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Potassium and sulfur availability and lime potential of ash co-product of corn cellulosic ethanol processing

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Potassium and sulfur availability and lime potential of ash co-product of corn cellulosic ethanol processing

by

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DEDICATION

I would like to dedicate this Thesis to my Family and my God. My family for their continued support through these last 2 ½ years and my God for giving me this opportunity to come back and continue my education where I learned so much and made a lot of great friendships that will last forever.

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CHAPTER 1: GENERAL INTRODUCTION

Introduction

As the United States strives to become a more sustainable country in terms of energy usage, more attention is being given to biofuels as a way to decrease the carbon dioxide released into the atmosphere by non-renewable resources. One of the main biofuels, ethanol, is mainly produced through the conversion of corn grain to ethanol. However, in recent years, ethanol produced from cellulosic material, such as corn residue, is gaining consideration because corn residue is already high in abundance and, unlike corn grain, is something that humans cannot digest. Therefore, it is not competing with the food market. At the end of the process of cellulosic ethanol, ash is leftover as a direct product of mainly lignin combustion. It has been shown that ash from lignin combustion can have positive effects on soil characteristics and at times on plant growth and yield (Etiegni et al., 1991; Ferreira et al., 2012; Ochecova et al., 2014).

Lower commodity prices in recent years, which many believe also for the foreseeable future, have farmers investigating other income options for their farms. Removing corn residue from fields and selling to cellulosic processing plants is another income for farmers. However, removal of residue increases removal of essential nutrients for plant growth and development. Because of this, more nutrients would need to be applied on fields to replace nutrients that are removed with the residue. Ash could provide a soil amendment or fertilizer option for farmers. Applying ash on soils deficient in nutrients that are recovered in ash would be more useful than disposing the ash in landfills where it has no value and would complete the cycle of cellulosic ethanol and make it more sustainable.

Research projects have focused on wood and bagasse ash application on soil characteristics, plant growth and grain yield; but no published research has been found using ash from corn residue with evaluation in a corn-soybean rotation at the field scale. Therefore, the objective of this study is to evaluate in the field the potassium and sulfur availability for corn (*Zea mays* L.) and soybean [(*Glycine max* L.) Merr.] as well as the liming potential of ash co-product of corn cellulosic processing and comparing it with industry products that are commonly used today.

Thesis Organization

This thesis is submitted as one paper suitable for the publication in the scientific journals of the American Society of Agronomy or Soil Science Society of America. The title of this paper is Potassium and Sulfur Availability and Lime Potential of Ash Co-Product of Corn Cellulosic Ethanol Processing. This paper contains sections for an abstract, introduction, materials and methods, results and discussion, summary and conclusions, reference list, tables, and figures. The paper follows a general introduction and closes with a general conclusion.

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CHAPTER 2: POTASSIUM AND SULFUR AVAILABILITY AND LIME POTENTIAL OF ASH CO-PRODUCT OF CORN CELLULOSIC ETHANOL PROCESSING

A paper to be submitted to Soil Science Society of America Journal

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Abstract

Lignin-derived ash obtained as a co-product of corn residue used for ethanol production may have value as a soil amendment. Preliminary laboratory analyses indicated that the ash had potential lime value and higher concentrations of K and S compared with other nutrients. The value of the ash to supply K and S and to increase soil pH was evaluated at two Iowa sites compared with commonly applied sources of K (KCl) and S (gypsum) and pure $CaCO_3$. At each site, three 2-year trials were initiated to assess the K, S, and lime values of the ash. Several rates of each material were applied only the first year at all trials. Corn (*Zea mays* L.) was planted in 2014 and soybean [*Glycine max* (L.) Merr.] in 2015. Soil samples (15-cm depth) were taken before treatment application, at the V6 stage of each crop, and after crop harvest. Soil was analyzed for K, S, and pH levels Leaf samples taken at the corn R1 growth stage and soybean at the R3 stage were analyzed for K and S concentration. There were large fertilizer and ash K effects on grain yield, soil K, and leaf K but no significant source differences. The ash had liming value comparable to pure $CaCO_3$ or higher. The results for S crop-availability were not conclusive mainly because there was little or no grain yield response to S, but soil and tissue test results suggested less early S supply compared with gypsum.

Abbreviations: ANOVA, analyses of variance; CEC, cation exchange capacity; CCE, calcium carbonate equivalent; ECCE, effective calcium carbonate equivalent; RCBD, randomized complete block design.

Introduction

Ash produced from burning of plant materials has been used as a source of plant nutrients or as a soil amendment for centuries. Recently, ash has become one of the byproducts of the biofuel industry. Ethanol derived from the processing of corn grain is the predominant biofuel in the USA. There is, however, increased interest in using lignocellulosic materials to produce ethanol, and one possible use of the mostly lignin residue is to burn it for electricity production. Wood chips, trees, and wood pulp have been used for the production of electricity for years with the ash material most commonly being disposed of in landfills. However, with increasing regulations enforced for landfills and increasing costs to dispose materials in landfills, research has been done at assessing the potential benefits these ash materials have on soil characteristics, plant growth and yield.

Brazil has long been a leader in processing sugarcane (*Saccharum officinarum*) for sugar and ethanol. A co-product that comes from sugarcane processing is called bagasse. Bagasse is the fibrous material that is left after the sugar has been pressed out of the sugarcane. It is estimated that around 163 million metric tons of bagasse was produced in the year 2013 (UN, 2016). The bagasse can be used in combustion to create bioelectrical energy to provide power for the entire processing plant with excess energy being incorporated into the electrical grid (Alonso-Pippo et al., 2008). The bagasse is burned in a boiler that produces steam which turns a turbine to create electricity. The ending product of this process being bagasse ash. There have been many different uses of this ash to complete the cycle of ethanol production from sugarcane. One of those uses is as a soil amendment. Ferreira et al. (2012) investigated the effect that ash material produced from sugarcane bagasse combustion had on the chemical properties of an oxisol soil. The pH of the ash was 9.25 and contained 21.41, 14.94, 36.46, and 3.01 g kg^{-1} of total P, K, Ca, and Mg, respectively. Four rates consisting of 0, 5, 15, and 30 Mg ha^{-1} were applied and incorporated into the soil and rice (*Oryza sativa*) was cultivated thereafter. Analysis of the soil before ash incorporation showed a pH of 6.45, Ca, Mg, and K 1499, 323, and 203 mg kg^{-1} (1 *M* KCl extraction), and 34 mg P kg^{-1} (Mehlich-1 test). Soil samples were taken 132 days after ash incorporation. Results showed statistically significant increases in soil pH, P, and K levels but only for the highest rate applied.

Naylor and Schmidt (1986) evaluated wood ash from paper mills and home wood stoves and compared its liming potential and K value with ground limestone and commercial potash fertilizer. This research was done in the greenhouse and used on two soils; a Mardin silt loam (Typic Fragiocrept) and a Burdett silt loam (Aeric Ochraqualfs). Materials were collected, analyzed for composition, mixed with 3 kg of soil and put into pots. The wood ash and commercial limestone materials were mixed at rates approximate to 2.24, 4.5, 9.0, 17.9, and 35.9 Mg ha^{-1} while the potash fertilizer was mixed with soil a rates equivalent to 34, 68, 135, 270, and 540 kg ha^{-1}. The soils were incubated at 25 °C for 60 days with watering occurring periodically to simulate wet and dry periods. After the incubation, soil samples were tested for pH and extractable nutrients. The wood stove ash contained higher levels of Ca and K (30 and 11%) than the boiler ash (20 and 3%). The materials application rates caused a linear increase in crop-available soil K as evaluated by soil testing. The K in the wood boiler and stove ash was available at a range of 18 to 35% and 51%, respectively, compared with potash fertilizer of 63-76%. The authors hypothesized that higher temperatures in the wood boilers caused the lower K availability by forming insoluble K compounds. The initial pH of both soils were 4.8 and 5.7 with ash and ground limestone being applied to the soil to raise the pH to levels that are suitable for crop growth based on each materials respective effective equivalent neutralizing value compared to $CaCO_3$ by considering the fineness of the materials. Both materials increased soil pH significantly but there was no significant difference between the two sources at any of the rates applied on either soil.

Etiegni et al. (1991) conducted a study in Idaho using ash material that was produced from the combustion of wood for electricity production. The ash collected was passed through a 35 mesh screen to collect only particles 1-mm or less in diameter. Six different soil types representing cultivated soils and forest soils of the state were collected and air dried for greenhouse trials. Each soil was mixed with ash at rates of 2, 4, 8, 16, and 32 percent of soil weight which was equivalent to 40, 80, 160, 320, and 640 Mg ha^{-1}, respectively. Wheat (*Triticum aeastivum* L.) seeds were planted in Palouse (Ultic Haploxerolls), Latahco (Argiaquic Xeric Argialbolls), and Westlake (Cumulic Ultic Haploxerolls) cultivated soils and poplar root cuttings were planted in Santa (Vitrandic Fragixeralfs), Helmer (Alfic Udivitrands), and Potlach (Aquic Haplocryalfs) forest soils. The poplar study was conducted for two months and the wheat study for 45 days after seedlings emergence. Soils were then tested at the completion of the wheat and poplar study to analyze the effects on soil characteristics. The ash pH was 13.1, calcium carbonate equivalent (CCE) was 92.4%, and had 331, 22.4, 13.6, 41.7, and 4.35 g kg^{-1} total Ca, Mg, P, K, and S. The initial pH of the soils ranged from 5.2 to 5.5. Soil pH increased with increasing rates of ash with the two highest ash rates increasing the pH above 10 for all soil types. The plant biomass, when compared with the control, was increased by the lowest ash application rate, was decreased by the intermediate rates, and no biomass was produced when the two highest rates were applied.

Ochecova et al. (2014) set up a 3-year pot experiment designed to determine the effect wood ash that was burned for electricity production had on two soils that had levels of potentially toxic elements due to contamination from mining and smelting industry activities. One soil was a Cambisol soil as defined by the FAO (referred to as an Inceptisol in the USA) and the other a sandy clay loam Fluvisol (referred to as Entisol or Inceptisol in the USA). Rates of ash applied to the both soils ranged from 0.2 to 1.0% was on a weight basis. The wood ash had a pH of 11.5 and 3.34 g K kg^{-1}. Application of wood ash did not affect vegetative growth or grain yield of wheat. However, ash application significantly increased the pH and K levels in both soils. In the Cambisol, pH was increased from 5.6 in the control to 7.5 by the highest treatment. The pH of the Fluvisol was also increased but not as much as in the Cambisol because the Fluvisol was less acidic, and the increase was from 7.10 in the control to 7.32 by the high ash rate. Available K in the soil was increased significantly over the control for both soils, with increases from 120 to 253 mg K kg^{-1} in the Cambisol and from 79.5 to 116 mg K kg^{-1} in the Fluvisol soil.

The reviewed information showed that ash produced from combustion of plant material used for energy production supplies plant nutrients and increases soil pH but can be detrimental to plant growth when applied in large quantities. Also, the effects on soils and crops depend a great deal on the plant material used and the industrial process. The ash used in our study resulted from the processing of corn stover for ethanol production and subsequent combustion to produce energy, and $CaCO_3$ was added during the combustion process. The N and P concentrations of the ash were very low, but had higher concentrations of K and S. Therefore, our study focused on the K, S, and liming value of ash.

Potassium deficiencies as well as the need for K fertilization are common in many states of the US and other regions of the world. In 2011, 4,166 Mg of potash fertilizer (60% K_2O) was used in the USA (Nehring, 2013). Iowa research has shown frequent and large corn and soybean responses to K fertilization except in the western region of the state where soil-test levels are optimum or higher (Mallarino and Blackmer, 1994; Barbagelata and Mallarino, 2013; Clover and Mallarino, 2013; Oltmans and Mallarino, 2015). This and other research has been used to establish Iowa soil-test K interpretations and fertilization (Mallarino et al., 2013).

Sulfur is classified as a secondary nutrient and is deficient in soils of many regions of the world, but early research in areas of the north-central region of the U.S. west of Indiana and Michigan showed that crop response to S fertilization was infrequent (Hoeft at al., 1985; Hoeft and Fox, 1986). However, the frequency of S deficiencies are increasing in the north-central region, probably due to reduced industrial S emissions as a result of increasing pollution controls (Franzen, 2015). Research with alfalfa (*Medicago* *sativa*) and corn in Iowa since the early to middle 2000s mainly in northern and northeast Iowa have shown frequent and significant yield responses (Sawyer and Barker, 2002; Lang et al., 2006; Sawyer et al., 2009; Franzen, 2015).

Soil acidity is a very important factor in crop production as it affects nutrient availability, phytotoxicity potential of certain elements, and the microbial activity in soils (Foy, 1984; Marschner, 1995). Soils can become acidic through leaching of basic cations over time and in a large extent from the nitrification of ammonium in N sources containing ammonium or compounds that transform into ammonium. McLean and Brown's (1984) and Voss (1991) summarized liming field research in the Midwest from the 1950s until 1990 and concluded that corn and soybean frequently would benefit from lime application in soils with pH < 6.0 and much less frequently in soils with higher pH. Iowa research in recent years (Kassel, 2008; Henning, 2004a; Henning, 2004b; Henning, 2008a; Henning, 2008b; Pagani and Mallarino, 2012; Pagani and Mallarino, 2015) has confirmed that liming is a needed practice in many soils, and the information has been used to update soil pH interpretations and liming guidelines in Iowa (Mallarino et al., 2013).

Given the characteristics of the ash of interest for our study, the objective of this research was to evaluate in the field the K and S crop-availability and soil acidity neutralizing capacity of ash resulting from the processing of corn stover for ethanol production and subsequent combustion to produce energy. The evaluation was based on the comparison of effects of ash and commonly used sources of these two nutrients and calcium carbonate ($CaCO_3$) on selected chemical properties and crop yield.

Materials and Methods

Sites and treatments

Field experiments were established at two sites at an Iowa State University Research Farm in Boone County, Iowa, having different soils and previous corn and soybean sequence. Table 1 shows the soils at each site and the properties measured before applying the treatments and Table 2 shows precipitation information. The previous crop was corn at Site 1 and soybean at Site 2, and both had been harvested for grain. Three, 2-year independent trials adjacent to each other were conducted at each site to evaluate separately the K, S, and lime value of the ash material. Corn was planted the first year at both sites, and soybean was planted the second year. Both sites were managed with chisel plowing of cornstalks in the fall and disking of both corn and soybean residue in the spring. This type of tillage system is the most common in Iowa. The chisel plow used had shanks that tilled the soil 15 to 30 cm deep and were spaced 30 cm apart. Corn (in 2014) was planted on 6 May and the hybrid used was DeKalb 57-75. Soybean (in 2015) was planted on 16 May and the variety used was Pioneer 92Y75. Both crops were planted with a row crop planter with row units spaced 76 cm apart, using seeding rates recommended by Iowa State University, and managed with appropriate pre-emergent and post-emergent herbicides.

The ash was produced from combustion in a fluidized bed reactor of residues of ethanol production from corn stover (after grain harvest) by a proprietary fermentation process. The solid material remaining after distillation was largely composed of lignin, but also included denatured proteins and mineral constituents that entered the process with the corn stover material. This solid material was produced by mechanically pressing liquid out of the solid material, and a semisolid material was produced by evaporating the liquid remaining after pressing the solid material. Both materials at a ratio of approximately 70% solids and 30% semisolids materials plus $CaCO_3$ were combusted at approximately 1370 °C in a fluidized bed reactor.

The capability of the ash to supply K and S and its liming values was compared with that of commercial potash fertilizer (KCl), mined finely ground gypsum, and pure finely ground $CaCO_3$. The target application rates for trials at both sites were 0, 38, 76, 114, and 152 kg K ha^{-1}; 0, 17, 34, 51, and 68 kg S ha^{-1}; and 1.12, 2.24, 3.36, and 4.48 Mg ECCE ha^{-1}. The use of ECCE is required in the State of Iowa for ag lime quarry certification, and assess the neutralizing power of limestone by quantifying combined effects of particle size and neutralizing value (IDALS, 2008). The K and S application rates for the reference sources were calculated on the basis of composition indicated in the bags of the commercial products used. The K, S, and ECCE target application rates with the ash source were similar to those used for the reference materials and were based on preliminary analysis of bulk ash received. The chemical composition and ECCE of the ash (Table 3) was determined at the Iowa State University Soil and Plant Analysis Laboratory. The total concentration of various elements in the ash was analyzed using a microwave digestion technique (USEPA, 2007) and measurement by inductively coupled plasma (ICP). Water-extractable K and S was determined by shaking 0.5 g of dried ash material with 50 mL water during 2 hours and measuring K and S with ICP. However, analysis of three ash samples taken during the application differed from the target rates. Therefore, the K, S, and ECCE application rates with the ash and the reference materials differed somewhat, but we have the best estimate possible of the nutrients rates applied with the ash. Table 4 shows actual nutrient and ECCE applied with each source.

Application of all materials was done only in spring of the first year (2014) before corn planting. No treatments were applied the second year (2015). The sources and application rates combinations at each trial were arranged in a randomized complete block design (RCBD) with three replications. Plot size was constrained by the amount of ash material that was available, and was 3.05 m in width (4 crop rows) and 6.1 m in length. Non-limiting rates of P (135 kg P ha^{-1}) and N (280 kg N ha^{-1}) were applied to all plots the first year. Uniform rates of S (50 kg S ha^{-1}) and $CaCO_3$ (3.4 Mg ECCE ha^{-1}) were applied across all plots of the K trials. Uniform rates of K (179 kg K ha^{-1}) and $CaCO_3$ (2.2 Mg ECCE ha^{-1}) were applied across all plots of the S trials. In the lime trials, no K was applied to the highest two ash rates due to the high amount of K that was applied via the ash. Rates of 84 and 34 kg K ha^{-1} were applied to 1.12 and 2.24 Mg ECCE ha^{-1} rates, respectively, since these plots had lower amounts of K applied through the ash and we needed to make sure there were unlimited rates of K. All plots also received a uniform rate of S (50 kg S ha^{-1}).

Soil, plant, and grain yield measurements

Initial soil characteristics were determined by taking a composite sample from each of the three replications at each trial and site using soil cores 15-cm in depth. These samples were analyzed separately, and the averages are shown in Table 1. Soil samples were dried at 40 °C, crushed to pass through a 2-mm sieve, and were analyzed for P, extractable cations (K, Ca, Mg, and Na), pH, extractable sulfate (SO_4-S), pH, buffer pH, and cation exchange capacity (CEC) following procedures recommended for the North Central Region by the NCERA-13 regional soil testing and plant analysis regional committee. Soil-test P was measured by the Bray-P1 method (Frank et al., 1998) but results are not shown because a non-limiting P fertilizer rate was applied across all plots. Soil-test K and extractable Ca, Mg, and Na were measured by the ammonium-acetate extractant and measuring concentrations in extracts by inductively-coupled plasma (ICP) spectrometry (Warncke and Brown, 1998). Soil pH was measured by the 1:1 soil-water ratio method (Peters et al., 2012). Extractable sulfate was measured by the monocalcium phosphate ($Ca(H_2PO_4)_2$) method (Franzen, 2015). Soil organic matter was measured by a combustion method described by Wang and Anderson (1998). The CEC of the soils was estimated as suggested by the NCERA-17 committee by summation of extractable Ca, Mg, K, Na, and neutralizable soil acidity (Warncke and Brown, 1998). Soil samples also were collected from each plot of each trial (12 cores, 15-cm depth) each year in late spring at the corn or soybean V6 crop growth stage (Pedersen, 2004; Abendroth et al., 2011) and in the fall (October) after each crop harvest. Soil analyses of these samples depended upon the trial where the samples were collected using the same procedures described for the initial soil samples. Soil-test K was measured in samples from the K trials, extractable sulfate was measured in samples from the S trials, and pH was measured in samples from the lime trials.

Plant height was measured only in the first year 49 days after corn was planted in all plots of all trials. Height was measured on three plants in the center two rows of each plot from the ground level to the tip of the tallest leaf when lifted to be perpendicular to the ground. The average of the three measurements was used as a representative height for each plot. Height was not recorded in 2015 when soybean was planted. Plant tissue samples were taken in both years from all plots of the K and S trials. For corn in 2014, the leaf blade below and opposite to the primary ear leaf was taken from ten plants of each plot at the R1 growth stage (Abendroth et al., 2011). In 2015, the soybean newest fully developed trifoliate leaf, including the petiole, was taken from ten plants of each plot at the R3 growth stage (Pedersen, 2004). The leaf samples were dried in a forced-air oven at 60 °C and ground to pass through a 2-mm sieve. Samples from the K trials were tested for total K concentration and samples from the S trials were tested for total S. The concentrations of both nutrients in the plant tissue were measured by digesting samples in concentrated HNO_3-H_2O_2 (Zarcinas et al., 1987) and measuring concentrations by ICP spectrometry.

Grain was harvested by hand harvesting from a central area (two rows by 5 m) of each plot. Weight and moisture of grain was recorded for each plot to determine yield. Corn yield was adjusted to a grain moisture of 150 g kg^{-1} and soybean yield was adjusted to a grain moisture of 130 g kg^{-1}.

Data management and statistical analyses

Treatment effects on soil and crop measurements for each trial and year were assessed by analysis of variance (ANOVA) for a RCBD using the mixed procedure of SAS assuming fixed source and rate effects and random block effects (SAS Institute, 2011). Since the application rates differed between the two sources, the analysis performed for each measurement included source as a categorical variable (ash and the reference material), application rate as a continuous variable using the actual rates applied for each source, and the interaction between source and rate. When the ANOVA indicated a significant effect ($P \leq 0.05$) for application rate or the interaction source by rate, the response to rate was further studied by fitting response models. A single response model was fit across data for both sources when there was significant effect of rate but no significant source or interaction source by rate; otherwise two models were fit. The models linear, quadratic, quadratic-plateau, and exponential asymptotic to a maximum were fit using the REG or NLIN procedures of SAS (SAS Institute, 2011) or Sigmaplot 11.0 (Systat Software Inc., 1735 Technology Drive, Suite 430, San Jose, CA 95110, USA). A curvilinear model was chosen to describe the response only when its residual sums of squares were significantly smaller ($P \leq 0.05$) than for the linear model, which was tested by *F* test of the model residual sums of squares. When this was the case, we fit the curvilinear model with the highest R^2 value.

Results and Discussion

Potassium trials

First-year treatment effects

Analysis of variance of the results from the first year spring soil tests, tissue tests, plant height, grain yield, and post-harvest soil tests showed that all the measurements had significant responses to K supplied by KCl or ash sources at both trials, but no significant interaction ($P \leq 0.05$) between source and application rate. Therefore, both sources had statistically similar effects on all measurements, and a single response model was fit across data from both sources for each measurement and site. Figure 1 shows data and response models fit for all measurements made in 2014. The results of the analysis of the soil samples taken in the spring (41 days after the K application) show that soil-test K increased linearly with increasing application rates at both sites (Fig. 1). It must be noted that at Site 2 both source and rate effects were significant, although the interaction was not, but source was not significant in a supplemental ANOVA that excluded the highest KCl rate. The soil-test K levels for the highest KCl rate were 140 mg kg^{-1} at Site 1 and 135 mg kg^{-1} at Site 2. This compares with soil-test K values for the highest ash rate of 119 mg kg^{-1} at Site 1 and 118 mg kg^{-1} at Site 2. These differences between the highest KCl and ash K rates are explained by the lower rate of K applied with the ash material.

Corn plant height was measured in all plots 49 days after planting, and showed a significant positive rate effect with higher rates of K applied at both sites (Fig. 1). The application of KCl or ash increased plant height up to the highest rate applied but with decreasing increments as the rate increased. Although plant height is not a good tool to estimate grain yield, the results showed that the K supplied by KCl and ash sources were equivalent for vegetative growth. The K concentration in ear-leaves of corn at the R1 growth stage increased linearly as the K application rate increased at both sites (Fig. 1). A linear increase for leaf K concentrations but a curvilinear increase with decreasing increments for plant height suggest luxury K uptake for vegetative growth. Both sites showed a very large corn grain yield response to K application (Fig. 1). We expected to see a response of crop grain yield at both sites because the initial soil-test K values were below the optimum range according to interpretations in Iowa (Mallarino et al., 2013). At Site 1 there was a linear response up to the highest rate used, whereas at Site 2 there was a curvilinear response with decreasing increments but no yield plateau was reached.

The post-harvest soil-test K levels showed a large residual effect of the pre-plant K applications at both research sites (Fig. 1). However, the overall soil-test K levels were higher at Site 1 than at Site 2, and the increase with increasing application rate was curvilinear with increasing increments at Site 1 but linear at Site 2. Different residual soil-test K levels and either a linear or curvilinear trend could be expected depending on soil properties and K removed with harvest, which was not measured. However, the lower soil-test K levels at the Webster soil in Site 2 are reasonable because this site had finer texture, higher extractable Ca and CEC (Table 1) and this soil is more poorly drained than the Clarion soil at Site 1.

Second-year treatment effects.

Soil and soybean measurements taken in 2015 (Fig. 2) showed a large residual effect of the K applied before the 2014 corn crop. As in 2014, ANOVA for all measurements taken in 2015 showed statistically significant ($P \leq 0.05$) rate effects but no significant interaction between source and application rate. Therefore, both sources had statistically similar effects on all measurements, and a single response model was fit across data from both sources for each measurement and site.

Results of the analysis of the soil samples taken in the spring of 2015 show (Fig. 2), as expected, approximately similar soil-test K levels and residual responses to results from the fall soil sampling in 2014. As in fall 2014, at Site 2 both source and rate effects were significant, although the interaction was not, but source was not significant in a supplemental ANOVA that excluded the highest KCl rate. Results of tissue testing of soybean leaves at the R3 growth stage showed that leaf K concentrations increased curvilinear with increasing increments as the K rate increased at both sites (Fig. 2). The overall leaf K concentrations and the rate of increase were smaller at Site 2, however. The soybean grain yields showed large residual responses to K at both sites (Fig. 2), which was expected since initial soil-test K was low and the higher rates applied more K than what would be removed with corn grain harvest. The grain yield increase was linear at both sites, and the overall yield levels was higher at Site 2. Results for the fall post-harvest soil sampling in 2015 also showed a residual effect of K applied in 2014 on soil-increasing increments at both sites, and as was observed for the previous sampling dates the overall levels were lower in Site 2.

Therefore, for comparable application rates, the K supply by ash material and KCl fertilizer were similar concerning effects on soil-test K values, corn early vegetative growth as estimated by plant height, and for grain yield. These results compare in different ways to the results of previous research. Our results showing that even low ash rates increased soil-test K and pH were approximately similar to those reported by Naylor and Schmidt (1986) for K and Etiegni et al. (1991), who used different types of wood ash. The ash we used had more significant effects on soil chemical properties than Ferreira et al. (2012) reported when using ash from sugarcane bagasse since they found a soil K increase only for the highest rate applied of 30 Mg ha^{-1}. These authors did not use a reference material, however, and soils had very different properties. The ash used by Naylor and Schmidt (1986) had similar K composition compared to the ash used in this experiment which is twice as much K than the ash used by Ferreira et al. (2012).

Sulfur trials

First-year treatment effects.

Analysis of variance of the results from both sites for the spring soil SO_4 at the corn V6 growth stage, the corn leaf S tissue test results at the R1 growth stage, and the post-harvest SO_4 soil test results showed significant responses ($P \leq 0.05$) to S applied by gypsum or ash sources ($P \leq 0.05$) but only at Site 2 for corn grain yield (not shown). Furthermore, in all these instances there was significant effects of S source or source by application rate interaction. Figure 3 shows data and response models fit for all measurements made in 2014.

Analysis of the soil samples taken in the spring (41 days after the S application) show that a significant interaction between source and application rate for soil SO_4 was explained by a clear response to S supplied by gypsum but not by the ash at both sites. Soil-test SO_4 increased linearly with increasing rates of S applied for the gypsum source ($P \leq 0.05$). There was no significant model fit for the ash source at Site 1, and a linear model was fit at Site 2 but was significant only at the $P \leq 0.06$ level and the increases were very small.

No significant rate or interaction effect for corn plant height at either site was observed, therefore no model was fit (Fig. 3). The S concentration in the ear-leaves of corn at the R1 growth stage showed a curvilinear response with decreasing increments for both sources at both sites, but the increases were greater for gypsum than for the ash (Fig. 3), a difference confirmed by a significant source by rate interaction. A high plateau was reached for the gypsum source, but this was not clear for the ash probably because of the actual rates of S applied with ash were lower. The steep increase in soil S along with the large increase in the lowest application rate for the leaf S concentrations at both sites suggest a high solubility and uptake potential for gypsum which agrees with soil S measurements earlier in the spring. The smaller leaf S increasing increments for the ash compared with gypsum agrees with results for the soil SO_4 results in earlier in the spring but the difference was not as marked as for the soil test results. This confirms the lower solubility of ash S (Table 3) and increased availability as the season progressed.

The grain yield results (Fig. 3) showed no significant response to S at Site 1 and a significant but very small response at Site 2. A linear response with a very small rate of increase with the gypsum source and a curvilinear response with decreasing increments with the ash source with increasing rates of S applied was confirmed by a significant source by rate interaction. The slightly larger yield response to ash S than to gypsum S at Site 2, and a similar but smaller and non-significant difference at Site 1, does not have an obvious explanation but confirms comments made before about increasing crop-availability of ash S as the season progressed. However, this possibility does not agree with post-harvest soil S results in Fig. 3, because they show statistically significant and large residual effects at both sites for the gypsum source but not for ash. With increasing rates of gypsum S applied, there was increasing increments representing an exponential model. Therefore, either the small grain yield differences in favor of ash S at Site 2 was a random result or the measurement of extractable soil SO_4 does not assess well the crop-availability of soil S, at least for the ash source. The soil SO_4 values decreased from the spring to the fall, which can be explained by leaching, crop removal, or changes to other S forms.

Second-year treatment effects.

Soil and soybean plant measurements taken in 2015 (Fig. 4) showed no residual rate, source or interaction effects of the S applied before corn in 2014. This difference from results in 2014 is plausible for the ash material as there were few measurements that showed a statistically significant increase. For the gypsum source, however, a lack of residual response by any measurement in 2015 is surprising because there were statistically significant increases at 7 of the 10 measurements in 2014, and especially with an increase of post-harvest soil SO_4. The lack of residual effects in 2015 could be due to SO_4 leaching from precipitation that was received during the fall of 2014 and spring 2015. However, the precipitation during these months was not much higher than the long-term average, although the total annual precipitation was higher than normal in both years (Table 2). Other soil processes, such as immobilization of SO_4 by soil microorganisms could also explain such a decrease.

The comparison of the ash and gypsum as S sources was not conclusive due to the conflicting results observed for effects on the different measurements. Application of gypsum resulted in higher soil and tissue S than for ash but was not significantly different or less efficient than the ash at increasing grain yield. No previous research done with wood ash or bagasse ash studied the effects of ash S had on soil tests or plant growth. The measurements made do not explain with certainty the lower apparent crop-availability of ash early in the growing season compared with gypsum as evaluated by soil or tissue testing. Bennett and Adams (1972), Keren and Shainber (1981) and others have shown that gypsum has very little solubility in water but becomes more soluble in soils and solutions with higher ionic strength or that mimic soil solutions. Therefore, a lower early crop-availability of ash, which had 519 g kg^{-1} water-extractable S is difficult to explain. We speculate that undetermined forms of S in the ash have slow solubility in the soil or that ash chemical properties reduced the solubility of S after application. For example, results from this study presented below showed that ash application increased soil pH.

Lime trials

First-year treatment effects.

Analysis of variance of the results from the first year showed significant ($P \leq 0.05$) application rate effects by both sources at both sites for spring soil pH at the corn V6 growth stage, corn plant height 49 days after planting, and post-harvest soil pH in the fall at both sites, but not for corn grain yield (not shown). Figure 5 shows data and response models fit for this year.

Application of $CaCO_3$ and ash greatly increased ($P \leq 0.05$) spring soil pH at both sites (Fig. 5). At Site 1, there was a significant source difference (greater pH for ash) but in a supplemental ANOVA the source became not significant when the highest ash rate was dropped. At Site 2 however, there was a source difference even when the highest ash rate was not included. Therefore, one linear model was fit across data for both sources at Site 1, but two models were fit at Site 2. At Site 2, the pH increase for $CaCO_3$ was linear and the increase for ash was curvilinear with smaller increases with the higher ECCE rates. The effect on pH for approximately similar rates was higher for ash than for $CaCO_3$. The maximum pH reached was higher for the highest ECCE application rate with ash than for $CaCO_3$. Perhaps the ECCE method of assessing neutralizing power of limestone does not correctly assess the liming value of the ash. The Na content of the ash was not very high but the ash pH was 12.7 (Table 3). Application of ash resulted in an extractable soil Na content of 46 mg kg^{-1} in fall 2014 with a decrease to 26 mg kg^{-1} in fall 2015 as compared with an initial 14 mg kg^{-1}. At this early sampling dates, 41 days after applying the materials, all the application rates with the only exception of the lowest $CaCO_3$ rate increased pH to levels higher than pH 6.0, which is the optimum for corn or soybean in this region (Mallarino et al., 2013).

Corn plant height showed a similar negative correlation ($P \leq 0.05$) with increasing rates of ECCE applied at both sites (Fig. 5). Site 1 showed a linear decrease and was significant with or without the highest ash rate. In Site 2, however, there was no significant decrease when the highest ash rate was excluded but there was a curvilinear decrease with larger decreases with the higher rates of ECCE applied. No source or rate significant effects ($P \leq 0.05$) in corn grain yield was observed at either site (Fig. 5). This can be expected in central Iowa soils with a calcareous subsoil (Pagani and Mallarino, 2015; Mallarino et al., 2013).

Results for post-harvest, fall 2014 pH at Site 1 were similar to the spring pH results in that there was a significant ($P \leq 0.05$) linear ECCE rate effect but no differences between the sources. At Site 2, the fall pH values showed a significant rate effect, and also a difference between sources that became not significant in a supplemental ANOVA the excluded the highest ash rate. Therefore, one model was fit to the data of both sources, and a linear model showed the best fit. At this sampling date, about six months after applying the materials, all application rates increased pH to levels higher than the optimum pH 6.0 and, in fact, the pH of the controls was slightly higher than pH 6.0 and that in the previous spring.

Second-year treatment effects.

Measurements taken in 2015 showed large and significant ($P \leq 0.05$) residual effects on soil pH from both ash and $CaCO_3$ applied before the corn crop in 2014, but no residual effect on corn grain yield (Fig. 6). Similar to 2014 all measurements had significant ($P \leq 0.05$) rate effects except soybean grain yield. One model was fit to the data when there was no significant source or interaction effect. At both sites, the spring soil pH showed a significant rate effect, and also a higher average pH for the ash that became not significant when a supplemental ANOVA excluded the highest ash rate applied. Therefore, one linear model was used to describe the increase in pH with increasing rates of ECCE applied at both sites, and the increasing trend was linear. Soybean grain yield results showed no significant ($P \leq 0.05$) rate or source effect at either site (Fig. 6). This lack of response in 2015 has the same explanation given for results in 2014 when no response was observed. The post-harvest, fall pH results at both sites showed significant ($P \leq 0.05$) ECCE rate effects, and one response model was fit to the data across both sources because there was significant source or interaction either by including or excluding the highest ash rate. A linear model showed the best fit at both sites.

At comparable rates of ECCE applied, the ash and $CaCO_3$ were approximately similar as liming materials for agricultural production. The ash increased soil pH to slightly higher levels only at one site and only the first year. The highest rates of both materials, which was higher than recommended for the initial pH of the soils, decreased early plant height the first year (corn) at both sites but did not affect grain yield at any site or year. Etiegni et al. (1991) reported substantial plant growth decreases with high application rates of wood ash. Etiegni et al. (1991), Ochecova et al. (2014), Naylor and Schmidt (1986), and Ferreira et al. (2012) all reported significant soil pH increases with application of sugarcane or wood ash.

Summary and conclusions

Results in 2014 from the K trials at both sites revealed significant increasing linear or curvilinear response to K application for spring soil-test K, plant height, ear-leaf concentration, grain yield, and post-harvest soil-test K with no differences between sources. Second year measurements showed strong residual effects to the application in spring of the previous year. All measurements, except height that was not measured in 2015, were significantly increased with increasing rates of K applied with no significant source differences.

Results in 2014 from the S trials showed significant source differences for spring soil-test SO_4, corn leaf S concentration, and post-harvest soil-test S measurements at both sites and for grain yield only at one site. A significant rate response was observed for gypsum and smaller or no response for the ash, probably due to a lower early crop-availability of ash S. The gypsum was more efficient at increasing soil SO_4 and leaf S concentration, at one site the ash was slightly better than gypsum at increasing corn grain yield, but the overall response and the yield difference was very small. No significant residual effects of S applied the first year was observed for any measurement in 2015.

Evaluation of the liming value of ash in the first or second year ear of the study showed significant soil pH increases for both sources for all sampling dates, and the sources differed only at one sampling date of one site where the ash increased soil pH slightly more than the $CaCO_3$. The higher rates of both sources decreased corn plant height, but no source or application rate affected crop grain yield in any site or year.

Overall, the study showed that ash resulting from the combustion of lignin and mineral residue after distillation of corn residue for ethanol production had liming value comparable to pure $CaCO_3$ or higher, similar K availability to the commonly used KCl fertilizer. The results for S crop-availability were not conclusive mainly because there was little or no grain yield response to S, but soil and tissue test results suggested less early S supply from ash compared with gypsum.

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Tables

Table 1. Trial sites location, soils, and selected physical and chemical properties.†

Site Information	Site 1	Site 2
Soil Series	Clarion	Webster
Soil Classification	fine-loamy, mixed, superactive, mesic typic Hapludolls	fine-loamy, mixed, superactive, mesic typic Endoaquolls
Textural Class	loam	clay loam
pH	6.13	5.99
Organic Matter (g kg^{-1})	3.85	5.30
Mehlich-3 K (mg kg^{-1})	138	141
Mehlich-3 Ca (mg kg^{-1})	3940	4478
Mehlich-3 Mg (mg kg^{-1})	547	528
Mehlich-3 Na (mg kg^{-1})	12.2	14.9
CEC (cmol $100g^{-1}$)	27.1	31.2
SO_4-S (mg kg^{-1})	5.1	6.5
K test category‡	Low	Low

† For soil samples taken from the top 15 cm.
‡ Iowa State University interpretation K categories for corn and soybean (Mallarino et al., 2013)

Table 2. Precipitation information.

Year	Precipitation†													
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total	Diff‡
	mm													
2014	4	29	32	121	108	225	73	145	140	95	26	30	1027	126
2015	7	20	6	87	115	175	151	209	128	32	69	137	1138	237
	30-Year Average													
	17	22	50	101	120	128	116	122	84	62	48	31	901	

† Data from the closest climate station and similar for both sites (http://mesonet.agron.iastate.edu/climodat).

‡ Diff, difference from the average annual rainfall across 30 years (1985-2015).

Table 3. Ash chemical properties.

Property	Concentration
Moisture (g kg^{-1})	0.0
P (g kg^{-1})	5.1
K (g kg^{-1})	37
Ca (g kg^{-1})	222
Mg (g kg^{-1})	71
Na (g kg^{-1})	27
Fe (g kg^{-1})	4.0
Mn (g kg^{-1})	0.3
Al (g kg^{-1})	4.2
S (g kg^{-1})	47
Si (g kg^{-1})	1.5
Zn (mg kg^{-1})	114
Cu (mg kg^{-1})	36
Total C (g kg^{-1})	16.3
Total N (g kg^{-1})	0.40
CCE (g kg^{-1}) †	893
ECCE (g kg^{-1}) ‡	698
pH	12.7
Water extractable K(g kg^{-1})	768
Water extractable S (g kg^{-1})	519

† CCE, calcium carbonate equivalent.
‡ ECCE, effective CCE. The ash material passing screen sizes of 4.75, 2.36, and 0.25 mm were 100, 100, and 63.8%, respectively (IDALS, 2008).

Table 4. Nutrient applications rates.

K Trials			S Trials			Lime Trials†		
Potash	Ash	Ash Material	Gypsum	Ash	Ash Material	$CaCO_3$	Ash	Ash Material
--- kg K ha^{-1} ---		kg ha^{-1}	--- kg S ha^{-1} ---		kg ha^{-1}	-- kg ECCE ha^{-1} --		kg ha^{-1}
0	0	0	0	0	0	0	0	0
38	30	958	17	11	233	1121	1430	2048
76	60	1917	34	22	466	2242	2860	4096
114	90	2875	51	33	700	3363	4290	6143
152	120	3833	68	44	933	4484	5720	8191

† ECCE, effective calcium carbonate equivalent

Figures

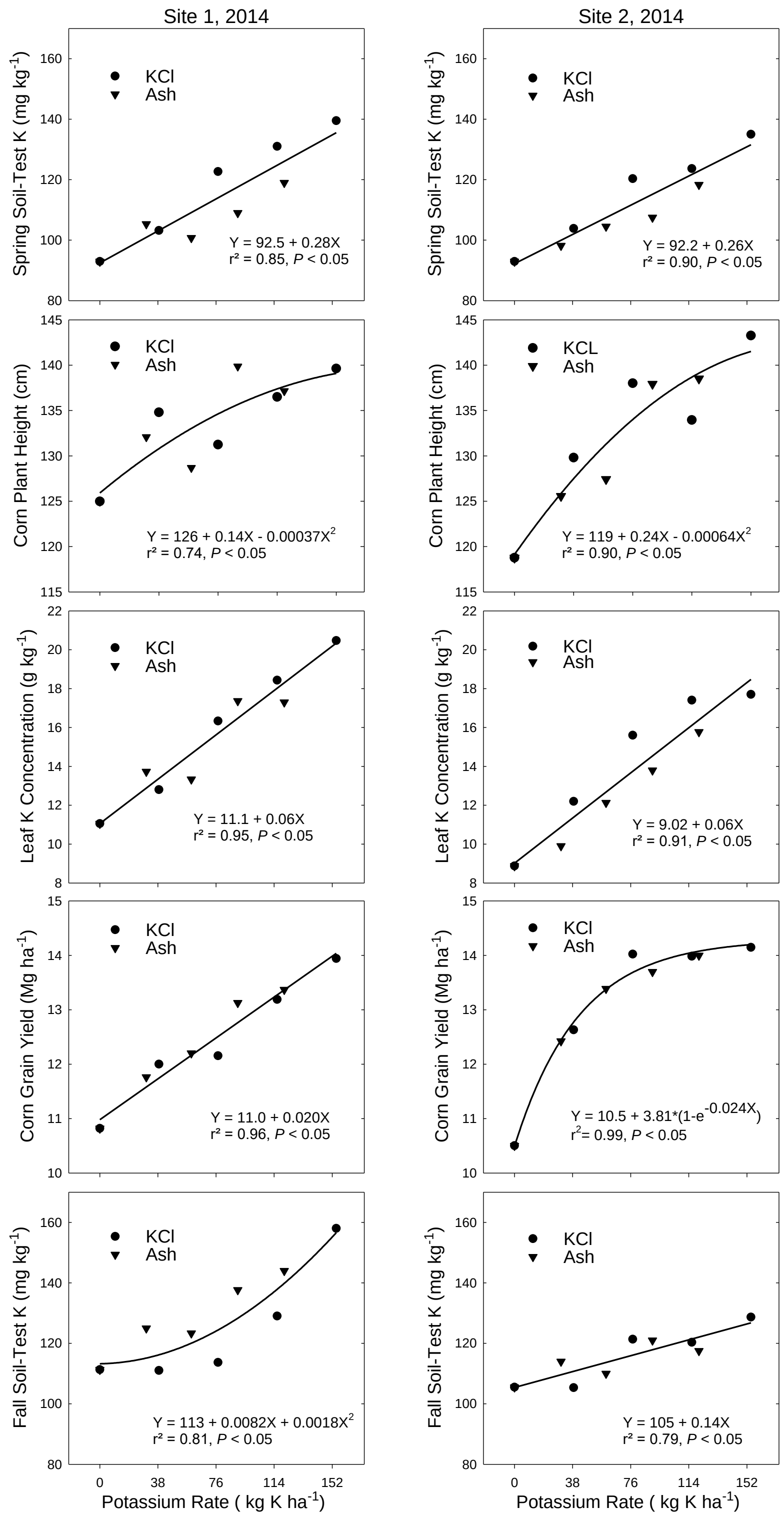

Fig. 1. Effect of K applied with ash or KCl fertilizer on soil and corn measurements in 2014. There was no significant ($P \leq 0.05$) interaction source by application rate for any measurement.

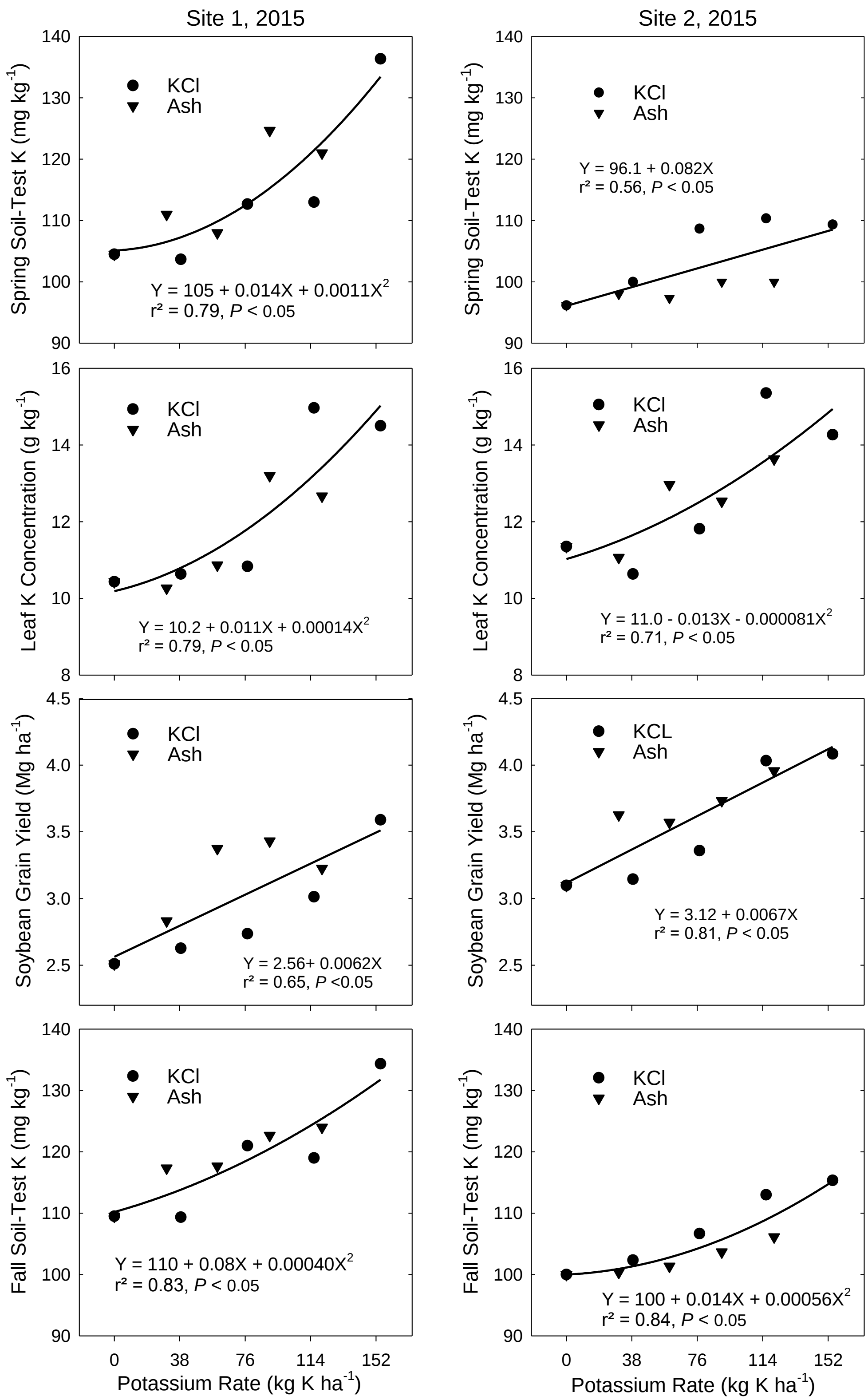

Fig. 2. Residual effect of K applied with ash or KCl fertilizer before the previous year corn crop on soil and soybean measurements in 2015. There was no significant ($P \leq 0.05$) interaction source by application rate for any measurement.

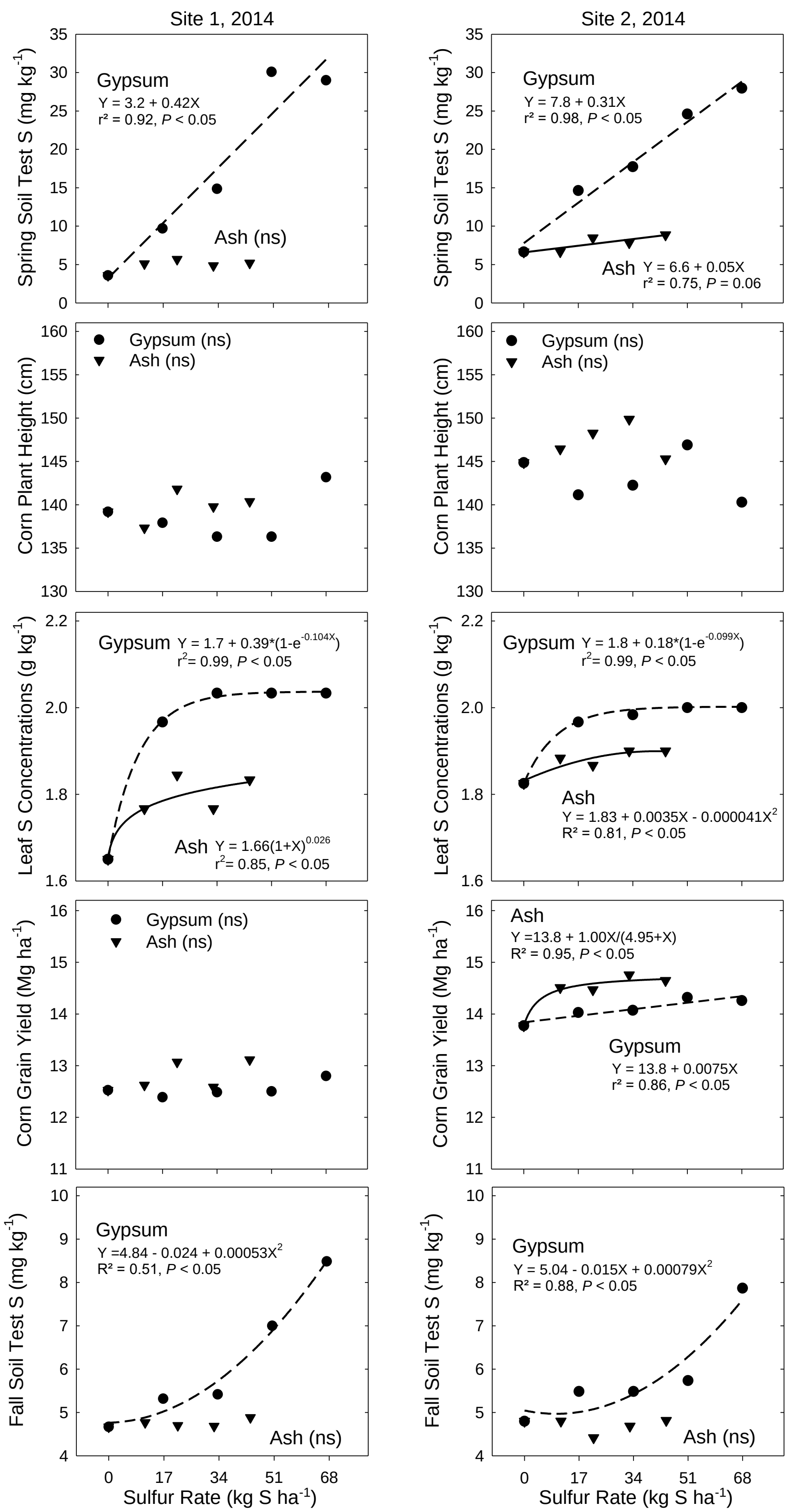

Fig. 3. Effect of S applied with ash or gypsum fertilizer on soil and corn measurements in 2014.

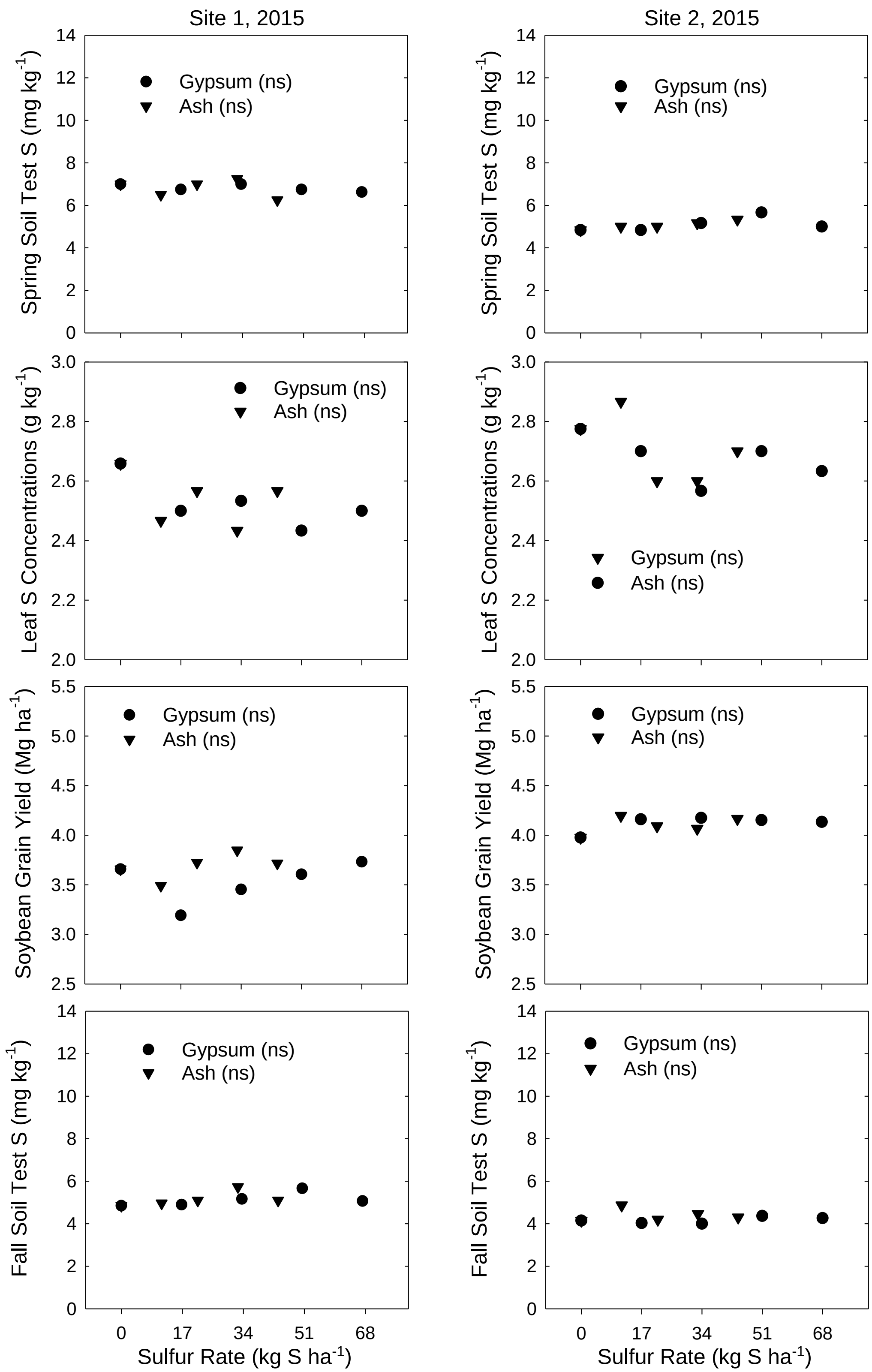

Fig. 4. Residual effect of S applied with ash or gypsum fertilizer before the previous year corn crop on soil and soybean measurements in 2015.

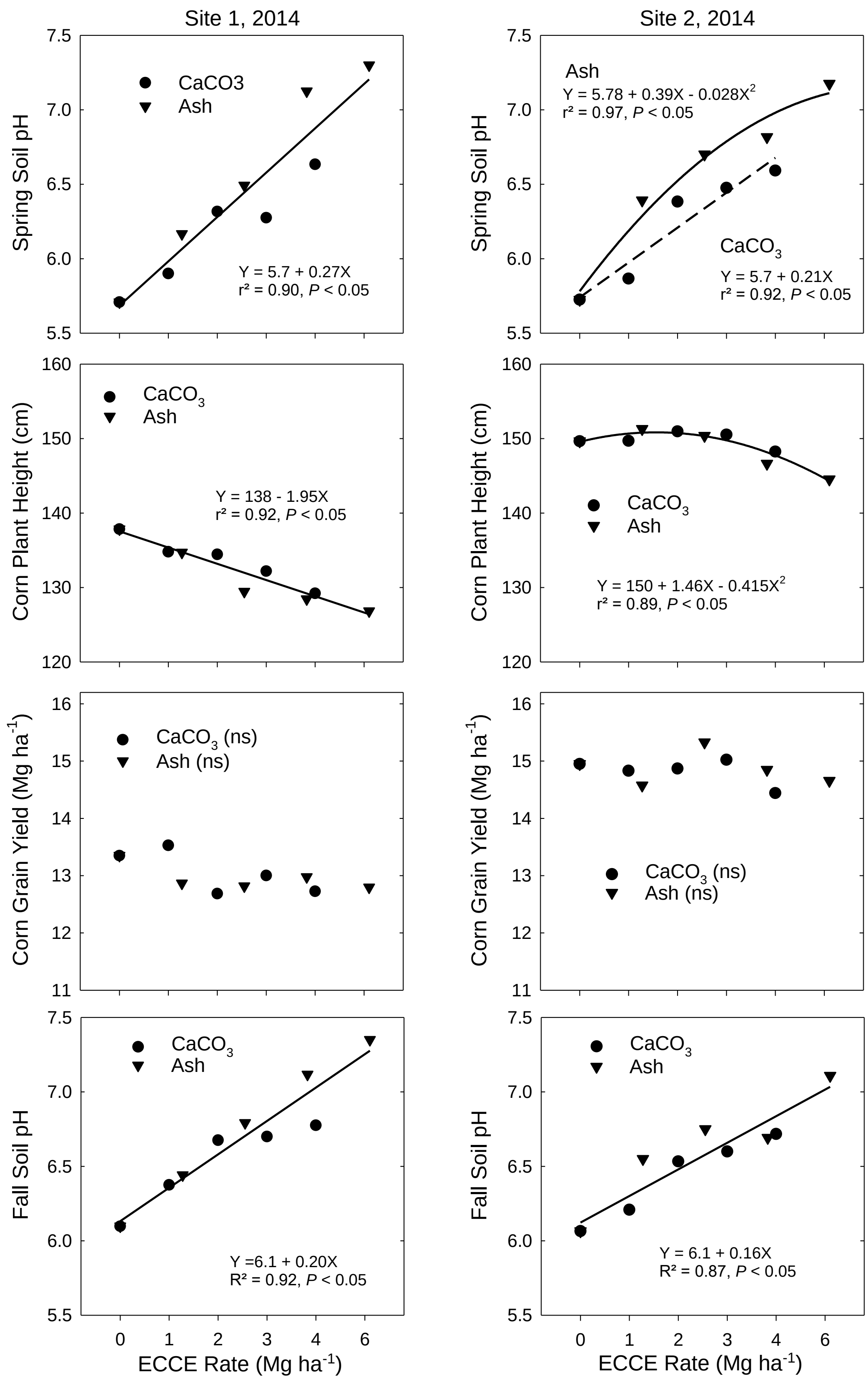

Fig. 5. Effect of ECCE applied with ash or $CaCO_3$ amendment on soil and corn measurements in 2014.

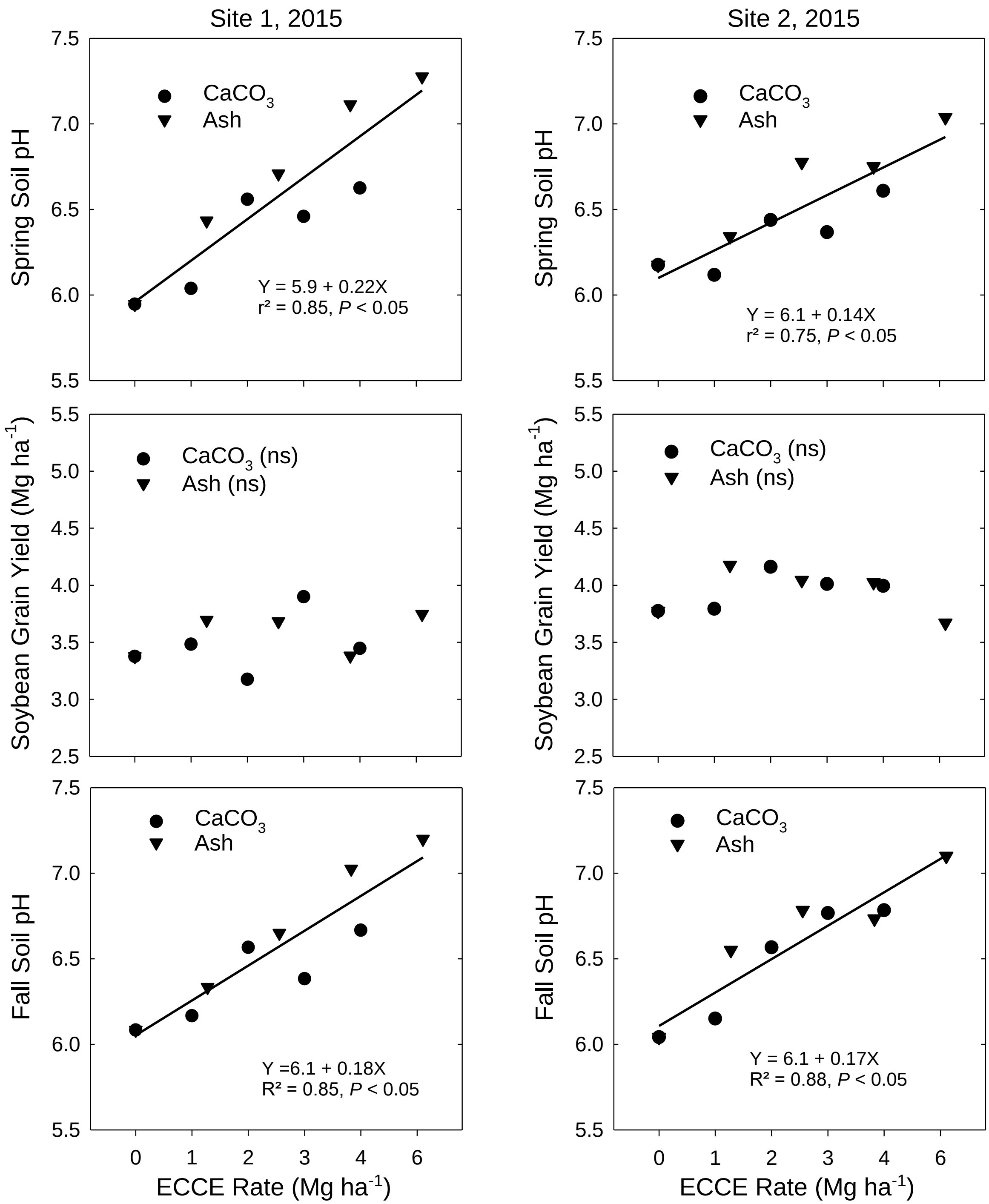

Fig. 6. Residual effect of ECCE applied with ash or $CaCO_3$ amendment before the previous year corn crop on soil and soybean measurements in 2015.

CHAPTER 3. GENERAL CONCLUSIONS

The objective of this research was to study the potassium (K) and sulfur (S) availability and liming effects ash material produced through the combustion of lignin cake from cellulosic ethanol processing had on soil properties and plant growth compared with common industry products of potash fertilizer, gypsum, and pure calcium carbonate, respectively. This objective was achieved by establishing two-year field plot trials with corn-soybean rotations at 2 sites in Boone County in Central Iowa. The sites chosen had two common Central Iowa soils that tested low in soil test K according to Iowa State interpretations (Mallarino et al., 2013). Each site was evaluated for two years where the first year (2014) was to evaluate the immediate effects of the ash and fertilizer and the second year (2015) was to evaluate the residual effects of the same materials applied a year before. Three trials were established at each site to represent the K, S, and lime portions of the objectives. Each trial included several application rates of K, S, or effective calcium carbonate equivalent (ECCE). The composition of the ash sampled at the time of application showed the ash had 3.7% potassium, 4.7% sulfur and a 70% ECCE value. Measurements taken were spring and fall soil test K, S and pH for the K, S and lime trials, respectively, corn plant height (2014 only), leaf K and S concentration for the K and S trials, and grain yield.

Results in 2014 from the K trials at both sites revealed significant increases from K application for spring soil-test K, plant height, ear-leaf concentration, grain yield, and post-harvest soil-test K with no differences between ash and potash fertilizer sources. Second year measurements showed strong residual effects to the application in spring of the previous year. All measurements, except height that was not measured in 2015, were significantly increased with increasing rates of K applied with no significant source differences.

Results in 2014 from the S trials showed significant source differences for spring soil-test S, corn leaf S concentration, and post-harvest soil-test S measurements at both sites and for grain yield only at one site. A significant rate response was observed for gypsum and smaller or no response for the ash, probably due to a lower early crop-availability of ash S. The gypsum was more efficient at increasing soil S and leaf S concentration, at one site the ash was slightly better than gypsum at increasing corn grain yield, but the overall response and the yield difference was very small. No significant residual effects of S applied the first year was observed for any measurement in 2015.

Evaluation of the liming value of ash in the first and second year of the study showed significant soil pH increases for both sources for all sampling dates, and the sources differed only at one sampling date of one site where the ash increased soil pH slightly more than the $CaCO_3$. The higher rates of both sources decreased corn plant height, but no source or application rate affected crop grain yield in any site or year.

Overall, the study showed that ash resulting from the combustion of lignin and mineral residue after distillation of corn residue for ethanol production had liming value comparable to pure calcium carbonate or higher, similar K availability to the commonly used potash fertilizer. The results for S crop-availability were not conclusive mainly because there was little or no grain yield response to S, but soil and tissue test results suggested less early S supply from ash compared with gypsum. More research can be done to improve the understanding of mainly the S and lime value of this ash material.

For now though, as cellulosic ethanol plants become more common around the Midwest and the country, these results will be relevant for the owners of the processing plant and the producers near it to help close the cycle of cellulosic ethanol production by returning mineral nutrients to the soil.

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