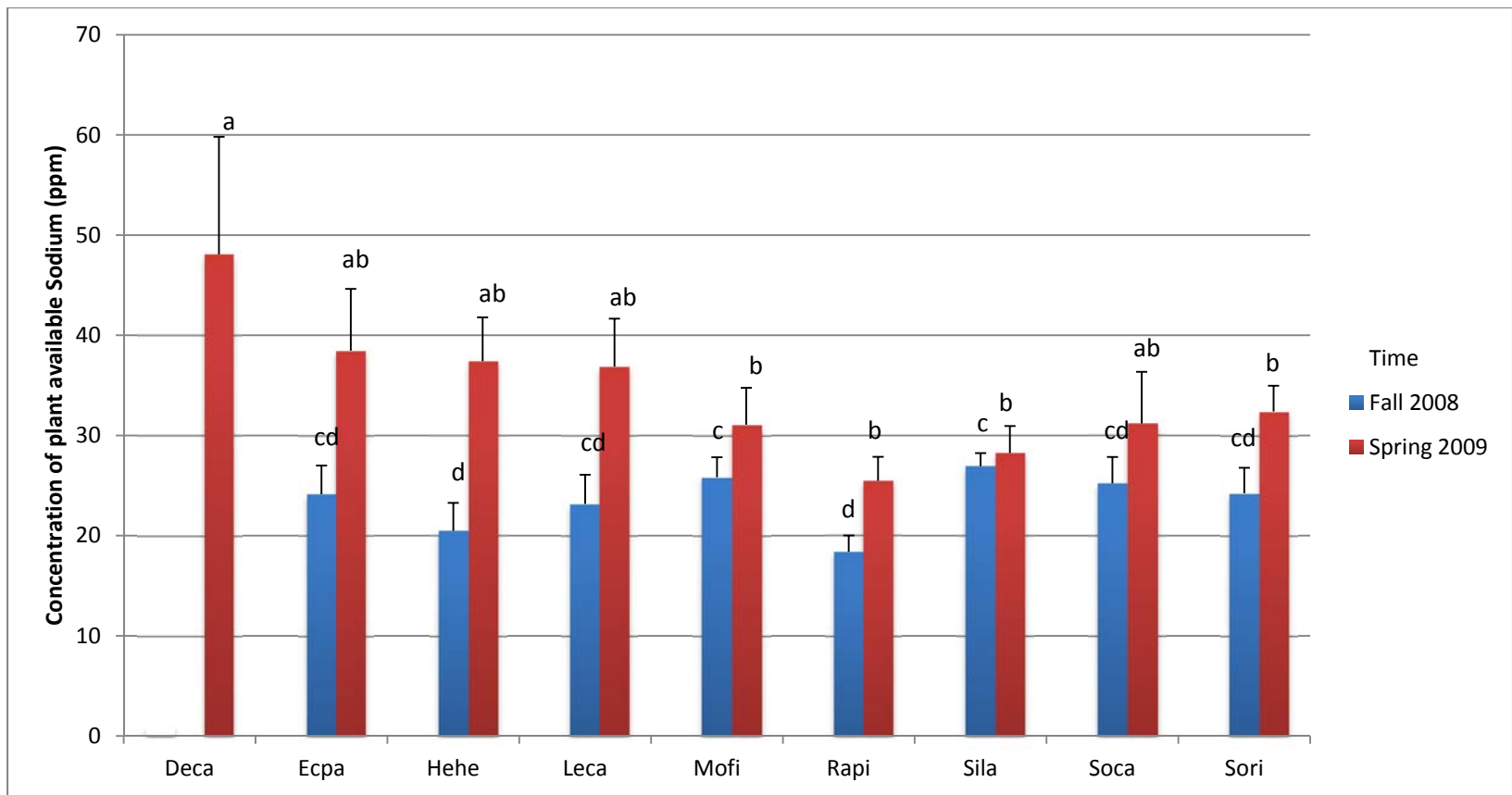


Figure B4. Mean concentration (ppm) of plant available sodium of selected soil samples near forbs sampled fall 2008 and spring 2009. The means of each sample were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

Soil Silicon

Table B3 and Figures B5 and B6 below show the mean concentrations of plant available silicon in soils adjacent to the test forbs during year 1, fall 2007 and spring 2008.

In the fall, the concentration of silicon in the soil surrounding *Heliopsis helianthoides* was the highest level of the soils sampled. It was significantly higher than that in the soils around *Lespedeza capitata*, *Solidago canadensis*, and *Echinacea pallida*. Silicon concentration in the soils around *Desmodium canadense*, *Monarda fistulosa*, *Ratibida pinnata*, *Silphium laciniatum*, and *Solidago rigida* were at intermediate levels. The concentration of silicon in the soil around *Lespedeza capitata* was significantly less than the other species.

In spring 2008, silicon concentration was again highest in the soil surrounding *Heliopsis helianthoides*, as in the fall. This silicon concentration was significantly higher than that in the soil around *Lespedeza capitata* and *Solidago canadensis*. Concentration in the soils around *Desmodium canadense*, *Echinacea pallida*, *Monarda fistulosa*, *Ratibida pinnata*, *Silphium laciniatum*, and *Solidago rigida* was similar to both levels, high and low.

Table B3. Mean concentration (ppm) of plant available silicon in soil surrounding selected species sampled during dormancy in fall 2007, spring 2008, fall 2008 and spring 2009. The means of each soil sample were independently analyzed with a one-way ANOVA to test significance between samples. A Tukey's Test was used to determine differences among means. NA represents data not available.

Mean concentration (ppm)/std. error of Si/sample time								
Species	N	F1(2007)	N	S1 (2008)	N	F2 (2008)	N	S2 (2009)
Deca	12	45.1 (4.79)	12	71.4 (9.13)		NA	6	78.0 (15.68)
Ecpa	15	38.2 (3.95)	15	59.1 (7.07)	6	83.7 (17.51)	12	81.8 (17.12)
Hehe	12	48.1 (3.66)	12	73.8 (8.21)	6	75.2 (17.81)	12	99.7 (15.44)
Leca	9	30.2 (1.89)	9	47.9 (14.80)	6	47.9 (3.20)	9	42.2 (2.03)
Mofi	15	43.2 (3.05)	15	59.7 (6.97)	6	110.3 (21.62)	12	89.0 (14.88)
Rapi	15	42.4 (3.31)	15	60.9 (6.75)	3	58.8 (9.07)	12	80.6 (10.40)
Sila	15	41.2 (3.22)	15	61.2 (6.87)	9	96.9 (6.40)	9	75.8 (7.43)
Soca	12	40.2 (3.95)	12	53.8 (10.74)	6	39.1 (2.09)	12	65.7 (9.39)
Sori	15	45.1 (3.13)	15	58.9 (6.52)	3	53.2 (2.69)	12	79.2 (11.85)
p-value		.122		.627		.003		.187

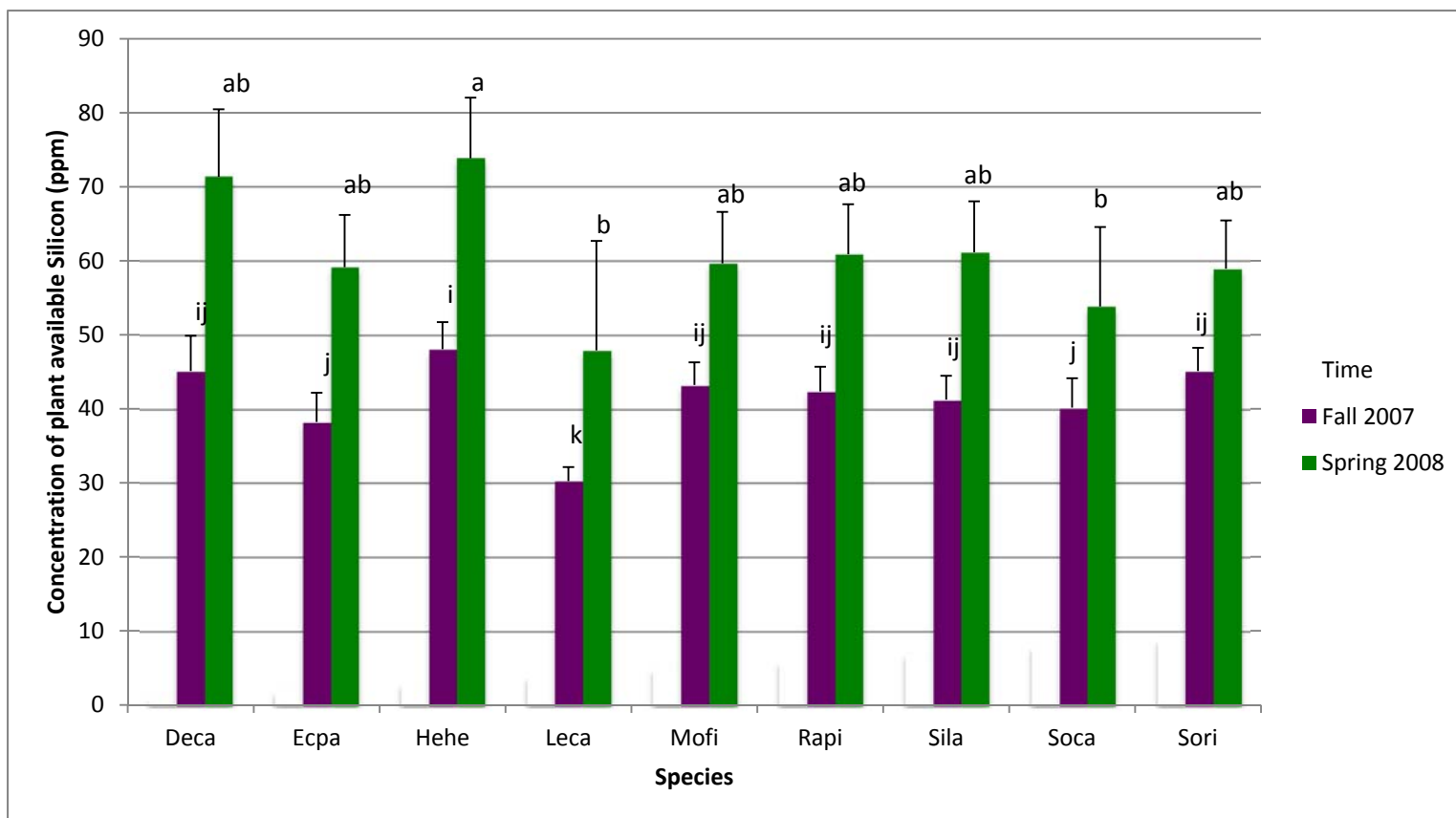


Figure B5. Mean concentration (ppm) of plant available silicon of selected soil samples near forbs sampled fall 2007 and spring 2008. The means of each sample were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

In fall 2008, the concentration of silicon in the soils around *Echinacea pallida*, *Monarda fistulosa*, and *Silphium laciniatum* was statistically higher than that around *Lespedeza capitata*, *Solidago canadensis* and *Solidago rigida*. The concentration of silicon in the soil around *Solidago canadensis* was significantly lower than the soil around the other forbs.

In spring 2009, the mean silicon concentrations in the soil around *Heliopsis helianthoides* and *Monarda fistulosa* were the highest. Their level was significantly higher than that in the soils adjacent to *Silphium laciniatum*, *Solidago canadensis*, and *Lespedeza capitata*. The silicon concentration in the soil around *Lespedeza capitata* was significantly lower than the soil around all the other forbs.

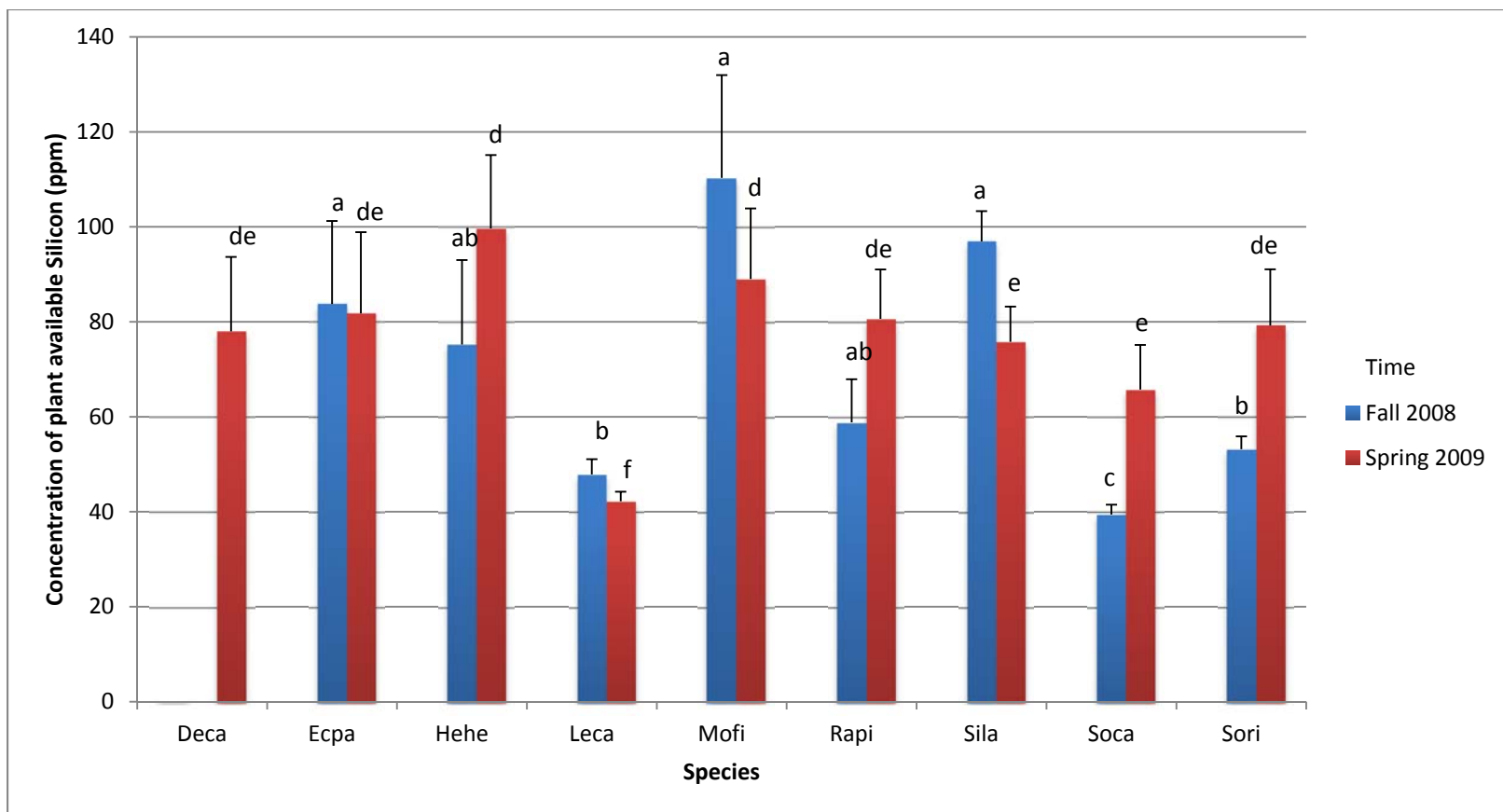


Figure B6. Mean concentration (ppm) of plant available silicon of selected soil samples near forbs sampled fall 2008 and spring 2009. The means of each sample were independently analyzed with a one-way ANOVA to test significance between means. A Tukey's Test was used to determine differences among means.

Table B4. Concentration of minerals present in composite samples from soils adjacent to selected forbs.

Mg of plant available mineral/kg of soil												
Species	Potassium				Sodium				Silicon			
	F ₁	S ₁	F ₂	S ₂	F ₁	S ₁	F ₂	S ₂	F ₁	S ₁	F ₂	S ₂
<i>Desmodium canadense</i>	225	193	NA	204	30	33	NA	21	21	17	NA	20
<i>Echinacea pallida</i>	216	293	172	185	37	33	15	18	21	24	20	25
<i>Heliopsis helianthoides</i>	255	352	106	155	33	42	18	21	26	31	23	36
<i>Lespedeza capitata</i>	207	257	107	125	47	53	19	20	18	19	21	15
<i>Monarda fistulosa</i>	251	377	224	209	31	41	19	23	21	28	31	28
<i>Ratibida pinnata</i>	288	388	144	247	28	40	21	17	20	26	21	20
<i>Silphium laciniatum</i>	304	333	269	273	29	37	18	16	24	24	28	23
<i>Solidago canadensis</i>	229	271	83	155	33	49	16	24	21	20	17	21
<i>Solidago rigida</i>	267	323	158	183	25	37	19	19	21	20	18	20

In most instances there is an increase in the mineral levels in the soil around the plants from fall to spring. Plant available potassium concentration decreased in the soil near *Desmodium canadense* from fall to spring. Due to a lack of sample data, we cannot compare the levels associated with this species in the next year. *Desmodium canadense* is the only species in the first year where this seasonal decrease takes place but it occurs again the second year for potassium in the soil near *Monarda fistulosa*. Plant available soil concentrations of sodium and silicon also decrease in several species each year, including *Echinacea pallida*, *Ratibida pinnata*, *Silphium laciniatum*, and *Lespedeza capitata*. When potassium or sodium levels decrease from fall to spring, silicon levels frequently do the same (two-thirds of the time), although some fluctuation in silicon concentration seems to occur independently

Table B5 a. Percent of potassium in ash and plant available potassium in composite soil samples.

Potassium	Fall 2007		Spring 2008		Fall 2008		Spring 2009	
Species	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg
Deca	3.72	225	1.48	193	4.08	NA	2.01	204
Ecpa	2.45	216	1.44	293	9.95	172	4.2	185
Hehe	9.88	255	3.45	352	10.8	106	3.86	155
Leca	9.76	207	3.86	257	13.4	107	7.6	125
Mofi	9.01	251	5.18	377	10.3	224	5.26	209
Rapi	4.87	288	2.32	388	5	144	3.14	247
Sila	7.15	304	3.49	333	6.55	269	6.3	273
Soca	20.8	229	10.7	271	16.4	83	11.9	155
Sori	11.3	267	5.55	323	9.18	158	5.8	183

Table B5 b. Percent of sodium in ash and plant available sodium in composite soil samples.

Sodium	Fall 2007		Spring 2008		Fall 2008		Spring 2009	
Species	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg
Deca	0.57	30	0.35	33	0.3	NA	0.6	21
Ecpa	0.2	37	0.27	33	0.59	15	0.72	18
Hehe	0.42	33	0.22	42	0.53	18	0.44	21
Leca	0.42	47	1.18	53	0.71	19	1.01	20
Mofi	0.37	31	0.49	41	1.23	19	0.91	23
Rapi	0.36	28	0.21	40	0.86	21	0.41	17
Sila	0.13	29	0.21	37	0.19	18	0.17	16
Soca	0.76	33	0.76	49	1.76	16	0.98	24
Sori	0.41	25	0.43	37	0.61	19	0.73	19

Table B5 c. Percent of silicon in ash and plant available silicon in composite soil samples.

Silicon Species	Fall 2007		Spring 2008		Fall 2008		Spring 2009	
	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg	Ash (%)	Soil mg/kg
Deca	6.09	21	7.88	17	4.98	NA	4.38	20
Ecpa	15.44	21	15.14	24	9.96	20	10.92	25
Hehe	18.54	26	23.96	31	17.27	23	12.09	36
Leca	17.33	18	17.35	19	10.67	21	12.01	15
Mofi	3.83	21	11.99	28	4.61	31	6.44	28
Rapi	15.27	20	17.34	26	116.36	21	21.32	20
Sila	16.22	24	22.23	24	9.27	28	10.96	23
Soca	17.99	21	19.86	20	15.57	17	11.82	21
Sori	22.08	21	31.6	20	20.75	18	23.81	20

Tables B6-B8 summarize the mineral concentration changes of potassium, sodium and silicon from fall to spring within the forbs and the adjacent soils. Organized by mineral, values in these tables are positive when a mineral increased in the tested material from fall to spring, and negative when the concentration fell from fall to spring.

Table B6. Change in concentration (ppm) of potassium in composite samples from forbs and adjacent soils from fall 2007 to spring 2008 and fall 2008 to spring 2009. Positive values indicate an increase from fall to spring and negative values indicate a decrease from fall to spring.

Changes in potassium concentration (ppm)				
	Fall 2007-Spring 2008		Fall 2008-Spring 2009	
	Plant	Soil	Plant	Soil
Deca	7310.3	4.2	-2361.0	NA
Ecpa	6367.6	28.1	-1259.6	1.1
Hehe	5418.2	26.8	-2565.6	-13.8
Leca	4179.1	-7.9	-2340.9	17.6
Mofi	4003.7	12.9	-1753.0	-4.6
Rapi	5285.9	32.3	-944.9	64.2
Sila	5100.3	33.5	-1324.5	-4.1
Soca	3734.1	-6.2	-1879.8	37.6
Sori	2693.4	36.7	-2862.8	41.5

The first year, potassium increased across the board in plant and plant available soil concentrations (Table B6). Just two soil samples decreased in concentration. The second year, each of the plants sampled decreased in potassium concentration from fall to spring. Soil concentrations were apparently unrelated to plant concentrations, with some increasing and some decreasing over time.

Table B7. Change in concentration (ppm) of sodium in composite samples from forbs and adjacent soils from fall 2007 to spring 2008 and fall 2008 to spring 2009. Positive values indicate an increase from fall to spring and negative values indicate a decrease from fall to spring.

Changes in sodium concentration (ppm)				
	Fall 2007-Spring 2008		Fall 2008-Spring 2009	
	Plant	Soil	Plant	Soil
Deca	-49.9	-11.6	48.7	NA
Ecpa	-27.3	-14.8	10.2	14.4
Hehe	-35.7	-2.4	-112.0	16.9
Leca	50.0	4.6	84.5	13.7
Mofi	-5.3	-20.0	-46.5	5.3
Rapi	-43.5	-19.6	-166.7	7.1
Sila	-26.2	-6.1	34.9	1.3
Soca	77.0	-6.1	-19.2	6.0
Sori	-1.5	-31.7	-49.0	8.2

Concentrations of sodium in all of the plant material except *Lespedeza capitata* and *Solidago canadensis* decreased from fall to spring the first year (Table B7). The second year all of the soil concentrations increased but the concentrations decreased in vegetation for half of the species.

Table B8. Change in concentration (ppm) of silicon in composite samples from forbs and adjacent soils from fall 2007 to spring 2008 and fall 2008 to spring 2009. Positive values indicate an increase from fall to spring and negative values indicate a decrease from fall to spring.

Changes in silicon concentration (ppm)				
	Fall 2007-Spring 2008		Fall 2008-Spring 2009	
	Plant	Soil	Plant	Soil
Deca	-126.0	26.3	-290.6	NA
Ecpa	-571.6	20.9	-157.0	-2.0
Hehe	-772.9	25.8	-264.4	24.5
Leca	-208.2	17.7	-278.6	-5.7
Mofi	-52.2	16.4	-100.8	-21.3
Rapi	-706.9	18.5	-197.2	21.8
Sila	-455.5	19.9	-268.1	-21.1
Soca	-426.2	13.6	-310.8	26.3
Sori	-674.1	13.8	-129.1	26.1

Silicon behaves most consistently within plants, always decreasing from fall to spring. Plant available silicon in the soil increased in each soil sample the first year as my hypothesis suggested, but in several instances there was a decrease in plant available silicon in the soil the second year.

To assess whether or not there is a correlation between soil and vegetation mineral concentrations, simple Pierson's Correlation Coefficient statistical analysis has been done.

Table B9. Correlation between mineral concentrations of plant species and adjacent soils of individual sites.

P-Value			
Species (Soil/vegetation) Samples	Potassium	Sodium	Silicon
1	0.413	0.199	0.005
2	0.026	0.512	0.012
3	0.005	0.730	0.014
4	0.025	0.125	0.345
5	0.008	0.057	0.011
6	0.000	0.517	0.002
7	0.159	0.685	0.004
8	0.717	0.712	0.120
9	0.000	0.108	0.013

The data of samples from individuals sites presented in the following three graphs are comprised of the mean of the samples each species. (Ex. The mean of all the *Desmodium canadensis* for fall 1 would be 1 point. This data was used to create the year 1 and year 2 graphs in the previous section.

Comparing the plant available mineral content of soil directly to the mineral content of the vegetation in a scatter plot, it is easier to see if the soil affects the plant material or not. Figures B7-B9 are comprised of the data from individual sites. Figures B10-B12 are numbers provided by the composite data.

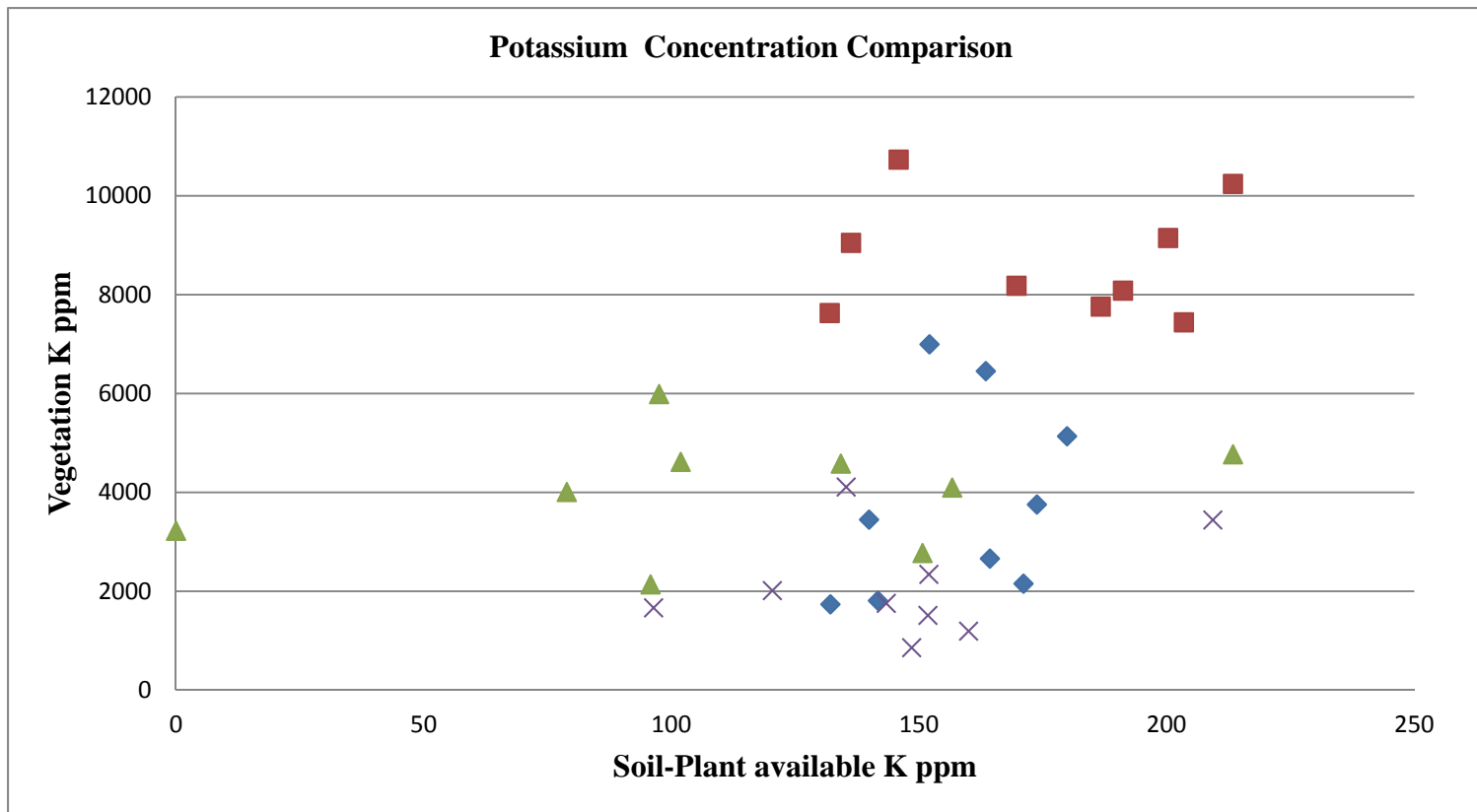


Figure B7. Scatter plot of potassium concentration in vegetation and plant available potassium in the soil from individual sites.

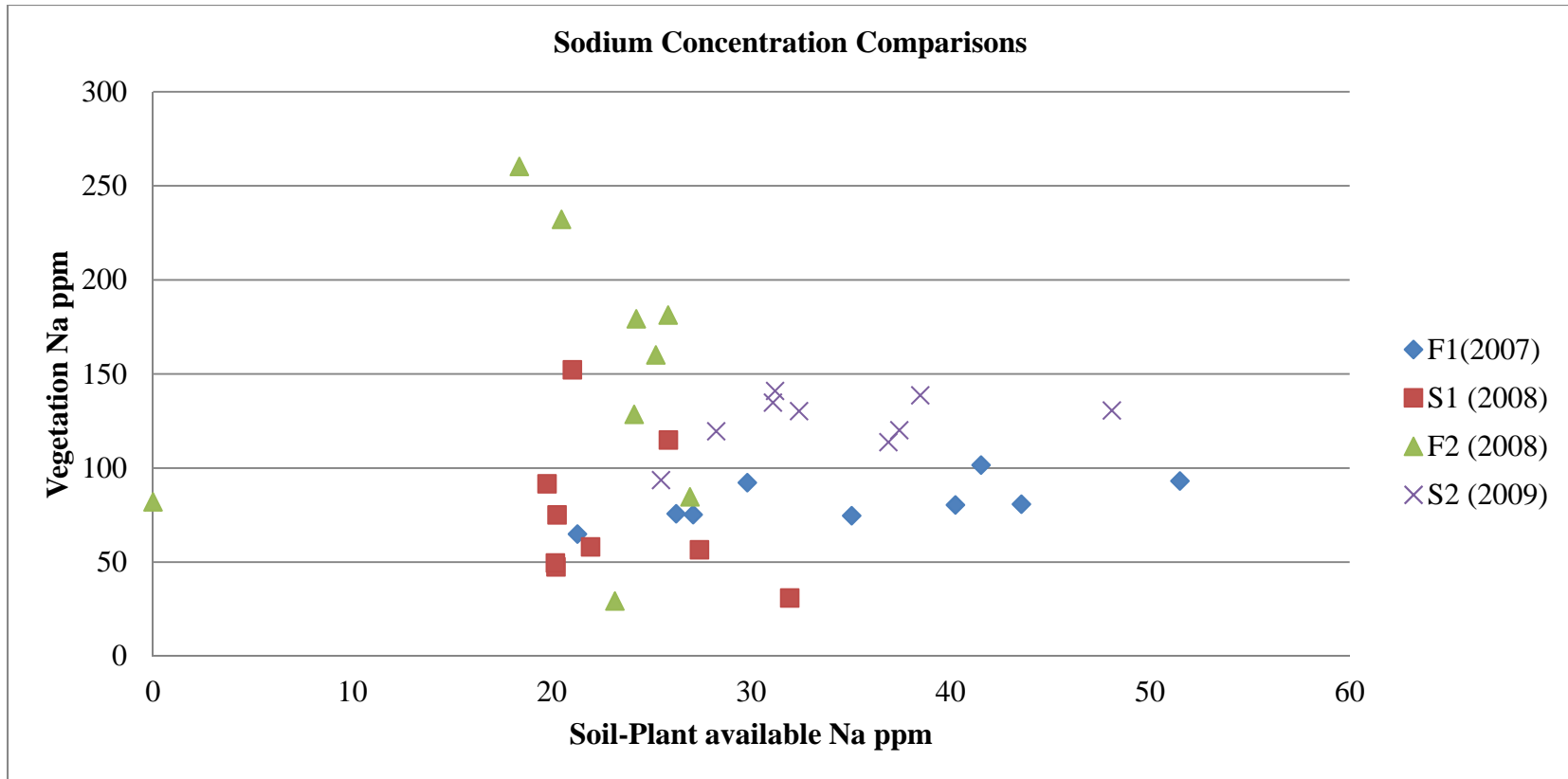


Figure B8. Scatter plot of sodium concentration in vegetation and plant available sodium in the soil from individual sites.

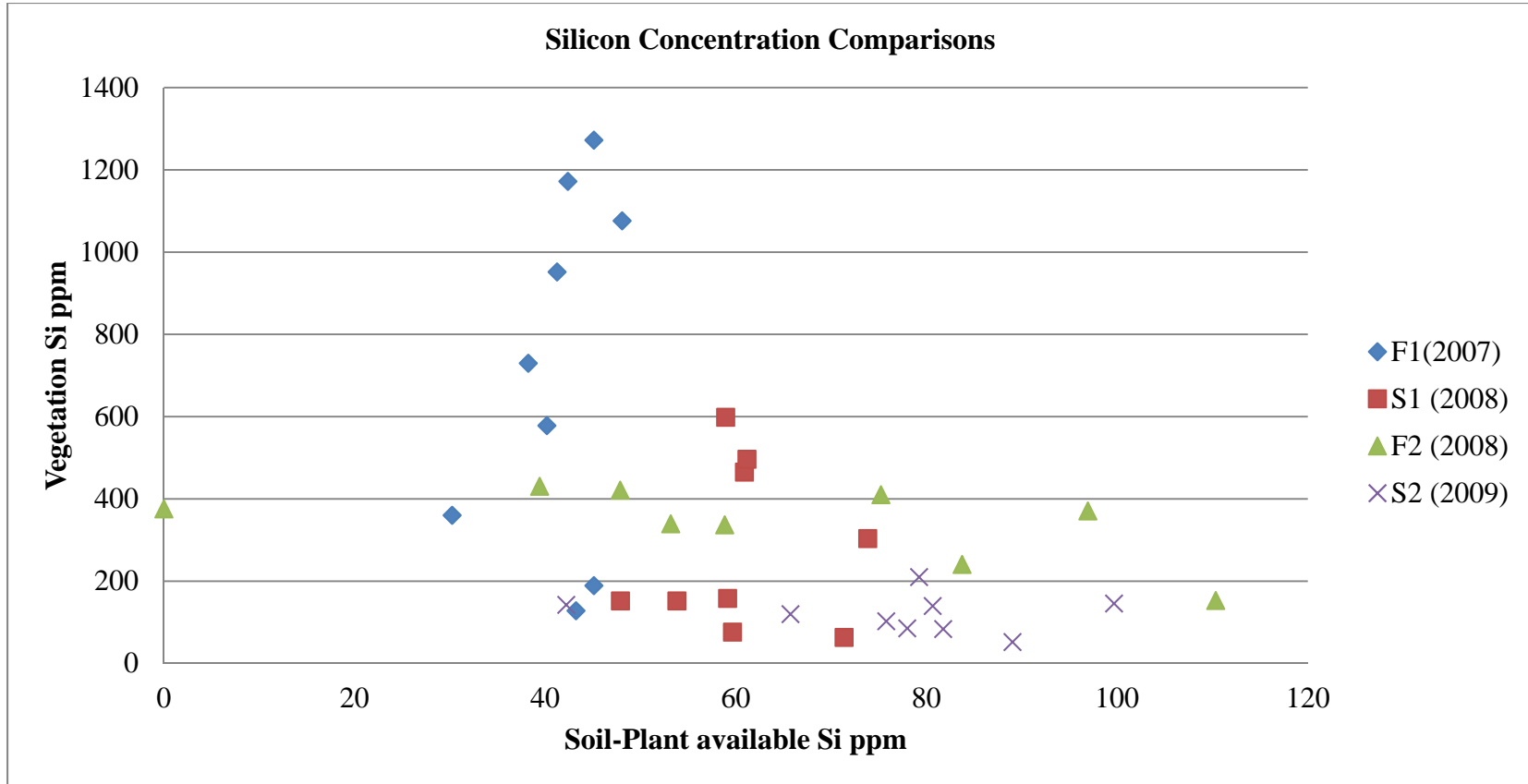


Figure B9. Scatter plot of silicon concentration in vegetation and plant available silicon in the soil from individual sites.

Figures B10-B12 show that there is very little if any correlation between vegetation mineral content and soil available mineral content. In general, the data show horizontal patterns indicating that over the total range of plant available minerals at each site, the minerals stay the same. The only slight deviations of this are potassium in spring 1, and sodium in fall 2. These show a slight pattern, but not in any consistent way. Figure 31 has similar data except for fall 1, which has a similar plant available soil concentration for all concentrations of vegetation.

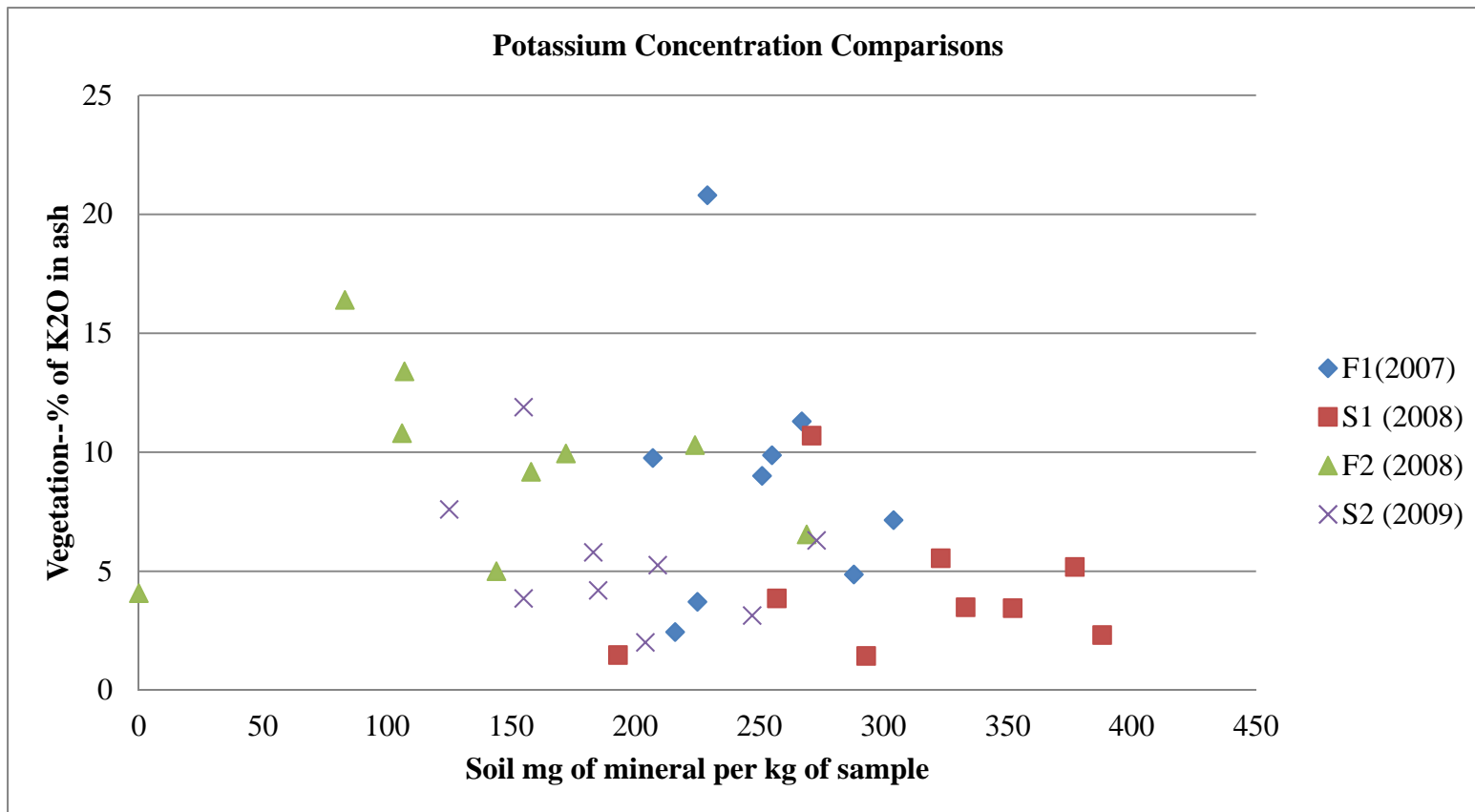


Figure B10. Scatter plot comparing potassium concentrations in plant species and adjacent soils of composite samples.

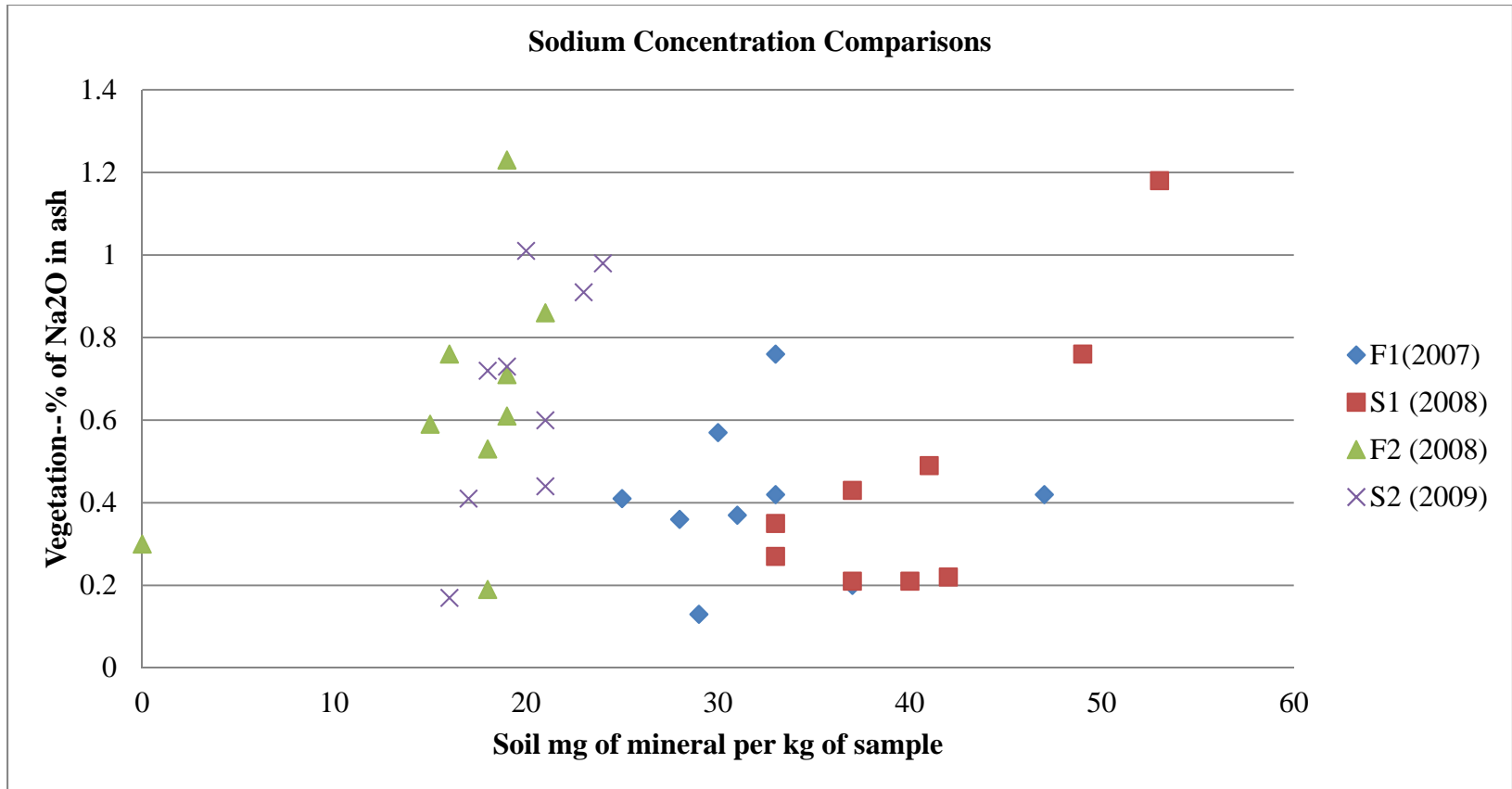


Figure B11. Scatter plot comparing sodium concentrations in plant species and adjacent soils from composite samples.

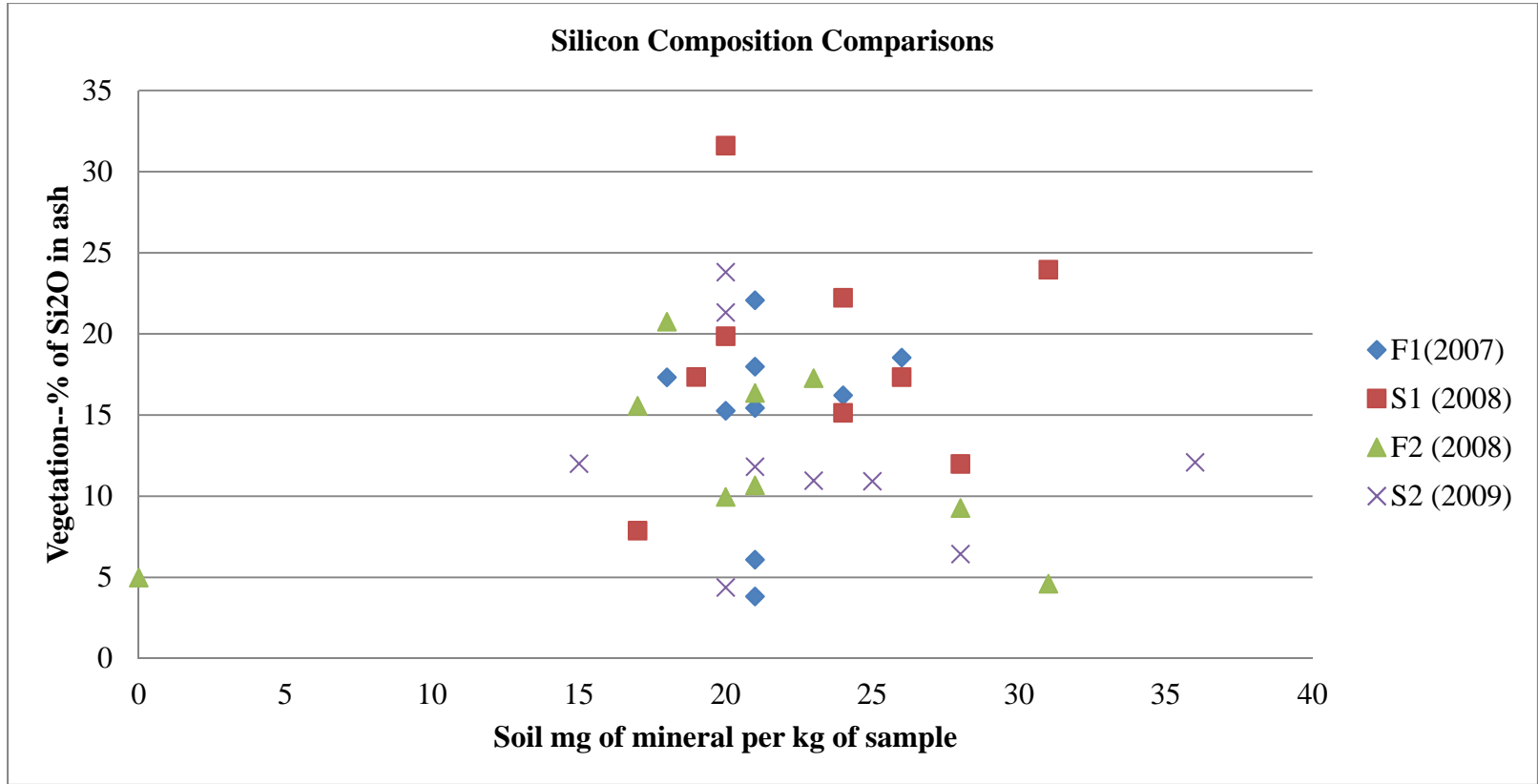


Figure B12. Scatter plot comparing silicon concentrations of plant species and adjacent soils from composite samples.

Using the composite data, or minerals after combustion, fall 2008 potassium in Figure 34 shows a slight reverse correlation that was not present in the individual site data. Spring 2008 sodium and silicon both show a bit of a correlation as well, but not entirely. Again, the other times and minerals do not show a correlation.

Relationship of Minerals in Soils With Minerals in Plants

The mineral concentrations varied when comparing mineral content of the plants with the mineral content of the soils. Potassium and sodium concentrations of the plants tended to be 5-20 times higher, occasionally more, than concentrations in the adjacent soil. Silicon concentrations of the plants tended to be about 2-3 greater than the adjacent soil although in spring 2009 there were a few instances in which the concentration in the plants was quite similar to that of the adjacent soil.

I hypothesized that amount of mineral in the soil would affect the mineral content of the plant tissue. I assumed that decreases in minerals in plants would be reflected by increases in adjacent soils. I further assumed that high mineral concentrations in the soil would result in higher mineral concentrations in the adjacent plants unless something prevented uptake of the minerals.

Overall there is very little correlation between the concentration of the minerals in the plants and in the adjacent soils for the individual species samples. In the composite samples, the correlation of sodium in plants and soils is evident in the individual species samples in that five of the nine species (*Echinacea pallida*, *Heliopsis helianthoides*, *Ratibida pinnata*, *Silphium laciniatum*, and *Solidago canadensis*) show a positive correlation, two of the species (*Heliopsis helianthoides* and *Solidago canadensis*) have a

very strong positive correlation and *Solidago laciniatum* is almost a strong positive. In the individual species samples the only correlation was a very strong one between potassium in *Solidago canadensis* and the adjacent soil.

According to Bakker and Elbersen (2005), the deposition of inorganic elements in the plant tissue is dependent on the texture of the soil in which it is grown. Switchgrass grown on sandy soil consistently showed lower potassium content. When sampled under natural conditions species from infertile sites generally have lower tissue nutrient concentrations than species from fertile sites, owing to reduced availability and absorption of nutrients (Auclair 1977). This raise suggests that the concentration of minerals in plant tissue is affected by the concentration of the minerals in the soil. Conversely, if the mineral content within the plants is high and large amounts are leached out of the dead plant this could affect the concentrations of the minerals in the soil adjacent to the plants. Therefore, it is possible that the concentrations determined by any of the following; the amount of mineral available in the soil, how much of the mineral is taken up, and utilized and/or how much re-enters the soil from the plant.

Interpretation of the relationship between plants and soils may not be as straightforward as originally anticipated. Mineral concentrations in soil solution and therefore mineral absorption by plants fluctuate considerably during the year. In nonagricultural soils there is generally a predictable spring nutrient flush and in some areas also an autumn or winter flush associated with the leaching and breakdown of fresh litter, a spring increase in microbial activity, and freeze-thaw or wetting-drying cycles

that dissolve microbial cells. As sampling was done well after the first killing frost (Oct. 25, 2007 and Oct. 21, 2008) and before re-growth in the spring, changes in mineral concentration would be physical in nature and not involve metabolic processes. Therefore, moisture and temperatures related to freezing and thawing would be factors affecting leaching of the minerals from the plants and soils.

Potassium ions within plants do not enter into permanent organic combinations, but exist as highly mobile soluble organic and inorganic salts (Lawton and Cook 1954). In early fall as senescence is occurring, potassium ions move from older dormant tissue in the phloem to the roots and diffuse into the soil. Furthermore, potassium ions are readily leached from dormant tissue by rain or dew. Hinnant and Kothmann (1982) found that as little bluestem reached senescence potassium was translocated and readily leached early in the fall. The higher concentrations in tissue of the plants than the soils I observed suggest that leaching from the soils may have already occurred prior to the first sampling each year. This may also be true for sodium and silicon although they are not as mobile as potassium.

“The difference in total ash content among these soil types can be largely explained by the higher soluble silica level in clay soils, which results in higher ash levels in crops grown on clay soils,” (Bakker and Elbersen, 2005).