

Evaluating Potential Agricultural Use of Industrial Byproducts

by

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Abstract

The large quantity of byproducts produced by the U.S. industry requires environmentally friendly and economical means of disposal. Integration of certain byproducts (e.g., papermill lime mud and calcium silicate slag) into agriculture may provide mutually beneficial solutions to the disposal problem. However, industrial byproducts significantly vary in chemical (e.g., calcium carbonate equivalent and trace contaminants) and physical (e.g., particle size) properties and may not meet the current regulations for liming materials and/or sludge and biosolids. As a result of these factors, several studies were conducted to evaluate beneficial effects and environmental risks of selected industrial byproducts. Soil incubation and rice culture studies were conducted at the Plant Science Research Center at Auburn University, AL, in 2015 and 2016. Eleven ground limestones, 6 papermill byproducts, 2 slags from steel industry (steel slag), and 1 slag from phosphorus fertilizer industry (P slag) were evaluated for their liming ability. The P slag was further analyzed for rates (0, 1000, 2000, and 4000 mg kg⁻¹) and application method (surface application and incorporation) using two typical soils (Sharkey clay and Pahokee muck) for rice/sugarcane production. Results indicated that the relative neutralizing value (RNV) is an adequate indicator of actual liming ability for ground limestones and industrial byproducts, if particle size can be accurately analyzed. Papermill mud is a suitable alternative liming agent. The P slag may also serve as a liming material if the particle size is reduced. Applied P slag increased plant available Si and rice biomass in both soils and Si in plant tissues in the organic soil. Plant available Mn and Mn in plant tissues decreased with

increasing slag rate, possibly due to the liming effect; however, deficiency was not observed. Trace contaminants (e.g., Cd, Cr, and Pb) and radioactivity in soils and rice grain were not affected by P slag application. The P slag increased transpiration and photosynthesis rates, canopy density, soluble sugars (i.e., glucose, fructose, and sucrose), and carbon isotope discrimination ($\Delta^{13}\text{C}$), and decreased proline accumulation of drought-stressed rice leaf. These results suggest that Si in the P slag is available to plant, and trace contaminants are unlikely to cause environmental risks for rice production. The P slag may also provide benefits on mitigating drought stress.

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I. Literature review

Introduction

Industries in the United States produce millions of metric tons of waste that must be either disposed or utilized. For example, paper and pulp mills are estimated to have produced ~5.3 million dry metric tons of solid waste as sludge and boiler ash in 1995, and half of which was produced in the southeastern United States (NCASI, 1999). With expanding industries, safe disposal of these byproducts is becoming a greater challenge. Surveys have shown that an average of 64% of the papermill byproducts are buried in landfills, and only 6% are used for agriculture and silviculture purposes (Morris et al., 2000; Muse and Mitchell, 1995). Stringent environmental regulations, as well as increasing cost from stockpiling wastes and overloading landfills forces industry to seek cost-effective and environmentally friendly means of disposal. Many industrial byproducts, such as calcium silicate slag from phosphate refining and lime mud from paper and pulp processing, have substantial value if used appropriately in agriculture. Utilization of byproducts in agriculture may offer a mutually beneficial solution to the disposal problem. However, concerns associated with certain industrial byproducts, such as highly varied liming ability and potential trace contaminants, may impede their application in agriculture. Analysis of physical and chemical properties of the industrial byproducts before commercial usage is necessary to address those issues.

Conventional liming materials

The principle function of a liming material is to neutralize natural soil acidity. Therefore, materials that have good alkalinity and are economically viable are the most desirable. Ground limestone is the most commonly used liming material, and is generally referred to as “Ag-lime”.

Limestones containing mostly Ca are calcitic (CaCO_3), and those containing both Ca and Mg are dolomitic [$\text{CaMg}(\text{CO}_3)_2$]. The calcium carbonate equivalent (CCE) is used to compare liming materials and represents the acid-neutralizing capacity expressed as a weight percentage of pure CaCO_3 (i.e., calcitic lime). The CCE of dolomitic limestone (109%) is slightly higher than calcitic lime (100%), but the dolomitic lime has a lower solubility and thus dissolves more slowly (Havlin et al., 2014). Ground limestones are usually slow to react, but the liming effect persists for a long time in the soil. Hodge and Lewis (1994) suggested that it often takes agricultural limestones > 4 years after field application to lose their liming effect.

The CCE for pure calcium oxide (a.k.a. burnt lime or quick lime) and calcium hydroxide (a.k.a. slaked lime or hydrated lime) is 178 and 135%, which is higher than calcium carbonate. Calcium oxide and calcium hydroxide also have higher reactivity than ground limestone, due to their higher solubility. However, they are less popular because of their higher cost and greater caustic nature, which makes them more difficult to handle.

Paper and pulp industry byproducts

Background information

The U.S. currently produces roughly 30% of the world's paper and paperboard (US EPA, 2002). The nation's 70% pulp production capacity is concentrated in the Southeast, where 4.7×10^{10} kg pulp is produced each year (USDA, 2000).

The Kraft process, which is used by most pulp and paper mills in the southeastern United States, produces a series of solid wastes. Organic residuals mainly include primary and secondary sludge. Primary sludge is generated when the pulp enters the paper machine. The major component is cellulose fiber. Secondary sludge is a mixture of varied materials that have

gone through some degree of decomposition (Morris et al., 2000). Paper and pulp mills also produce inorganic solids known usually as lime mud, grit, dregs, and green liquor dregs (Muse and Mitchell, 1995; Morris et al., 2000). These by-products are produced during the spent-liquor purification process (Simson et al., 1981). The spent liquor is reacted with $\text{Ca}(\text{OH})_2$ to recover high-cost chemicals, yielding NaOH and CaCO_3 . Since CaCO_3 is sparingly soluble, it precipitates out of the solution and is termed lime mud. After the concentrated black liquor passes the recovery furnace, the remaining is mixed with water and becomes green liquor. Sediments of the green liquor are called green liquor dregs or simply dregs and consist of mainly elemental C and CaCO_3 . Grit is the precipitant from the slaker and is primarily NaOH , CaSO_4 , and SiO_2 (Muse and Mitchell, 1995; Morris et al., 2000). Boiler ash, a mixture of fly ash and bottom ash from the wood-burning furnace, is another important byproduct (Ohno and Erich, 1993; Morris et al., 2000). The paper and pulp industry in the United States generates 4.6×10^9 kg of sludge and 3.3×10^9 kg of ash annually (Lynde-Maas, 1997).

Liming ability

Byproducts from paper and pulp processing have been extensively studied in the United States and Europe in the past a few decades for their liming ability (Simson et al., 1981; Ohno and Erich, 1993; Muse and Mitchell, 1995; Morris et al., 2000; Demeyer et al., 2001; Cabral et al., 2008; Lalande et al., 2009; He et al., 2009; Makela et al., 2012). Papermill byproducts significantly differ in chemical and physical properties depending on the type of raw materials (e.g., woods and fillers) and the processes from which they are made. Several sources of information on composition of papermill residues are available (Muse and Mitchell, 1995; Camberato et al., 1997; Morris et al., 1997). For example, ash samples from 14 paper mills were alkaline with pH ranging from 7.3 to 12.7 and CCE ranging from 13 to 69% (Muse and Mitchell,

1995). The CCE of inorganic residues, particularly lime mud (91 to 109%), approached that of pure CaCO₃ (Camberato et al., 1997). Organic residuals, such as primary and secondary sludge, usually have lower alkalinity (1 to 76% CCE) than inorganic residues (Morris et al., 1997).

Soil incubation studies have shown that papermill byproducts (e.g., ash and lime mud) are highly reactive possibly due to the solubility of oxides and hydroxides (Simson et al., 1981). Soil pH rapidly increases shortly after application (e.g., within 24 h) then decreases within a few weeks. Soil pH remains relatively consistent afterward and is still significantly higher than the untreated control at the end of the incubation (Simson et al., 1981; Muse and Mitchell, 1995; He et al., 2009). In contrast, ground limestones react slowly. Previous research showed that it took a 3-year reaction period for conventional agricultural limestone to reach equilibrium (Love et al., 1960). The liming effect of ground limestone was found to last for >4 yr after field application (Hodge and Lewis, 1994). Field studies found that the duration of liming effect of papermill byproducts was comparable to ground limestone (Simson et al., 1981; Muse and Mitchell, 1995).

Loading rates for papermill byproducts in previous studies were almost solely based on their CCE relative to ground limestone. Overliming due to the rapid rate of reaction of the papermill byproducts could be a potential problem at high loading rates (Simson et al., 1981; He et al., 2009). Quantification of liming ability of a particular papermill byproduct and actual field experiment may be necessary to determine the correct loading rate.

Carbon and nitrogen in organic residuals

Papermill sludges are mostly (~90%) composed of cellulose, hemicellulose, and lignin (Rashid et al., 2006); therefore, decomposition of papermill sludges is similar to other organic materials commonly added to the soil, which can be explained by a two-compartment decay model (Chantigny et al., 2000a, b; Fierro et al., 1999). The initial phase involves decomposition

of cellulose and hemicellulose and is fast. The second slow-decay phase is mostly driven by lignin decomposition. Field studies found that ~51% of the initially applied sludge decomposed within the first 4 mo after application. But after 2 yr, the remaining sludge in the soil still accounted for 43% of its initial mass, indicating that a large proportion of the total carbon in papermill sludges is biologically inert (Fierro et al., 1999). Mean residence time of the recalcitrant carbon was estimated to be 8.5 yr in the soil (Chantigny et al., 1999).

The composition of organic material added to the soil, especially C/N ratio, affects its decomposition. If the C/N ratio exceeds ~25:1, delayed decomposition and induced nitrogen immobilization may occur (Brady and Weil, 2008). Application of primary sludge with a high C/N ratio resulted in a significant decrease in extractable N in a laboratory incubation study (Zibliske, 1987). Shimek et al. (1988) found that growth of several crop plants decreased at C/N ratio >40. Addition of N as mineral fertilizer helped overcome induced N deficiency by sludge application and improved biomass of wheat grass (Fierro et al., 1999) and yield of barley (Simard et al., 1998a) and winter cabbage (Simard et al., 1998b).

Nitrogen contents and the C/N ratio of papermill sludges vary widely. Primary sludges usually contain $\leq 0.3\%$ N by dry weight with a C/N ratio >100:1 (Bellamy et al., 1995). Decreased yield of lupine (Vasconcelos and Labral, 1993) and corn (O'Brien et al., 2003) following application of primary sludges was observed, which was likely due to immobilization of N. Growth suppression dissipated after 10 to 12 mo indicating biodegradation of the applied materials. Secondary and mixed sludges contain partially decomposed organic materials and may have C/N ratio low enough (e.g., <20:1) to serve as a source of plant available N (Morris et al., 2000; Simard, 2001). Crop responses to land-applied secondary sludge and combined sludge have been variable and depend on the application rate, N concentration, and C/N ratio

(Camberato et al., 1997). Land-applied secondary or combined sludge has been found to increase yield and/or N uptake of corn (Bellamy et al., 1995; N'Dayegamiye et al., 2003), winter cabbage (Simard, 2001), alfalfa (Arfaoui et al., 2001), and blueberry (Gagnon et al., 2003).

Plant nutrients and trace contaminants

Besides liming ability, papermill byproducts often contain plant nutrients including N, P, K, Ca and Mg, but the concentrations vary greatly. Nitrogen in organic residuals (3.0 to 19.8 g kg⁻¹) is typically higher than that in inorganic residuals (0.3 to 7.7 g kg⁻¹). Phosphorus is typically <2 g kg⁻¹, which is too low to be used as a fertilizer (Muse and Mitchell, 1995; Camberato et al., 1997; Morris et al., 1997).

Papermill byproducts are usually high in Ca and low in Mg (Muse and Mitchell, 1995; Camberato et al., 1997; Morris et al., 1997). In soils, Ca and Mg compete for binding sites and plant uptake. Over-application of Ca may reduce Mg availability to plants (Simson et al., 1981; Nunes et al., 2008). Acid soils in the southeastern Coastal Plain are typically low in Mg; therefore, analysis of soil and byproduct to be applied is necessary to determine the appropriate loading rate and avoid induced Mg deficiency.

Sodium is universally present in all papermill byproducts (Muse and Mitchell, 1995; Camberato et al., 1997; Morris et al., 1997) and is typically high in concentration (>10 g kg⁻¹). However, Na is not of immediate concern unless exchangeable sodium percentage (ESP) is greater than 15% (U.S. Salinity Laboratory, 1954), which typically results in pH >8 and no need for liming agents. If used, high Ca in the byproducts may eventually replace Na on soil exchangeable sites, allowing Na to be leached from soil and preventing Na accumulation (Muse and Mitchell, 1995; Cabral et al., 2008). Thus, the potential negative effects on soil physical characteristics due to the presence of high Na level is unlikely for Coastal Plain soils.

Concentrations of trace elements, such as As, Fe, Mn, Cr, Cd, and Pb, are low in papermill byproducts (Muse and Mitchell, 1995; Morris et al., 2000), compared to USEPA's Part 503 Rule, which regulates land application of sludge and biosolids (USEPA, 1993). However, it has been criticized that trace elements at levels approaching the EPA limits are potentially harmful to many crops long term (McBrid, 1995). In addition, the total metal concentration is not a good indicator of the bioavailability, mobility, or toxicity of trace elements. These properties are strongly dependent on their chemical speciation in papermill byproducts. Therefore, in order to determine the environmental impact of the papermill byproduct, it is necessary to not only know the total concentrations, but also the distribution of the trace elements in different fractions. Soil environment is continuously changing due to factors such as pH, temperature, redox potential, microbial activity, and leaching, which also affect fate of trace elements in the soil.

Calcium silicate slag

Calcium silicate slag is a generic name that includes slags from iron and steel industry (i.e., steel slag) and from phosphate refining (i.e., P slag) that are primarily calcium silicate. Similar to papermill byproducts, calcium silicate slag may be used as an alternative liming material. The liming effect is caused by free oxides and hydroxides in the slags. Previous studies found calcium silicate slag to be as effective or slightly superior to conventional agricultural limestones in neutralizing soil natural acidity (Rogers, 1948; Carter et al., 1951; Jones and Edwards, 1954; Rodriguez et al., 1994; Oguntoyinbo et al., 1996; Munn, 2005; Makela et al., 2012; Ning et al., 2016). In addition to Ca and Si, calcium silicate slag contains other nutrient elements, such as Mg, Fe, and Mn.

Calcium silicate slag has been widely used as a Si supplement for rice and sugarcane. Previous studies have demonstrated that calcium silicate slag added to organic or mineral soils under rice production: i) increases plant height, plant biomass, and yield (Gascho, 1977; Elawad et al., 1982; Snyder et al., 1986; Anderson et al., 1987); ii) reduces susceptibility to disease and pest (Datnoff et al., 1997; Savant et al., 1997; Ning et al., 2014); and iii) increases Si accumulation in the leaf (Anderson et al., 1987; Kato and Owa, 1997; Ning et al., 2016). In sugarcane, Mg deficiency has occurred with application of slag causing reduced yield, possibly due to an imbalance of soil Ca and Mg resulting from the high ratio of Ca to Mg in the applied slag (Anderson, 1991).

Calcium silicate slag from phosphorus refining (i.e., P slag) usually contains $<10 \text{ g kg}^{-1}$ unrecovered P (Korcak, 1998), which makes it a significant source of P at high loading rates (e.g., 4480 kg ha^{-1} , typical rate used in Florida). There have been concerns over adverse environmental effects from excessive P fertilization. Anderson and Snyder (1992) investigated the fate of P applied from calcium silicate slag. At application rates up to 20 Mg ha^{-1} , P applied in slag was found to be biologically unavailable and unlikely to contaminate surface water. Calcium tends to form insoluble precipitates with P, which lowers P solubility. However, P solubility is specific to the form(s) of P within the slag, as well as the properties of the soil to which it is applied.

Steel slags contain various concentrations of trace elements (e.g., Cr, Cd, and Pb) depending on the type of steel produced and the procedures used. Application of steel slag was found to elevate total concentrations of Cr and V in a forest soil, but Cd, Cu, Pb, Ni, and Zn was not affected (Makela et al., 2012). Additionally, $>80\%$ of the total Cr in the slag was in residual fraction, which is biologically inactive; however, 46% of the total V was bioavailable (Makela et

al., 2012). Another study reported that residual fraction of Cd and Pb accounted for 89.1 and 94.5% of the total concentration in the slag (Ning et al., 2016). Applied steel slag was found to significantly decrease exchangeable Cd in a paddy soil and Cd accumulation in rice grain, possibly due to the liming effect of the steel slag (Ning et al., 2016). Few studies have investigated trace contaminants in the P slag. Mortvedt (1986) determined bioavailability of ^{226}Ra in a P slag containing $\sim 1 \text{ Bq } ^{226}\text{Ra g}^{-1}$, which is a concentration commonly found in P slag. Results indicated that uptake of ^{226}Ra by fescue and wheat into aboveground tissue was not affected by P slag application. These results indicated that land-applied calcium silicate slag may not pose potential risks to the environment or crop production.

Quality of liming materials

The quality of agricultural liming materials is primarily determined by purity and fineness. Purity is expressed as calcium carbonate equivalent (CCE), which represents the total alkalinity of the material. Pure CaCO_3 is the standard against which other liming materials are measured, and its neutralizing value is 100%. Fineness is referred to as particle size distribution, which represents the particles passing through or retained on a specific sieve size. The smaller the particle size, the higher the effectiveness of a given liming material. Crushing limestones to increase the proportion of fine particles also increases the cost of the material. Regulations governing the quality of agricultural limestones are defined at the state level and typically vary from state to state. For example, all agricultural liming materials sold in Alabama should have a minimum CCE of 90%, i.e., $\geq 90\%$ of the particles should pass 10 mesh, and $\geq 50\%$ of the particles should pass 60 mesh screen (Alabama Department of Agriculture and Industries, 1982). While in Virginia, the minimum CCE is 85%, and ≥ 90 , 50, and 30% of the particles should pass 20, 60, and 100 mesh screen, respectively (Mullins et al., 2009). Industrial byproducts

significantly differ in chemical (i.e., CCE) and physical properties (i.e., particle size) and may not be addressed by state lime laws regulating ground limestone.

Relative neutralizing value (RNV), a.k.a. effective neutralizing value (ENV), or effective calcium carbonate equivalent (ECCE), represents percentage of effective materials in liming materials based on their particle size. It is the sum of the percentages of each particle size fractions multiplied by a pre-determined efficiency factor. Each state in the U.S. has adopted their own efficiency factors specified by particles sizes (Table 1). The most widely adopted sieve sizes are 10, 60, and 100 mesh across the U.S. The RNV allows comparison of different ground limestones using standard product information (i.e., CCE and particle size), but this is untested on industrial byproducts. Munn (2005) found that the effectiveness of three different types of slag to raise soil pH was greater than their size efficiency would have predicted, suggesting that particle size distribution of the slag particles was not as good a predictor of overall acid neutralizing effectiveness. Due to the limited information on byproducts, it is worthy of further study to determine whether the RNV is indicative of actual liming ability of industrial byproducts.

Characteristics and bioavailability of trace contaminants in the soil

Cadmium (Cd)

Cadmium is considered as one of the most toxic metals because it exhibits great adverse effects on the environment and the quality of food. Cadmium(II) is dominant in the environment. In soil solutions, it may present as cationic (e.g., CdCl^+ and CdOH^+) and/or anionic species (e.g., CdCl_3^-) with ligands (Kabata-Pendias and Sadurski, 2004). In addition to

inorganic species, Cd also occurs in complexes with various organic acids (e.g., humic acid and fulvic acid) in soil solutions (Welch and Norvell, 1999).

The mobility of soil Cd is significantly correlated to soil pH (Taylor and Percival, 2001). In acidic soils (pH <5.5), adsorption of Cd to soil colloids, hydrous oxides, and organic matter is minimal (Adriano et al., 2005). Under these conditions, 55 to 90% of Cd in soil solution is present as free ions and is readily available to plants (Taylor and Percival, 2001). In alkaline soils, Cd in soil solution precipitates as sparingly soluble CdCO_3 and/or $\text{Cd}_3(\text{PO}_4)_2$ under oxidized conditions (Martin-Garin et al., 2002) and CdS under anaerobic conditions (Christensen and Huang, 1999). Increasing pH also results in increased adsorption of Cd by insoluble organic matter (Kabata-Pendias, 2010). Therefore, bioavailability of Cd decreases with increasing soil pH. Soil organic matter is another important factor in determining availability of Cd. Studies have demonstrated high sorption affinity of organic matter for Cd (Sauve et al., 2003; Ge and Hendershot, 2005). Land use also affects Cd speciation and mobility. The mobility and plant availability of Cd in wetland soils differs from that of upland soils. The uptake of Cd by higher plants is greater under dryer conditions, indicating it is more available to plants under upland conditions (Grambrell, 1994).

Although Cd is not an essential element for metabolic processes of higher plants, it is effectively absorbed by both root and leaf systems. Terrestrial plants tend to accumulate Cd in the roots where it is bound to the cell wall. Sorghum was able to transport more of the adsorbed Cd to the shoots than the other plant species (Kabata-Pendias, 2010; An, 2004). The ability of plants to absorb Cd significantly varies. The difference in Cd content of crops grown in the same soil with 10 mg Cd kg^{-1} exceeded 100-fold. The lowest concentration was in rice plants, Sudan grass, and clover, and the highest was in spinach and turnip (Chaney and Hornick, 1977).

Chromium (Cr)

Naturally occurring Cr compounds have principal valences of +3 (chromic) and +6 (chromate). The two oxidation states of Cr allow the formation of both anionic (e.g., CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$) and cationic species (e.g., Cr^{3+} and CrOH^{2+}), as well as organic complexes, which vary considerably in their solubility and plant availability (Kabata-Pendias and Sadurski, 2004). The speciation of Cr is Eh–pH dependent under most environmental conditions. Chromium(III) is slightly mobile only under very acidic conditions, and it is almost completely precipitated as a hydroxide at pH 5.5. Its compounds are considered to be very stable in soils (Bartlett and Kimble, 1976a). On the other hand, Cr^{6+} is very soluble in soils and is easily mobilized in both acid and alkaline soils (Bartlett and Kimble, 1976b). The speciation and mobility of Cr in soils may be also affected by soil organic matter. Dudka et al. (1993) demonstrated that exchangeable and OM-bound forms of Cr increased by 8 to 52% and 9 to 31% of the total Cr content when organic matter (i.e., sewage sludge) was added to the soil. Chelation of Cr^{3+} ions to organic acids (e.g., humic acid and fulvic acid) increases solubility and mobility (Laborga et al., 2007). Chelation of Cr^{3+} by other organic acids (e.g., citric acid and malic acids) from root exudates can also increase Cr^{3+} solubility and mobility (James and Bartlett, 1983a, b).

Most Cr (>80% of total content) occurs in soils as immobile residual fraction and is slightly available to plants (Kabata-Pendias, 2010). Cr(VI) is more toxic than Cr(III) due to its high solubility and high oxidizing potential (Pawlisz et al., 1997). Higher plants can take up both Cr(III) and Cr(VI), but the mechanism is different. Cr(III) is absorbed by simple passive diffusion at cation exchange sites of the cell wall (Skeffington et al., 1976). Uptake of Cr(VI) is still poorly understood. Zayed et al. (1998) found that sulfur-loving plants in the Brassicaceae family accumulated more chromate compared to other plants (e.g., pea and strawberry) grown in

the same hydroponic solution, suggesting Cr(VI) may be actively taken up via sulfur mechanism. A subsequent study by Kim et al. (2006) found enhanced Cr accumulation by overexpression of sulfate transporter genes in transgenic tobacco (*Nicotiana tabacum* L.), indicating chromate may be taken up by sulfate transporter.

A majority of absorbed Cr is concentrated in roots. Zayed et al. (1998) found total concentrations of Cr were ~100-times higher in root than in shoot. However, Cr³⁺ is the primary form found in plant tissues whether plants were treated with Cr³⁺ or CrO₄²⁻, and intermediate Cr(V) have been detected in suggesting reduction of CrO₄²⁻ to Cr³⁺ occurs in the plant (Howe et al., 2003). Chromate-treated plants accumulated slightly more Cr in plant tissues than Cr³⁺-treated plants (Zayed et al., 1998; Howe et al., 2003).

Lead (Pb)

Lead(II) is the most common and reactive oxidation state of Pb in the environment. It occurs as both cationic species (e.g., Pb²⁺ and PbCl⁺) and anionic species (e.g., PbCl₃⁻) in the soil solution (Kabata-Pendias and Sadurski, 2004). In the soil, Pb is mainly associated with clay minerals, hydrous oxides, and soil organic matter (SOM). Soil organic matter has a strong affinity for Pb and plays a decisive role in Pb mobility in soils. The formation of Pb-OM complexes may increase its availability (Basta et al., 2005). The Fe/Mn hydroxides demonstrate great propensity to fix Pb. The Pb concentration in Fe-Mn nodules could be as high as 20,000 mg kg⁻¹ (Kabata-Pendias, 2010).

Soil pH greatly affects solubility of Pb. Martinez and Motto (2000) showed increased solubility of Pb with decreasing soil pH. At high soil pH (pH >6), Pb precipitates as hydroxides or with phosphates or carbonates, and thus has a low bioavailability.

A majority of Pb in the soils is difficult to phytoextract. Davies (1995) reported that only about 0.005 to 0.13% of Pb in the soil solution is available to plants. Uptake of Pb by plants depends on soil properties particularly pH and SOM content. Zimdahl (1976) suggested Pb is passively absorbed by plants. Some plants, such as corn and sunflower, can accumulate more Pb (Huang and Cunningham, 1996). When Pb is taken up by plants, it is concentrated in root tissues and the translocation to above-ground parts is greatly limited. Zimdahl (1976) reported that only 3% of the Pb in roots is translocated to shoots. Guillen et al. (2009) suggested that the radioactive isotope of Pb (i.e., ^{210}Pb) is taken up by the same pathway as stable isotopes of Pb.

Atmospheric deposition is also a major source of Pb in the environment. Dusts and vapors of Pb can enter the atmosphere from natural and anthropogenic sources. It has been calculated that up to 95% of the total Pb content of plants may be from aerial deposition on leafy plants (Dalenberg and van Driel, 1990).

Polonium (Po)

Seven Po isotopes occur naturally, but only ^{210}Po with the half-life of 138.4 d is relatively ubiquitous in the environment. The ^{210}Po in soils originates either as a product of the radioactive decay of ^{238}U present in the soil or the result of deposition from the atmosphere as a decay product of ^{222}Rn (Persson and Holm, 2011). The dominant oxidation states of Po in the environment are +2 and +4. In aqueous solution, Po(II) is slowly oxidized to Po(IV). Polonium and its compounds (e.g., PoH_2 and PoCl_2) are highly volatile (Housecroft and Sharpe, 2012).

In the soil, Po is almost irreversibly sorbed on metal hydroxides and/or sulfides and is very immobile; however, sorption is pH dependent with stronger sorption in neutral and alkaline soils and weaker sorption in strongly acid soils (Kabata-Pendias, 2010). The Po content of soil

also varies with soil type. Organic soils have been reported to contain more Po than mineral soils, because Po tends to be bound by SOM (Birsen and Kadyrzhanov, 2002).

The natural abundance of ^{210}Po in terrestrial plants ranges from 8 to 12 Bq kg⁻¹ (Bowen, 1979). Cereals and legumes have generally low transfer factors compared to the other crops. A transfer factor is the concentration of radionuclide in the plant divided by its concentration in the soil. The average TF for Po is 5.6×10^{-3} , suggesting very low bioaccumulation of ^{210}Po from the soil (Vandenhove et al., 2008). Most of the natural radioactivity content in wild leafy plants is ^{210}Po resulting from the direct deposition of decayed ^{222}Rn from atmospheric deposition (Hill, 1960). Relatively widespread use of radioactive phosphate fertilizers may be increasing levels of radioactive Po in plants (Kabata-Pendias, 2010). Greater accumulation of Po in tobacco relative to other plants has been reported, possibly due to its large leaf area, which is better able to capture atmospheric deposition (Moore et al., 1976; Shacklette et al., 1978).

Radium (Ra)

Radium is a naturally occurring metal and is ubiquitous in all environments. The most stable isotope is ^{226}Ra . It exists mainly as divalent cation in soils, and has similar geochemistry to Ca^{2+} . Radium can also form complexes (e.g., RaOH^+ and RaCl^+) in soil solutions (Kabata-Pendias, 2010). Clay minerals, Fe/Mn hydroxides, and SOM have great affinity for Ra and significantly decrease its exchangeable fraction, particularly at neutral and alkaline pH (Greeman et al., 1999). Acid soils increase its bioavailability. When Ra from slags and sludges are mixed with acidic soils, the mobility of Ra complexed with soil is enhanced compared to its mobility in just the slag or sludge. During a 2-wk incubation study with an acidic moist top soil, >20% of the Ra present in the slag was solubilized (Frissel and Koster, 1990; Swann et al., 2004). Soil microorganisms may also affect Ra mobility. Under anaerobic conditions, sulfate-reducing

bacteria were found to rapidly dissolve RaSO_4 in a land-applied sludge and enhance Ra mobility (Pardue and Guo, 1998).

Radium is relatively easily taken up by plants, mainly through the root system, and is also easily translocated to the shoots (Gunn and Mistry, 2005). The ^{226}Ra concentration in crop plants is highly variable. Uchida and Tagami (2007) calculated the soil-to-crop TF of ^{226}Ra in 21 crops and vegetables (e.g., wheat, barley, cabbage, lettuce, etc.). The TFs ranged from $<1.1 \times 10^{-3}$ to 5.8×10^{-2} , with the lowest value for potato and the highest for green leek. Plant availability and plant uptake of Ra is also influenced by Ca, since Ra and Ca have similar geochemistry (Gerzabek et al., 1998).

Thorium (Th) and Uranium (U)

Thorium and uranium are two most abundant actinides in the terrestrial environment, and their distribution and bioavailability has received much attention. The mobility of Th and U in soils may be limited due to both the formation of slightly soluble precipitates (e.g., phosphates, oxides) and sorption on clays, hydrous oxides (e.g., goethite), and SOM (Greeman et al., 1990). A sequential extraction study found that $>80\%$ of total Th in soils was distributed in the residual fraction, whereas 11% was bound to organic matter and only 0.1% was associated with the exchangeable fraction, indicating bioavailability of Th in soils is low (Blanco et al., 2004).

The two important oxidation states of uranium are U(IV) and U(VI). The U(IV) is insoluble under oxidizing conditions, and is an important species (i.e., UO_2) only in reduced soils. Ionic speciation of U(VI) is highly dependent on pH. In acidic soils, sorption of U(VI) is weak and cationic species such as UO_2^{2+} are dominant (Allard et al., 1982). As pH increases, hydroxyl complexes of U(VI), such as $(\text{UO}_2)_2(\text{OH})_2^{2+}$, become more important. Once the carbonate concentration in the soil solution becomes significant, the carbonate complexes of

U(VI) become dominant when $\text{pH} > 6$. Uranium(VI) can also form complexes with sulfate and phosphate ions, such as $\text{UO}_2(\text{SO}_4)^{2-}$ and UO_2PO_4^- . These complex ions tend to increase the solubility of uranium in the environment (Pulford, 2010). Mobility of U(VI) is also affected by SOM. Shcherbina et al. (2007) found that humic derivatives could reduce actinides in the presence of Fe hydroxides and thus decrease their mobility. The sorption and co-precipitation of U(VI) by calcium carbonate, as well as reduction to U(IV), controls U mobility in the terrestrial environment and is of great environmental importance.

Yoshida and Muramatsu (1997) suggested that both Th and U in soils were only slightly available to plants. The calculated TF is < 0.01 for Th (Garten, 1978; Torstenfelt, 1986) and 0.05 for U (Haneklaus and Schnug, 2005), indicating very low bioaccumulation of Th and U in plants from soil. Effects of the U and Th treatments on plant growth are variable and depend on different plants species and elements. Wheat exposed to U concentrations of up to 6 mg kg^{-1} showed increased yield compared to untreated control, but similar concentrations applied to tomato resulted a reduction in yield (Gulati et al., 1980). Applied Th in the growth medium has been found to decrease Ca in wheat seedlings (Shtangeeva et al., 2005). Increases of U in the nutrient solution (up to $1000 \mu\text{mol L}^{-1}$) may cause oxidative stress and cellular redox imbalance in plants (Vandenhove et al., 2006). Overall, Th and U do not tend to have significant detrimental effect on plants due to their low bioavailability.

Silicon nutrition of higher plants

Background information

Silicon comprises $\sim 28\%$ of the earth's crust and is the second most abundant element in soil after oxygen (Singer and Munns, 1999). The prevailing and plant-available form of Si over

the physiological range of soil pH is monosilicic acid (H_4SiO_4) with a solubility of $\sim 0.2 \text{ g L}^{-1}$ in water. The average Si concentration in the soil solution ranges 14 to 20 Si mg L^{-1} (Epstein, 1999), which is >100 -times higher than the average concentration of P in the soil solution (0.05 mg P L^{-1} ; Havlin et al., 2014). Once absorbed, Si is mainly deposited in the cell wall as amorphous silica (Currie and Perry, 2007).

All terrestrial plants contain some Si in their tissues. However, plant species differ considerably in their ability to accumulate Si in plant tissues, ranging from 1 to 100 g Si kg^{-1} on a dry weight basis (Epstein, 1999; Ma and Takahashi, 2002). In general, monocots have higher levels of Si accumulation (10 to 15%) compared to dicots ($\leq 0.5\%$). Members of the Gramineae (e.g., rice) and Cyperaceae (e.g., sedge) families are particularly high in Si accumulation ($>4\%$ Si, Hudson et al., 2005). Different parts of the same plant can also demonstrate great difference in Si accumulation. For example, Si concentration was found to be 0.5 g kg^{-1} in polished rice, 50 g kg^{-1} in rice bran, 130 g kg^{-1} in rice straw, 230 g kg^{-1} in rice hulls, and 350 g kg^{-1} in rice joints (Van Hoest, 2006).

Mechanisms of Si uptake

Differences in Si accumulation among species have been ascribed to differences in ability of roots to take up Si as well as different mechanisms of Si being loaded into the xylem (Ma and Yamaji, 2006, 2008). Three different mechanisms for Si absorption by higher plants have been proposed, including active (faster/higher Si uptake than water), passive (similar to water uptake), and rejective (slower/lower Si uptake than water) uptake, which vary based on plant species (Takahashi et al., 1990). Mitani and Ma (2005) investigated uptake of Si in rice, cucumber, and tomato, which differ greatly in their shoot Si concentrations. The root cell symplast was found to have a higher Si concentration than the external solution in all species; however, the

concentration in rice was 3- and 5-times higher than in cucumber and tomato, respectively. A further kinetic study showed that the radial transport of Si from the external solution to root cortical cells was mediated by a transporter with the same K_m (0.15 mmol L^{-1}) for all the species, but the V_{max} values were different in the order of rice > cucumber > tomato. In addition, Si uptake by all the three plants could be decreased by low temperature and a metabolic inhibitor (e.g., 2,4-dinitrophenol), suggesting that both active uptake and passive diffusion are involved in Si absorption (Mitani and Ma, 2005). Xylem loading was also compared among rice, tomato, and cucumber. The Si concentration of xylem sap in rice was 20- and 100-times higher than that in cucumber and tomato, respectively, indicating active transport in rice, but passive diffusion in cucumber and tomato. Results suggested that xylem loading plays a decisive role in accumulation of Si in rice shoot (Mitani and Ma, 2005).

Recently, transporters involved in Si uptake from the external solution to root cortical cells (Lsi1 and Lsi2) were identified in rice (Ma et al., 2006). Another transport, Lsi6, is expressed in leaf sheath and leaf blades and is responsible for xylem loading (Yamaji and Ma, 2009).

Role of Si in metabolism and its essentiality for higher plants

Although ubiquitously present in both soils and plants, most plant physiologists do not consider Si as an ‘essential’ mineral nutrient for higher plants, except for the members of the Equisetaceae family (Epstein 1994). This is partly because persuasive evidence that Si meets the universally adopted definition of essentiality for higher plants proposed by Arnon and Stout (1930) is still lacking. Visual symptoms, such as necrosis on mature leaves, wilting of plants, and reduced vegetative growth and grain production, have been documented in Si-deficient paddy rice (Lewin and Reimann, 1969). These deficiency symptoms suggest, but not prove, that

Si is essential for rice, because failure to complete the life cycle was not observed. A recently-modified definition of nutrient essentiality for higher plants was proposed by Epstein and Bloom (2005). Based on this new definition, an element is essential if it fulfills either one or both of the two following criteria: i) the element is part of a molecule that is an intrinsic component of the structure or metabolism of the plant, and ii) the plant can be so severely deficient in the element that it exhibits abnormalities in growth, development or reproduction, i.e., “performance”, compared to plants with milder deficiency. Since Si deficiency causes various abnormalities in a wide variety of plant species (Ma and Takahashi, 2002; Ma and Yamaji, 2006), Si is considered a “quasi-essential” nutrient for higher plants.

It is almost impossible to purify nutrient solution cultures to be completely free of Si. Even highly-purified water contains 2×10^{-5} mmol Si L⁻¹ (Werner and Roth, 1983). Consequently, plants grown in conventional nutrient solutions always contain some Si in their leaves, which may lead to erratic results in experiments designed to investigate Si nutrition (Epstein, 1994, 1999). A few studies have used germanic acid, a specific inhibitor of Si uptake, to investigate role of Si in metabolism. In the absence of Si, the proportion of lignin in wheat root cell walls decreased, but the phenolic compounds increased (Jones et al., 1978). Parry and Kelso (1975) suggested that Si influences the concentration and metabolism of polyphenols in xylem cell walls indicating that Si may play a role in lignin biosynthesis and cell wall structure.

Beneficial effects of Si

Supplementation with Si has demonstrated a number of beneficial effects on growth in many plant species, which include improvement of leaf exposure to light (Ma and Takahashi, 2002), resistance to lodging (Idris et al., 1975), decreased susceptibility to pathogens and pests (Datnoff et al., 1997; Savant et al., 1997), and amelioration of abiotic stresses such as P

deficiency (Roy et al., 1971; Ma and Takahashi, 1990a, 1990b, 1991), drought (Gong et al., 2003; Gong et al., 2005; Hattori et al., 2005; Kaya et al., 2006; Crusciol et al., 2009; Gunes et al., 2008; Chen et al., 2011), and metal toxicity (Wu et al., 2013). This review will focus on Si-mediated resistance to disease and pest, alleviation of drought stress, and metal toxicity with particular emphasis in rice.

Resistance to disease and pest

Numerous studies have shown that supplemental Si could effectively reduce plant susceptibility to disease caused by both fungi and bacteria in many plant species. Silicon was found to reduce severity of sheath blight, brown spot, leaf blast, leaf scald, and stem rot in rice; powdery mildew in cucumber, barley, and wheat; ring spot in sugarcane; rust in cowpea; leaf spot in Bermuda grass; and gray leaf spot in St. Augustine grass and perennial ryegrass (Fauteux et al., 2005; Rodrigues et al., 2015). Silicon also suppresses insect pests such as stem borer, mites, leaf spiders, and various hoppers (Savant et al., 1997).

Two mechanisms have been proposed for Si-induced resistance to diseases and pests. Absorbed Si deposits beneath the cuticle and forms as a Si-cuticle double layer (Ma and Yamaji, 2006). Over the years, it has been assumed that this layer, as well as polymerized Si in the cell wall, acts as a physical barrier and blocks penetration of fungi and bacteria, thereby inhibiting the infection. However, no evidence has ever directly linked cell wall reinforcement with penetration failure by the fungus. Fauteux et al. (2005) argued this theory may not be sufficient to explain the observed protective effect.

Recent evidence indicates that soluble Si might be able to trigger the natural defense mechanisms of the plant. This was first reported in cucumber. Plants that received additional Si had enhanced activity of chitinases, peroxidases, and polyphenol oxidases as well as increased

concentration of flavonoid phytoalexins, all of which may protect against fungal pathogens (Cherif et al., 1994; Fawe et al., 1998). Wheat (Belanger et al., 2003) and rice (Rodrigues et al., 2003) are also able to produce similar antimicrobial chemicals such as glycosylated phenolics and diterpenoid phytoalexins in Si-treated plants. Kauss et al. (2003) found elevated production and accumulation of proline-rich proteins at the site of the attempted penetration by fungi into epidermal cells in cucumber plants, which may help improve polymerization of Si in the cell wall and thus impede the infection. These biochemical responses were induced only by soluble Si, suggesting that soluble Si plays an active role in enhancing host resistance to diseases (Fauteux et al., 2005). A model proposed by Fawe et al. (2001) suggested that soluble Si may serve as activator/secondary messenger of systemic acquired resistance (SAR) and may regulate the activity of post-elicitation intracellular signaling systems. To date, pathways of Si-induced pathogen defense is still largely unclear.

Si-induced mitigation of metal toxicity

Silicon has been well documented to alleviate phytotoxicity of metals, including Mn, Fe, Al, Cd, Cr, Pb, Cu and Zn, among which the possible roles of Si in enhancing tolerance to Mn and Al have been extensively investigated. In general, two types of mechanisms (i.e., external and internal) have been proposed to explain how Si regulates plant resistance and/or tolerance to metal toxicity.

Manganese (Mn) and iron (Fe)

Manganese and Fe are plant essential micronutrients, but they can be toxic at high concentrations. Manganese and Fe toxicity occurs frequently in highly reduced soils (i.e., submerged soil) or in highly weathered acidic soils of tropical and subtropical areas. Silicon has

been reported to reduce Mn toxicity in many plant species, such as rice (Okuda and Takahashi, 1962; Li et al., 2012), barley (Williams and Vlamis, 1957; Horiguchi and Morita 1987), maize (Doncheva et al., 2009), wheat (Vlamis and Williams, 1967), sugarcane (Fox et al., 1967), and cucumber (Shi et al., 2005; Feng et al., 2009).

In rice, many mechanisms have been proposed. Okuda and Takahashi (1962) suggested that Si might enhance the oxidation power of rice roots by facilitating O₂ transport from shoot to root, and reduce solubility and availability of Mn in rhizosphere. Horiguchi (1988) reported that in addition to Si-decreased Mn uptake, Si also decreased peroxidase activity and thus necrotic spots in Mn-stressed rice seedlings, indicating Si increased internal tolerance to excessive Mn in plant tissues. Recently, Si was found to increase Mn in the roots of a Mn-sensitive rice cultivar but decrease Mn in both shoot and root of a Mn-tolerance rice cultivar (Li et al., 2012). Che et al. (2016) suggested that Si-induced Mn mitigation may be attributed to down regulation of Mn transporter gene and decreased Mn transport from root to shoot presumably by forming Mn-Si complex in root cells.

Different mechanisms have been proposed for other plant species. In barley and common bean, Mn uptake was not affected, but Mn was more uniformly distributed in the leaf blade. The mechanism for this homogeneous distribution is still unclear, but may be attributed to decreased apoplastic Mn resulting from Si-enhanced binding capacity of the cell wall (Horst et al., 1999). In cucumber and pumpkin, alleviation of Mn toxicity by Si may also be related to triggering antioxidative defense systems of the plant against cell damage (Iwasaki et al., 2002; Shi et al., 2005; Feng et al., 2009).

Silicon has also been reported to significantly mitigate Fe toxicity symptoms in rice (Okuda and Takahashi, 1965; Fu et al., 2012; Dufey et al., 2014). Decreased Fe uptake in the

root with the addition of Si has been reported, but the avoidance mechanism is still unclear (Fu et al., 2012; Dufey et al., 2014). Similar to Si-induced alleviation of Mn toxicity, increased root oxidation power may partially contribute to reduced Fe uptake (Okuda and Takahashi, 1965).

Aluminum (Al)

Aluminum is a major constituent of most mineral soils. While Al may show beneficial effects on certain plant species (e.g., tea plant), it is generally considered a major constraint for plant growth especially in acid soils (e.g., southeastern Coastal Plain soils in the United States). Mitigation of Al toxicity by supplemental Si has been observed in sorghum (Li et al., 1996), barley (Liang et al., 2001; Morikawa and Saigusa, 2002), maize (Ma et al., 1997; Kidd et al., 2001), rice (Rahman et al., 1998; Singh et al., 2011), and wheat (Cocker et al., 1998b).

Excessive Al severely inhibits root growth and nutrient uptake and limits crop production. Supplemental Si has been reported to reduce Al toxicity by reinstating root growth, but this beneficial effect is dependent on genotype and timing of Si application (Kidd et al., 2001; Wang et al., 2004; Zhang et al., 2009). In maize, enhanced root elongation with Si treatment was significant only for the Al-sensitive variety (Kidd et al., 2001). Alleviation of Al-induced inhibition of root elongation in maize was not observed when Si was applied as a pretreatment (Wang et al., 2004). However, Zhang et al. (2009) found that both Si pretreatment and continuous Si supply significantly reduced the inhibitory effect of Al on root elongation for all 5 varieties of *Stylosanthes*.

Both internal and external mechanisms for Si-induced alleviation of Al toxicity have been proposed. Ma et al. (1997) found that toxic Al^{3+} concentrations in hydroponic nutrient solution were decreased by the addition of silicic acid, suggesting an interaction between Si and Al occurs due to the formation of non-toxic hydroxyaluminosilicate complexes in the solution. Other

studies indicated that Si-induced plant detoxification, such as co-deposition of Al with Si within the plant may also contribute to reducing Al toxicity. Silicon has been found to stimulate exudation of organic acids, particularly malate. These organic acids may chelate Al and reduce its activity and toxicity (Cocker et al., 1998a, b).

Cadmium (Cd)

In the past decades, numerous studies have demonstrated that Si can significantly mitigate Cd toxicity symptoms and improve the growth of higher plants (Liang et al., 2005; Song et al., 2009; Nwugo and Huerta, 2008, 2011; Feng et al., 2010; Rizwan et al., 2012; Shi et al., 2010). Silicon and Cd interactions are genotype dependent. Song et al. (2009) found that the alleviative effect of Si on plant growth was more significant in the Cd-tolerant cultivar than in the Cd-sensitive cultivar.

Many reports have attributed Si-mediated alleviation of Cd stress to the improvement in photosynthesis (Nwugo and Huerta, 2008, 2011; Feng et al., 2010). Nwugo and Huerta (2008, 2011) suggested that Si may reduce Cd toxicity to components of photosystem II (PSII) by regulating key proteins related to photosynthesis process. In addition, Feng et al. (2010) reported that exogenous Si could effectively relieve Cd-induced damage to photosynthesis by preventing chloroplast swelling, protecting thylakoids and chloroplast membrane, and increasing pigment contents. Stimulation of the antioxidant defense system by Si has also been reported (Song et al., 2009; Shi et al., 2010; Farooq et al., 2016). Under Cd stress, added Si increased activities of superoxide dismutase (SOD), peroxidase (POD), and /or catalase (CAT) in cabbage (Song et al., 2009) and peanut (Shi et al., 2010). Farooq et al. (2016) found that with additional Si, genes encoding members of the stress-associated protein (SAP) family (e.g., phytochelatin synthase 1) was down-regulated in rice.

Chromium (Cr) and lead (Pb)

Recently, Si has been reported to be effective in mitigating Cr toxicity in rice (Zeng et al., 2011; Tripathi et al., 2012), barley (Ali et al., 2013) and cabbage (Zhang et al., 2013), and Pb toxicity in banana (Li et al., 2012) and cotton (Bharwana et al., 2013). Mechanisms have not been extensively studied. Supplemental Si has been suggested to inhibit uptake and translocation of Cr and Pb, improve photosynthesis, and enhance enzymatic antioxidant activities and thereby mitigating Cr and Pb toxicity (Ali et al., 2013; Bharwana et al., 2013).

Si-induced drought alleviation

Drought is considered the single most devastating abiotic stress limiting plant growth and productivity, especially in arid and semiarid areas, which occupies approximately 30% of the world land surface. Current climate models have predicted increased severity and frequency of drought in several regions around the world under the ongoing global climate change scenarios (IPCC 2007; Walter et al., 2011). With the progressing growth of the world population, it is urgent to increase the drought tolerance of crops to maintain adequate food supplies. Silicon has exhibited the ability to reduce the impact of drought stress. Recent progress has been made in the understanding of mechanisms for Si-mediated drought stress at the physiological and biochemical levels.

Transpiration and photosynthesis

Under drought stress, the water potential and water content of plants are substantially decreased. The addition of Si can improve the water status of plants under drought stress (Farooq et al., 2009). Gong et al. (2008) found that the application of Si increased the leaf water potential in wheat under drought stress in the field. Similar results were also obtained in wheat

(Pei et al., 2010) and sorghum (Liu et al., 2014) under water-deficit stress induced by polyethylene glycol (PEG) in hydroponic nutrient solutions.

Supplemental Si can also decrease transpiration rate of drought-stressed plants (Agarie et al., 1998; Ma et al., 2001; Gao et al., 2006). Because leaves of wheat seedlings under drought stress were thicker as a result of Si addition, it was suggested that the formation of a silica-cuticle double layer on leaf epidermal tissue might contribute to the reduction in leaf transpiration (Gong et al., 2003). However, supplemental Si has also been reported to increase transpiration rate in rice (Chen et al., 2011), sorghum (Hattori et al., 2005, 2007, 2008), and wheat (Gong et al., 2005, 2008) under water-deficient conditions. These contradictory results in the effect of Si on transpiration rate were attributed to differences in Si accumulation among plant species and the proportion of cuticular transpiration to total transpiration (Liang et al., 2015). Growth conditions (i.e., hydroponics and soil culture) may also contribute to the differences in transpiration (Hattori et al., 2008).

Both stomatal (i.e., stomatal closure) and non-stomatal (i.e., decreased capacity of C fixation by chloroplast) limitations contribute to inhibited photosynthesis under drought stress (Yordanov et al., 2000). Gong et al. (2005) observed that drought stress depressed the wheat photosynthetic rate, but Si application reinstated it to a normal rate. Since intercellular CO₂ was not different between water-sufficient and drought-stressed plants, stomatal limitations do not explain inhibited photosynthesis. Similar results were observed in drought-stressed sorghum (Hattori et al., 2005). In rice, Chen et al. (2011) suggested that both stomatal and non-stomatal factors were involved in Si-mediated improvement of photosynthesis of drought-stressed plants. Gong and Chen (2012) reported a diurnal pattern of photosynthetic gas exchange in wheat. Non-stomatal factors were the main contributor to reducing drought stress early in the morning (i.e.,

before 0930 h), while stomatal closure was the main contributor to differences for most of the day.

Chlorophyll is responsible for light capture and plays a key role in photosynthesis. Addition of Si was found to maintain or increase the level of chlorophyll in pepper (Lobato et al., 2009), rice (Chen et al., 2011) and sorghum (Yin et al., 2014). Chlorophyll fluorescence is indicative of efficiency of photosynthesis. Chen et al. (2011) found that added Si increased both basal quantum yield and maximum quantum efficiency of photosystem II (PSII) of rice plants subjected to drought stress. Results suggest that Si application could alleviate photosynthetic apparatus damage under stress and increase the photosynthetic efficiency.

Nutrient uptake

The improvement of plant growth by the application of Si under drought stress may be related to nutrient uptake and transport in addition to improvements in transpiration and photosynthesis. Nutrient uptake by roots and transport to shoots is limited by water deficiency, and Si may help maintain the balance of uptake and transport of mineral nutrients in drought-stressed plants.

Potassium plays an important role in osmotic adjustments, and Ca serves as a second messenger and is related to the expression of osmotic stress responsive genes (Zhu, 2002). Supplemental Si has been reported to increase the concentrations and/or total accumulation of Ca and K in the leaves of water-stressed maize (Kaya et al., 2006), wheat (Pei et al., 2010), and rice (Chen et al., 2011). This increase may be attributed to the decreased permeability and increased H⁺-ATP activity of the plasma membrane by added Si (Kaya et al., 2006; Liang et al., 2015).

Previous studies reported inconsistent results over Si-mediated N and P uptake under drought stress. Added Si was found to decrease P uptake in maize (Gao et al., 2004), but

increased P uptake was observed in wheat (Gong and Chen, 2012) and forage grasses (Eneji et al., 2008). In rice, Deren (1997) observed decreased N concentrations in all plant parts with Si application. However, Detmann et al. (2012) reported that Si could increase N use efficiency (NUE). This issue is worthy of further investigation.

Improved root traits due to applied Si may help improve water and nutrient accessibility under drought stress. Increased biomass and anatomical traits of root (e.g., length and volume) with exogenous Si was observed in rice (Chen et al., 2011) and sorghum (Hattori et al., 2005), but not in wheat or sunflower (Gong et al., 2003; Gunes et al., 2008; Pei et al., 2010). These inconsistent results may be explained by the differences in culture conditions and the plant species/cultivars used. However, the mechanisms of Si-enhanced root growth are poorly understood.

Osmotic regulators

Osmotic adjustment plays an important role in water uptake under water-deficit conditions. Compatible solutes, such as proline, a non-protein amino acid, and sugars, act as osmotic regulators and tend to accumulate in leaf when plants are subjected to drought stress (Greenway and Munns, 1980). It has been suggested that active accumulation of soluble sugars and amino acids (i.e., alanine and glutamic acid) was responsible for the osmotic adjustment in Si-treated plants under drought stress (Sonobe et al., 2011; Ming et al., 2012).

Inconsistent results have been reported with proline accumulation. Crusciol et al. (2009) found that added Si increased proline in drought-stressed potato leaves; however, the opposite result was reported by Pei et al. (2010) in sorghum. de-Lacerda et al. (2003) argued that the increase in proline level was an injury symptom rather than an indication of stress tolerance. Yin et al. (2014) observed that Si significantly decreased proline levels but increased sugar levels in

drought-stressed sorghum, whereas Crusciol et al. (2009) reported contrasting results in potato. These results may be attributed to differences in water deficit responses and uptake and function of Si among plant species, as well as specific environmental conditions of these studies.

Carbon isotope discrimination ($\Delta^{13}C$)

Water use efficiency (WUE) can be defined as the ratio of dry matter accumulation per unit time to amount of water transpired (transpiration efficiency) or as the ratio of photosynthesis to transpiration (instantaneous WUE, Moghaddam et al., 2013). Direct measurement of long-term WUE is extremely laborious. Carbon isotope discrimination has been proposed as a method for evaluating WUE (Farquhar et al., 1989).

There are two naturally occurring stable isotopes of carbon, ^{12}C and ^{13}C . A relatively small fraction of the CO_2 in the atmosphere is composed of the stable C isotope ^{13}C (~1.1%) with ~98.9% being ^{12}C . The isotopic ratio of ^{13}C to ^{12}C in plant tissue is less than that in the atmosphere, indicating that plants discriminate against ^{13}C during photosynthesis. The bias for ^{12}C occurs because the key enzyme in photosynthesis, ribulose-1,5-bisphosphate carboxylase (Rubisco) actively discriminates against ^{13}C due to the intrinsically lower reactivity of this heavier isotope (Farquhar and Sharkey, 1982). Furthermore, there is a diffusional discrimination against $^{13}CO_2$ across the stomatal pore. The discrimination is larger for C3 plants than C4 plants because of the CO_2 concentrating effect of the bundle sheath cells in C4 plants, which enhances fixation of ^{13}C .

Regardless of the method of carbon fixation, assimilation of CO_2 depends on the ratio of the intercellular (C_i) to atmospheric (C_a) CO_2 concentration (C_i/C_a), which is linked to stomatal conductance (Farquhar et al., 1982). Decreased stomatal conductance results in decreased C_i and concentration of ^{13}C in the intercellular spaces relative to ^{12}C . This concentrating effect causes

Rubisco to fix an increased proportion of ^{13}C relative to ^{12}C (Farquhar et al., 1982) similar in concept to observed differences between C3 and C4 plants.

The ratio of ^{13}C and ^{12}C in samples is typically expressed with respect to a standard reference material, PeeDee Belemnite (PDB), and noted as $\delta^{13}\text{C}$ (Eq. 1).

$$\delta^{13}\text{C}(\text{‰}) = \left[\frac{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{sample}}}{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{standard}}} - 1 \right] \times 1000 \quad [1]$$

In contrast to $\delta^{13}\text{C}$, carbon isotope discrimination ($\Delta^{13}\text{C}$) is defined as Eq. 2:

$$\Delta^{13}\text{C}(\text{‰}) = \frac{\delta_a - \delta_p}{1 + \delta_p} \times 1000 \quad [2]$$

where δ_a and δ_p are the $\delta^{13}\text{C}$ values of atmospheric CO_2 and plant, respectively. Thus, the $\Delta^{13}\text{C}$ better reflects the relationship between air and plant than $\delta^{13}\text{C}$ in a specific environment. While both $\delta^{13}\text{C}$ and $\Delta^{13}\text{C}$ both correlate with WUE, $\Delta^{13}\text{C}$ is more specific to the particular growing conditions.

There is a negative relationship between WUE and $\Delta^{13}\text{C}$. Plants subjected to drought stress have lower $\Delta^{13}\text{C}$ due to decreased stomatal conductance (Farquhar et al., 1989). The correlation between WUE and $\Delta^{13}\text{C}$ has been extensively studied in many crops, especially C3 crops such as wheat (Farquhar and Richards, 1984; Condon et al., 1990), peanut (Hubick et al., 1986; Wright et al., 1994), cowpea (Ismail and Hall, 1993), and rice (Impa et al., 2005). However, few studies have investigated the effect of Si on drought tolerance using $\Delta^{13}\text{C}$.

Summary

Industrial byproducts require environmentally friendly and economically viable means of disposal. Integration of certain byproducts into agricultural usage offers a mutually beneficial solution for the disposal problem. Some papermill byproducts and calcium silicate slags have

substantial liming ability and may be used as alternative liming materials in areas without readily available sources of ground limestones. However, byproducts vary considerably in their chemical and physical characteristics and may not meet the minimal quality requirement for ground limestones. Relative neutralizing value (RNV) reflects the proportion of effective materials in a potential liming agent according to particle size, and allows cross comparison of qualities of ground limestones. However, use of RNV is untested for industrial byproducts.

Calcium silicate slag from phosphate refining is not only a potential liming material, but also good source of Si. Silicon is a quasi-essential nutrient for higher plants and has shown numerous beneficial effects for plant growth (e.g., alleviation of metal toxicity and drought stress), particularly in rice. However, solubility and bioavailability of trace contaminants in this particular slag have not been determined. In addition, few studies have evaluated calcium silicate slag as a source of Si with rice for drought stress mitigation.

In order to address these issues, studies were conducted to i) evaluate liming potential of locally available industrial byproducts and to determine whether relative neutralizing value is indicative of actual liming ability of industrial byproducts; ii) evaluate effect of calcium silicate slag on bioavailability of Si and uptake of trace elements in rice production; and iii) evaluate effect of calcium silicate slag on drought stress in rice production.

Table 1.1. Efficiency factors for agricultural limestone in the United States

States in the U.S.	Particle size ---mesh---	Efficiency factor
AL	10-60	0.5
	<60	1.0
IA	4-8	0.1
	8-60	0.3
	<60	0.6
WV	20-60	0.5
	<60	1.0
MO	8-40	0.25
	40-60	0.6
	<60	1.0
NE	>8	0.1
	8-60	0.4
	<60	1.0
WA	10-60	0.3
	60-100	0.9
	<100	1.0
KY, MS	10-50	0.5
	<50	1.0
MA, PA, VA	20-60	0.4
	60-100	0.8
	<100	1.0
IN, KS, MI, NC	8-60	0.5
	<60	1.0
MN, OH, TX, WI	8-20	0.2
	20-60	0.6
	<60	1.0

II. Evaluation of soil liming materials

Abstract

Acid soils in the southeastern Coastal Plain require ground limestone or another type of liming material to reduce acidity. High-quality limestone deposits for agricultural purposes are limited in this region. Some industrial byproducts (e.g., papermill sludge and steel slag) are potential alternative liming materials, but their neutralizing ability is highly variable and may not be adequately addressed by state lime laws regulating ground limestone. Relative neutralizing value (RNV) represents the percentage of effective constituent in liming materials based on particle size and total alkalinity. The objective of this study was to evaluate the liming potential of 9 industrial byproducts and 11 ground agricultural limestones to determine if RNV is indicative of the actual neutralizing ability. The moisture content, ash, total C and N, total elements, total alkalinity expressed as calcium carbonate equivalent (CCE), and particle size were analyzed for each product. Three acid soils in Alabama were collected for an incubation study. The amount of each product needed to bring soil pH to 6.5 (recommended rate) was calculated according to soil pH titration curves and RNV of each product and according to the modified Adams-Evans buffer method typically used in the region. Each product was mixed thoroughly with soil at 0, 50, 100, and 200% recommended rates and incubated for 6 wk in a greenhouse. During the incubation study, soil pH initially increased within the 7 d and remained fairly stable afterward. The wide range in properties of the liming materials resulted in various abilities to raise pH. Acidity in the soils was underestimated by the titration curve method bringing soil pH to 6.5 only when applied at twice the recommended rate. The RNV was a good estimate of actual liming ability of most liming materials with accurate particle size analysis (i.e.,

wet sieving). Of the byproducts evaluated, lime mud from the papermill industry was the most effective alternative liming agent because of its high CCE and fine particle size. The P slag would also be a good liming agent if particle size can be reduced. Other byproducts have factors that will likely prohibit their use as liming materials.

Key words

Acid soil; Liming material; Relative neutralizing value; Papermill byproduct; Calcium silicate slag

Introduction

Moderate natural acidity in soils in the southeastern Coastal Plain is one of the major factors limiting crop production in this region. Liming materials are required to neutralize natural soil acidity and improve soil productivity. Ground limestones are the most commonly and widely used liming agents. Although the southeastern Coastal Plain is abundant in high-quality calcitic and dolomitic limestone deposits, only a limited proportion of these deposits are used for agricultural purposes. Half a million metric tons of ground limestone are used on agricultural fields in Alabama each year. However, soil tests suggested that 3.8 million metric tons are needed annually for all Alabama crops and forages (Mitchell and Bryant, 2003). In addition, it is costly to deliver ground limestone to areas that are remote from the limestone quarries and logistics centers (e.g., the southwestern region of Alabama).

Industries in the United States produce a large quantity of byproducts each year that require environmentally friendly and economical means of disposal. Some industrial byproducts, such as paper mill sludge and calcium silicate slag, may have substantial alkalinity and may be used as alternative liming materials in soils. Byproducts from paper and pulp

processing industries (e.g., sludge, ash, and lime mud) have been extensively studied for their liming potential in the past a few decades in the United States and Europe (Simson et al., 1981; Ohno and Erich, 1993; Muse and Mitchell, 1995; Morris et al., 2000; Demeyer et al., 2001; Cabral et al., 2008; Lalande et al., 2009; He et al., 2009; Makela et al., 2012). Papermill byproducts usually react with soil rapidly, but the liming effect typically has a shorter longevity relative to ground limestones (Simson et al., 1981; Muse and Mitchell, 1995; He et al., 2009). Calcium silicate slag is usually defined as a byproduct from the iron and steel industry or the phosphate fertilizer industry. Previous studies found calcium silicate slags to be as effective or slightly superior to typical agricultural limestones in neutralizing soil natural acidity (Rogers, 1948; Carter et al., 1951; Jones and Edwards, 1954; Rodriguez et al., 1994; Munn, 2005). Due to the presence of highly reactive oxides and hydroxides in those byproducts, over liming may occur at high loading rates (Ohno and Erich, 1993; He et al., 2009; National Slag Association, 2013).

The quality of an agricultural liming material is primarily determined by purity and fineness. Purity is expressed as calcium carbonate equivalent (CCE), which represents the total alkalinity of the material. Fineness refers to particle size. Different states in the United States have their own regulations on quality of ground limestones. For example, all agricultural liming materials sold in Alabama should have a minimum CCE of 90%, and ≥ 90 and $\geq 50\%$ of the particles should pass 10 mesh and 60 mesh screen, respectively (Alabama Department of Agriculture and Industries, 1982). While in Virginia, the minimum CCE is 85%, and ≥ 90 , 50, and 30% of the particles should pass 20, 60, and 100 mesh screen, respectively (Mullins et al., 2009). Industrial byproducts differ in chemical and physical properties due to the raw materials (e.g., woods and fillers) and the processes from which they are made (Muse and Mitchell, 1995;

Morris et al., 2000; Munn, 2005). However, state lime laws regulating ground limestone do not address these differences. Relative neutralizing value (RNV), a.k.a. effective neutralizing value (ENV) or effective calcium carbonate equivalent (ECCE), is a calculation that uses CCE and particle size to represent the effectiveness of a liming material. It was developed to compare different ground limestones using standard product information but is untested on industrial byproducts. Munn (2005) found that three different types of steel slag were more effective in raising soil pH than their size efficiency would have predicted, suggesting that RNV of the slag is not as good a predictor of overall acid neutralizing effectiveness. Therefore, objectives of this study were to evaluate the liming ability of locally available industrial byproducts and to evaluate whether the RNV could serve as a reliable indicator of the neutralizing ability of all types of liming materials.

Materials and Methods

Twenty materials, including 5 calcitic limestones, 6 dolomitic limestones, 6 papermill byproducts, 2 slags from steel industry, and 1 slag from the phosphorus fertilizer industry, were collected and evaluated for their liming ability in this study (Table 2.1). Some of the limestone samples were obtained from commercial sources. For example, Lime 5 is marketed by Tri-State Lime LLC from Georgia, and Lime 9 and 10 are products of Austinville Lime Co. from Virginia. Other products were obtained from lime quarries and industries for research purpose only. Materials were first analyzed for moisture gravimetrically. A subsample (25 g) of each product was weighed, dried in an oven at 105°C for 24 h, and weighed again to determine moisture content. Oven-dried samples were used for the following analyses. A 1 g subsample was weighed into a 50 mL beaker, covered with a watch glass, heated in a muffle furnace at 450°C for 24 h, and weighed again. The material remaining in the beaker represents the minerals (i.e.,

ash) in the sample. Samples were then ground using a mortar and pestle, sieved to pass a 2-mm screen, and microwave digested using a Mars Xpress microwave (CEM Corp., Matthews, NC) using EPA-3051 procedure (US EPA, 1994) prior to total element determination by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Spectro Ciros CCD, side on plasma, SPECTRO Analytical Instruments Inc., Kleve, Germany). Total carbon and nitrogen in each material was analyzed by Auburn University Soil Testing Lab using a vario Macro CHNS Element Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). Each material was also analyzed for particle size (10, 60, 100, and 200 mesh) and calcium carbonate equivalent (CCE) using Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC) 924.02 and 955.01B, respectively (AOAC, 1990). Four analytical replications were used for all the above-mentioned analyses.

Relative neutralizing value (RNV) of each product was calculated using Eq. 1 based on standard screen sizes currently used in Alabama:

$$\text{RNV} = [(\% \text{ between 10 and 60 mesh}) \times 0.5] + (\% \text{ passed 60 mesh}) \times \text{CCE} \quad [1]$$

Particles between 10 and 60 mesh are considered 50% effective and are thus multiplied by 0.5; particles < 60 mesh are considered 100% effective (Adams, 1959; Barber, 1984).

Three acid soils (0-15 cm depth) were collected: i) Marvyn loamy sand (Fine-loamy, siliceous, thermic Typic Kanhapludults) from Auburn, AL, ii) Benndale fine sandy loam (Coarse-loamy, siliceous, thermic Typic Paleudults) from Brewton, AL, and iii) Lucedale loam from Prattville, AL (fine-loamy, siliceous, thermic Rhodic Paleudults). All soils came from unlimed treatments in long-term soil fertility experiments that have been in continuous production since 1911 (Marvyn series) or 1929 (Benndale and Lucedale series). After plant

residuals were removed, soils were dried at 65°C for 48 h in an oven and ground using a pulverizer to pass a 2-mm screen.

The lime requirement of each soil was evaluated using a pH titration curve. A subsample (10 g) of each soil was weighed and titrated with standardized 0.01 M Ca(OH)₂ solution to establish a pH titration curve (Fig. 2.1). This curve was used to estimate total amount of Ca(OH)₂ necessary to achieve a target soil pH of 6.5, which was defined as the recommended rate of Ca(OH)₂ to be added. The RNV of reagent grade Ca(OH)₂ is assumed to be 135%, and the recommended rate for each liming material and each soil was calculated based on the RNV relative to it (Table 2.2).

In addition, the lime requirement of each soil was determined using the modified Adams-Evans buffer method (Huluka, 2005), which is the typical lime requirement method used in Coastal Plain soils. The modified Adams-Evans buffer method is suitable for weakly buffered acid soils with pH ≥ 4.4. Briefly, 10 g soil was mixed with 10 mL deionized water, and pH was measured (initial pH). Then 10 mL modified Adams-Evans buffer solution was added to the mixture and intermittently stirred for 10 min. The pH was measured again after 30 min (buffer pH). In this approach, acid saturation of the soil was obtained by solving Eq. 2 (Huluka, 2005) at both the initial pH (H_{sat1}) and desired pH (H_{sat2}).

$$\text{Soil pH} = 7.79 - 5.55H_{\text{sat}} + 2.27H_{\text{sat}}^2 \quad [2]$$

The lime requirement was then calculated using Eq. 3 (Huluka, 2005),

$$\text{CaCO}_3 (\text{kg ha}^{-1}) = \frac{8000 \times (8 - \text{buffer pH})}{H_{\text{sat1}}} \times (H_{\text{sat1}} - H_{\text{sat2}}) \times 2.24 \times 1.5 \quad [3]$$

where 2.24 is a factor converting mg kg⁻¹ to kg ha⁻¹ and 1.5 is a correction factor based on the premise that agricultural limestone is not completely effective in neutralizing soil acidity (i.e., requires 150% of prescribed amount). Because the initial soil pH of the Marvyn loamy sand (pH

3.9) was below the minimum applicable pH for this test, the lime requirement for this soil was calculated assuming the initial pH was 4.4.

An incubation study was replicated twice in 2015 at the Plant Science and Research Center (32.59° N, 85.48° W) at Auburn University, AL, using three selected acid soils and 20 liming materials. Each material was incorporated into soils at 0, 50, 100, and 200% recommended rate based on the titration curves. The soil and liming material were mixed well in plastic bags and incubated for 42 d. Soil moisture was maintained at field capacity daily with supplied tap water using gravimetric method. Soil samples were taken at 1, 2, 3, 4, 5, 7, 14, 21, 28, 35, and 42 d after initiation of the experiment. Collected soil samples were dried at 65°C for 48 h, ground using a mortar and pestle to pass a 2-mm screen. Soil pH was determined using a 1:2 ratio (w/v) of soil and deionized water (Hue and Evans, 1986). The change of soil pH over the 42-d incubation study was plotted for each soil.

The percent effectiveness of the RNV for each liming material was calculated based on the final soil pH at 42-d incubation using reagent grade Ca(OH)_2 as a reference standard:

$$\text{Effectiveness (\%)} = \frac{\text{Soil pH of each liming material}}{\text{Soil pH of Ca(OH)}_2} \times 100 \quad [4]$$

Values equal to 100 indicate that the calculated RNV was a perfect match for predicting the effectiveness of that material. Values >100 and <100 indicate that the material was more or less effective than predicted.

Results and Discussion

Product Characterization

Moisture, Ash, and Total Carbon and Nitrogen

The percent moisture contents in all evaluated ground limestones were <5%, except for lime 8 (7.2%, Table 2.3). Moisture is generally a minor concern in ground limestones because they do not tend to hold water. A 4 to 5% moisture content in ground limestones has been found to improve spreading uniformity by reducing the dust of fine (<100 mesh) particles (Alley et al., 1980). This is not the case with many of the byproducts. The byproducts, particularly the papermill sludges, were considerably higher in moisture content (22.5 to 208%) relative to ground limestones (Table 1.3). High moisture content reduces the effectiveness of liming materials on a weight basis and results in more shipping and handling difficulties compared to typical dry agricultural liming materials. This problem may be resolved with improved sludge dewatering technology (Chen et al., 2002; Yin et al., 2004).

The percent ash content represents the proportion of minerals in the liming materials. Ash content in most ground limestones ranged from 95 to 99%, except lime 6 (88.6%) and lime 9 (81.6%). The slags had comparable ash content to ground limestones. The primary sludge and paper sludge were very low in ash content (14 and 45%, respectively), which was expected because these two papermill byproducts are mostly composed of wood and cellulose fibers (Table 2.3).

The composition of organic material added to the soil affects its decomposition. If the C/N ratio exceeds ~25, delayed decomposition and induced nitrogen deficiency (i.e., immobilization) for plants uptake may occur (Brady and Weil, 2008). Therefore, total C and N

analysis was especially important for papermill byproducts due to their organic nature. Among all the evaluated liming materials, only the primary sludge showed a >25 C/N ratio (Table 2.3). This could be a concern for this byproduct, if it is land applied. Additional N fertilizer may be needed to ensure adequate N supply.

Elemental Analysis

The ash, lime mud, steel slags, and P slag contain Ca in amounts comparable to ground limestones (~200 to 400 g kg⁻¹), whereas Ca content in the K-lime, primary sludge, secondary sludge, and paper sludge was lower. Except for secondary sludge and paper sludge, all the byproducts contain some Mg, and the steel slags contained levels near that of some dolomitic lime materials (Table 2.4). In soils, Ca and Mg compete for binding sites and plant uptake. Over-application of Ca may reduce Mg availability to plants (Simson et al., 1981; Nunes et al., 2008). Many of the acid soils in the southeastern Coastal Plain are often low in Mg concentration; therefore, analysis of the soil and the actual liming material being applied will be required to determine the correct lime loading rate and Mg fertilization recommendation to prevent Mg deficiency.

Concerns have been raised regarding adverse environmental effects of excessive P fertilization. Of the byproducts tested, the P slag contained the highest concentrations of P (7.1 g P kg⁻¹; Table 2.4), which is a significant source of P at high soil loading rates. However, bioavailability of P in this slag is still unknown. The fate of P applied from a similar product has been studied in the Everglades Agricultural Area (EAA) in Florida. At application rates of up to 20 Mg ha⁻¹, P applied in the slag was found to be biologically inactive and not likely to contaminate drainage waters (Anderson and Snyder, 1992).

Concentrations of Fe and Al in the steel slags were higher than other products due to the processes from which they are produced. The Al concentration in the papermill byproducts also tended to be higher than the ground limestones, possibly because of the presence of soil in the samples, as Al is the main components of mineral soils. Manganese was especially high in K-lime, ash, secondary sludge, and the two steel slags (Table 2.4). However, this is of little concern from an agronomic standpoint, because availability of Fe, Al, and Mn is highly pH dependent. At high soil pH (i.e., pH >5.5), Fe, Al, and Mn tend to precipitate as oxides and/or hydroxides and thus become less available to plants.

The K concentration in the byproducts was generally low, except for the K-lime, which was 12 times higher than the next highest byproduct (16.7 g K kg⁻¹). The K-lime, ash, lime mud, and P slag contain higher levels of Na than other products (Table 2.4). However, Na is not of immediate concern unless exchangeable sodium percentage (ESP) is greater than 15% (U.S. Salinity Laboratory, 1954). Soils that may approach or exceed this ESP value are generally alkaline and liming materials would not be needed. High Ca in the byproducts may eventually replace Na on soil exchangeable sites, allowing Na to be leached from soil and preventing Na accumulation (Muse and Mitchell, 1995; Cabral et al., 2008). Thus, potential negative effects on soil physical characteristics due to the presence of high Na level are unlikely.

Trace elements, including Cd, Cr, Cu, Ni, Pb, and Zn were present in some ground limestones and industrial byproducts. Concentrations of Cd, Cr, Cu, Pb, and Zn were well below the ceiling concentration for sludge and biosolids applied to land in US EPA's Part 503 Rule (Table 2.5, US EPA, 1993). However, if applied at the recommended rate, loading rates of Zn in lime 9, lime 11, K-lime, ash, and secondary sludge, and loading rates of Cr in the steel slags would exceed the maximum limit per year (Table 2.5). The concentration of Ni in the steel slags

(433 mg Ni kg⁻¹) also exceeded the ceiling concentration (420 mg Ni kg⁻¹), which might preclude their further usage in agriculture.

Calcium Carbonate Equivalent (CCE), Particle Size, and Relative Neutralizing Value (RNV)

The evaluated ground limestones had a CCE that ranged from 79.3% for lime 11 to 107% for lime 9. lime 9 also had the highest RNV of 95.3% because of its fine texture. In contrast, the RNV for lime 10 was the lowest among evaluated ground limestones (43.7%), due to the coarse texture of this pelletized lime (Table 2.6).

The CCE, particle size, and RNV highly varied among the evaluated byproducts (Table 2.6). The lowest CCE was observed for the three different types of papermill sludges (12.5 to 36.9%). Due to the presence of wood and cellulose fibers in those sludges, they were coarse-textured and consequently had low RNV (0.1 to 8.6%). The lime mud had the highest CCE (102%) and the finest particle size among all the evaluated byproducts, thus its RNV was 100.1%. The ash had comparable RNV to ground limestones. Total alkalinity of the two steel slags (CCE ≥ 90%) exceeded the state requirements for ground limestones, but the calculated RNV was only 46 and 39% because of their large particle size. The P slag had a moderate CCE (58%), but the particle size needs to be reduced to improve its effectiveness (Table 2.6).

Incubation Study

Control and Ground Limestone Treatments

Initial soil pH for Benndale fine sandy loam, Marvyn loamy sand, and Lucedale loam was 5.3, 3.9, and 5.4, respectively. During the 42-day incubation study, the pH of the untreated control tended to increase slightly in the Marvyn loamy sand (Fig. 2.3A), and remained relatively consistent in Benndale fine sandy loam and Lucedale loam (Fig. 2.2A and 2.4A).

Due to the extremely low total alkalinity and large particle size, the primary sludge was not evaluated in the incubation study. The calcitic and dolomitic limestones performed similarly and thus data presented are averages of these two types of materials. All the liming materials and rates tended to increase pH of the three acid soils. For most liming materials, the pH rapidly increased within the first 14 d and remained relatively stable afterward (Fig. 2.2 to 2.10). This rapid reaction may be attributed to the low buffer capacity of the Coastal Plain soils, proper incorporation of the liming materials, and adequate daily water supply during this incubation study. A similarly fast reaction may not occur under field conditions due to the less than ideal mixing and moisture conditions that are likely to occur.

Paper Industry Byproducts

The paper sludge showed the best performance on increasing soil pH among all the evaluated liming materials. Soil pH was elevated to ≥ 6.5 by the paper sludge even at 50% recommended rate, and the trend was consistent among the three acid soils (Fig. 2.2B, 2.3B, and 2.4B). Since the waste fibers in the paper sludge have a large particle size, the calculated RNV was very low, resulting in a high recommended rate for this byproduct. However, the lime that coats the fibers was very fine-textured and has high alkalinity. Erratic particle size analysis significantly underestimated its actual liming ability and caused the over liming effect.

The ash and lime mud demonstrated comparable liming ability to ground limestones. The secondary sludge tended to be more effective than the ash and lime mud, whereas the K-lime showed consistently inferior performance than the other papermill byproducts (Fig. 2.2 to 2.10).

Steel and Phosphorus Industry Byproducts

The two steel slags had similar liming ability and tended to be more effective than the P slag. Soil pH amended with the P slag gradually increased and may continue to increase beyond the 42-d incubation study, possibly due to its large particle size and slow dissolution.

Lime Rate Evaluation

When applied at 50% recommended rate, $\text{Ca}(\text{OH})_2$, ground limestones, and most of the byproducts slightly increased soil pH relative to untreated control, which was expected as added liming materials were not sufficient enough to neutralize the natural acidity (Fig. 2.2B, 2.3B, and 2.4B). However, none of the evaluated liming materials, except for the paper sludge, raised pH of the three acid soils to the target of 6.5 when applied at the recommended rate based on the soil titration curves (Fig. 2.5, 2.6, and 2.7). The 200% recommended rate came closer to the target pH than the recommended rate (Fig. 2.8, 2.9, and 2.10). In order to more fully evaluate the correct lime rate, lime requirements were evaluated using the modified Adams-Evans buffer method (Huluka, 2005). This buffer method recommended 38, 77, and 162% more $\text{Ca}(\text{OH})_2$ than the titration curve method for a target pH of 6.5 in the Benndale fine sandy loam, Marvyn loamy sand, and Lucedale loam, respectively (Table 2.7). This result supported the findings from the incubation studies that the soil titration curves underestimated the potential acidity in all the three soils, particularly the Lucedale loam, which had a higher buffer capacity due to its finer texture.

Relative Neutralizing Value (RNV) Evaluation

Liming materials evaluated in this study showed consistent performance among all the three acid soils (Table 2.8). The average percent effectiveness of all liming materials and all

soils was 101%, indicating the calculated RNV was reliable in predicting the final pH for most ground limestones and byproducts evaluated in this study, except for the paper sludge and one ground limestone (lime 6; Table 2.8). The paper sludge was more effective (121%) than the calculated RNV would have predicted. This was expected because of the erratic particle size analysis resulting from the crumbly nature of this organic material. The lime 6, a ground marble, was the only liming material that was notably less effective (91%) than the calculated RNV would have predicted, possibly due to its more crystalline properties relative to other liming materials evaluated in this study (Table 2.8). Highly crystalline ground marble may not be as reactive as a less crystalline sedimentary limestone of similar total alkalinity and particle size (Dr. Daniel Olk, USDA-ARS, personal communication). The degree of crystallinity may be another parameter that should be evaluated when determining lime effectiveness.

This empirical correction factor (i.e., 1.5) in Eq. 4 works well with ground limestones that meet the state lime law of Alabama, but it may be inadequate for alternative liming materials (e.g., papermill lime mud and P slag) due to their highly varied actual liming ability. Since calculated RNV may more accurately predict the actual liming ability of most ground limestone and byproducts, the equation may be modified to Eq. 5:

$$\text{Liming material (kg ha}^{-1}\text{)} = \frac{8000 \times (8 - \text{buffer pH})}{H_{\text{sat1}}} \times (H_{\text{sat1}} - H_{\text{sat2}}) \times 2.24 \times \frac{100}{\text{RNV}} \quad [5]$$

Conclusions

Many of the locally available byproducts evaluated were not suitable alternative liming agents as provided. Papermill byproducts, except ash and lime mud, generally do not have enough CCE to be particularly effective. Lime mud is superior to ground limestone due to its high total alkalinity and fine particle size. However, the moisture content needs to be reduced

before it can serve as a good substitute of conventional ground limestones. The ash has decent CCE and RNV, but the Zn content may be prohibitively high for environmental loading rates, as well as for application to Zn sensitive crops, such as peanut. Papermill and other organic byproducts need to be analyzed carefully for particle size (e.g., wet sieving) to prevent underestimation of RNV that can lead to over liming. The steel slags have high total alkalinity, but their usage as liming agents may be precluded because of their Cr and Ni content. The P slag has moderate total alkalinity, but the particle size needs to be reduced to improve efficacy. While each product has a limitation to its use as a liming agent, limitations for lime mud and P slag are the most easily overcome through drying and crushing, respectively.

Assuming accurate particle size analysis (i.e., wet sieving) for liming material, the calculated RNV is an adequate indicator of actual liming ability for most ground limestones and industrial byproducts. This simple calculation might offer some benefits for consumers. Currently, most states in the United States only set a minimum standard for ground limestones, and products that fail to meet regulations for ground limestones cannot be sold as agricultural liming materials. If the RNV may be provided on the product label, some industrial byproducts can be marketed to consumers as substitutional liming agents, which will improve the accessibility of liming materials in areas where quality ground limestones are not readily available. In addition, ground limestones with superior quality (e.g., finer particle size) usually cannot compete with minimum-quality ones as they are more expensive. The RNV will allow consumers to directly compare the actual neutralizing value of different liming materials and choose products that are both effective in raising soil pH and economically viable.

Table 2.1. Name and type of product for evaluated materials

No.	Name	Type	Location
1	Lime 1	Calcitic limestone	AL
2	Lime 2	Calcitic limestone	MS
3	Lime 3	Calcitic limestone	AL
4	Lime 4	Calcitic limestone	AL
5	Lime 5	Calcitic limestone	GA
6	Lime 6	Dolomitic limestone	AL
7	Lime 7	Dolomitic limestone	AL
8	Lime 8	Dolomitic limestone	AL
9	Lime 9	Dolomitic limestone	VA
10	Lime 10	Dolomitic limestone	VA
11	Lime 11	Dolomitic limestone	TN
12	K-lime	A mixture of papermill ash and lime mud	NC
13	Ash	Byproduct of papermill	AL
14	Lime mud	Byproduct of papermill	AL
15	Primary sludge	Byproduct of papermill	AL
16	Secondary sludge	Byproduct of papermill	AL
17	Paper sludge	Byproduct of paper recycling	AL
18	Steel slag (old)	Byproduct of steel industry	AL
19	Steel slag (new)	Byproduct of steel industry	AL
20	P slag	Byproduct of P fertilizer industry	FL

Table 2.2. Recommended rate for each liming material and each soil to achieve a target pH of 6.5 based on the pH titration curve.

No.	Name†	Benndale fine	Marvyn	Lucedale
		sandy loam	loamy sand	loam
		-----g kg ⁻¹ -----		
1	Lime 1	0.46	1.09	0.80
2	Lime 2	0.60	1.43	1.05
3	Lime 3	0.39	0.93	0.68
4	Lime 4	0.38	0.92	0.67
5	Lime 5	0.54	1.28	0.94
6	Lime 6	0.43	1.02	0.75
7	Lime 7	0.42	1.02	0.75
8	Lime 8	0.41	0.97	0.71
9	Lime 9	0.29	0.70	0.52
10	Lime 10	0.64	1.53	1.13
11	Lime 11	0.42	0.99	0.73
12	K-lime	0.59	2.17	0.91
13	Ash	0.74	1.01	0.42
14	Lime mud	0.49	0.67	0.28
16	Secondary sludge	5.70	7.77	3.25
17	Paper sludge	14.3	19.5	8.17
18	Steel slag (old)	0.62	1.48	1.08
19	Steel slag (new)	0.72	1.73	1.27
20	P slag	7.36	10.0	1.20

† Primary sludge (No. 15) was not included in the incubation study due to its low alkalinity.

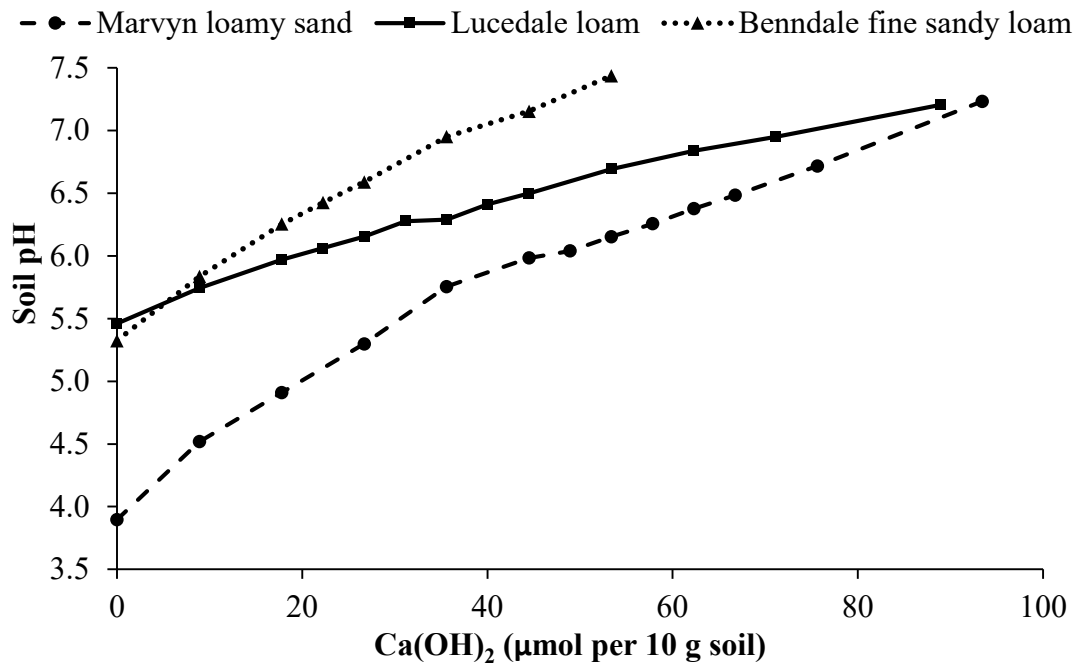


Figure 2.1. Titration curves for the Marvyn loamy sand, Benndale fine sandy loam, and Lucedale loam soils. Target pH is 6.5.

Table 2.3. Moisture, ash, total C and N, and C/N ratio in each liming material

No.	Name	Moisture	Ash	Total C	Total N	C/N	
		-----%-----					
1	Lime 1	0.1	98.3	10.9	0.67	16.3	
2	Lime 2	0.2	98.3	11.4	0.71	16.1	
3	Lime 3	0.1	98.3	11.3	0.87	13.0	
4	Lime 4	3.3	98.3	11.2	0.80	14.0	
5	Lime 5	0.6	97.7	10.5	0.68	15.4	
6	Lime 6	0.1	88.6	12.5	0.82	15.2	
7	Lime 7	4.0	96.0	10.8	0.63	17.1	
8	Lime 8	7.2	98.0	10.5	0.86	12.2	
9	Lime 9	0.2	81.6	12.5	0.83	15.1	
10	Lime 10	0.1	94.3	11.6	0.68	17.1	
11	Lime 11	1.9	98.7	9.1	0.76	12.0	
12	K-lime	22.5	85.6	1.4	0.99	1.4	
13	Ash	88.4	84.3	7.8	0.49	15.9	
14	Lime mud	34.6	98.7	8.3	0.72	11.5	
15	Primary sludge	208	14.0	13.2	0.43	30.7	
16	Secondary sludge	78.6	76.6	9.6	0.81	11.2	
17	Paper sludge	56.3	44.8	18.2	0.77	13.6	
18	Steel slag (old)	16.0	96.3	0.8	0.85	0.9	
19	Steel slag (new)	14.5	97.3	0.9	0.78	1.2	
20	P slag	8.0	98.7	1.6	0.76	2.1	

Table 2.4. Total concentration of elements in each liming material

No.	Name	Ca	Mg	P	Fe	Al	K	Na	Mn	Cu	Zn	Ni	Cr	Cd	Pb
		g kg ⁻¹						mg kg ⁻¹							
1	Lime 1	366	6	ND	2.1	1.8	142	5	67	11	ND	ND	2	ND	ND
2	Lime 2	388	10	0.1	1.2	1.5	127	17	26	8	ND	ND	ND	ND	ND
3	Lime 3	383	4	ND	0.7	1.2	74	14	29	9	ND	ND	ND	ND	ND
4	Lime 4	396	8	ND	0.5	1.0	55	6	17	6	ND	ND	ND	ND	ND
5	Lime 5	321	ND	0.2	4.0	2.0	414	ND	149	12	ND	ND	25	ND	ND
6	Lime 6	250	113	ND	1.2	0.8	15	8	89	8	ND	ND	ND	ND	ND
7	Lime 7	199	128	ND	2.5	1.2	133	3	102	11	ND	ND	ND	ND	ND
8	Lime 8	329	32	ND	2.1	1.4	118	ND	57	11	ND	ND	ND	ND	ND
9	Lime 9	213	142	ND	3.2	0.9	93	50	456	12	2452	ND	2	ND	30
10	Lime 10	281	66	0.3	4.7	1.4	79	ND	194	13	ND	ND	2	ND	ND
11	Lime 11	182	87	ND	1.3	1.0	286	ND	43	16	1519	ND	5	ND	ND
12	K-lime	108	6	2.4	4.2	8.9	16679	3434	1754	58	1720	ND	13	ND	ND
13	Ash	294	11	1.1	1.3	3.3	1138	1780	3424	54	2566	ND	3	ND	ND
14	Lime mud	385	5	1.3	0.8	2.1	401	3569	565	25	ND	ND	11	ND	ND
15	Primary sludge	37	8	0.2	2.2	2.1	447	440	330	20	ND	ND	6	ND	9
16	Secondary sludge	91	ND	0.8	4.8	7.9	552	555	1040	44	5377	ND	21	ND	19
17	Paper sludge	144	ND	0.1	1.2	5.1	295	69	62	65	ND	ND	10	ND	8
18	Steel slag (old)	352	47	ND	6.7	7.4	47	213	3268	52	ND	433	1235	ND	10
19	Steel slag (new)	324	48	ND	7.0	8.0	67	364	3428	50	ND	433	940	ND	13
20	P slag	299	2	7.1	1.5	6.0	1375	2625	155	7	40	75	105	34	9

Table 2.5. Ceiling concentration limit and maximum loading rate per year for sewage sludge and biosolids applied to land in US EPA's Part 503 Rule

Pollutant	As	Cd	Cr	Cu	Pb	Ni	Zn
	-----mg kg ⁻¹ -----						
Ceiling concentration	75	85	3000	4300	840	420	7500
	-----kg ha ⁻¹ -----						
Maximum loading rate limit per year	0.011	0.15	0.47	0.029	0.047	0.33	0.18

Table 2.6. Particle size, calcium carbonate equivalent (CCE), and relative neutralizing value (RNV) of each liming material

No.	Name	Particle size				CCE	RNV	Factor
		<10 mesh	<60 mesh	<100 mesh	<200 mesh			
		-----%-----						
1	Lime 1	85.4	46.6	29.5	11.9	92.9	61.3	--
2	Lime 2	77.4	18.4	7.7	3.5	98.1	47.0	Crystalline structure
3	Lime 3	99.9	46.5	17.8	5.0	98.3	72.0	
4	Lime 4	98.4	46.4	22.4	7.9	100.9	73.0	--
5	Lime 5	91.0	31.9	14.8	3.7	85.2	52.3	--
6	Lime 6	96.6	26.9	13.4	5.1	106.8	66.0	--
7	Lime 7	83.4	50.1	33.2	19.2	99.0	66.1	--
8	Lime 8	92.0	52.4	33.6	14.3	95.7	69.1	--
9	Lime 9	100	77.7	31.9	12.3	107.3	95.3	High Zn
10	Lime 10	89.1	1.6	0.4	0.2	96.4	43.7	--
11	Lime 11	99.9	70.4	42.0	11.8	79.3	67.5	High Zn
12	K-lime	96.5	60.5	44.8	28.1	39.4	30.9	High Zn and low CCE
13	Ash	94.8	58.4	44.7	23.1	87.0	66.7	High Zn
14	Lime mud	99.9	95.9	82.2	67.3	102.3	100.1	Moisture
15	Primary sludge	0.7	0.1	0.02	0.01	12.5	0.1	Low CCE
16	Secondary sludge	42.6	6.4	3.2	1.2	35.3	8.6	High Zn and low CCE
17	Paper sludge	17.9	0.7	0.1	0.02	36.9	3.4	Low CCE
18	Steel slag (old)	69.9	29.2	18.3	7.9	91.7	45.5	High Ni and Cr
19	Steel slag (new)	58.7	25.2	16.3	7.2	92.6	38.9	High Ni and Cr
20	P slag	22.1	0.9	0.6	0.4	58.1	6.7	Particle size

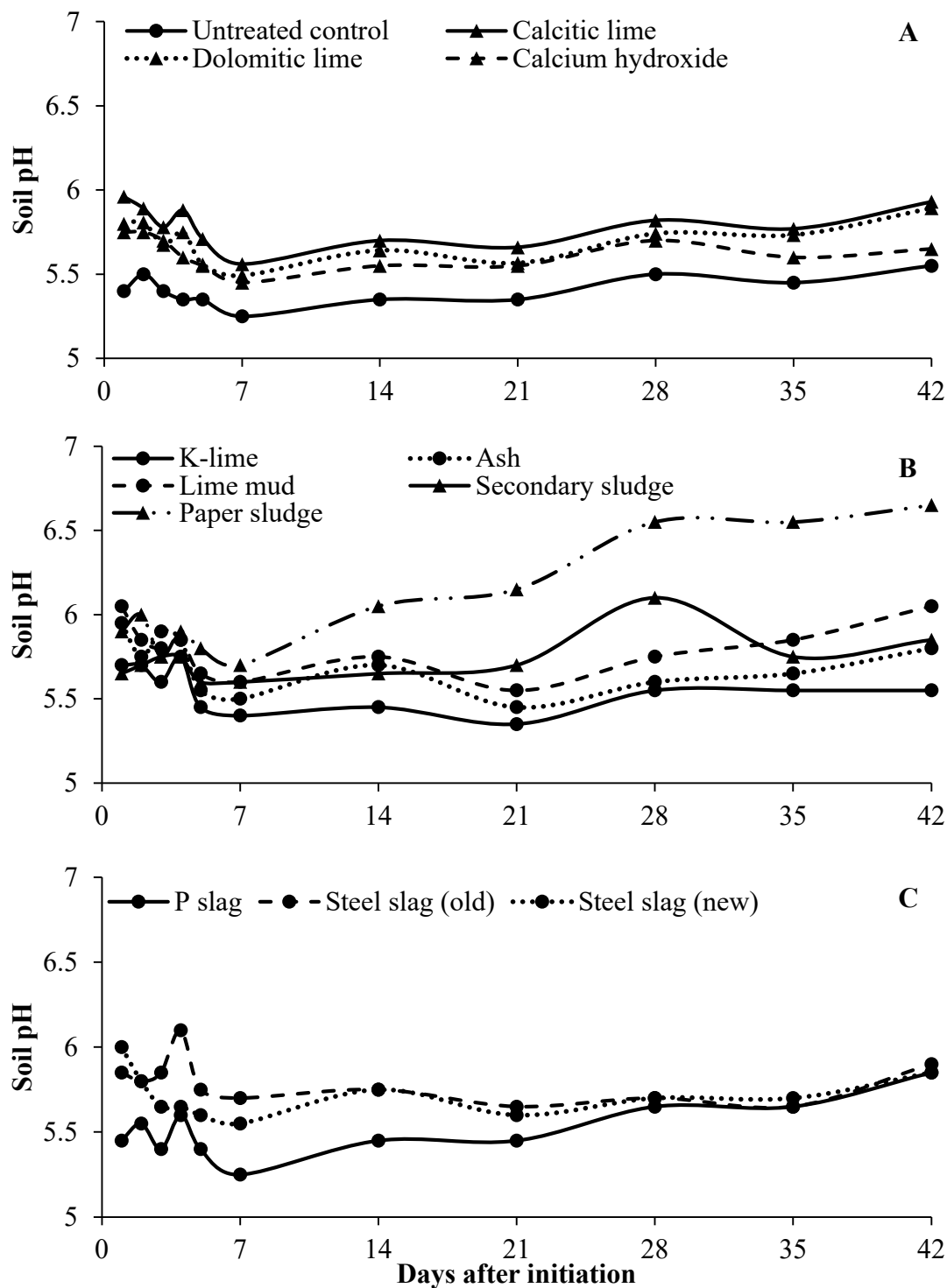


Figure 2.2. Soil pH of Benndale fine sandy loam over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at 50% recommended rate according to the titration curve.

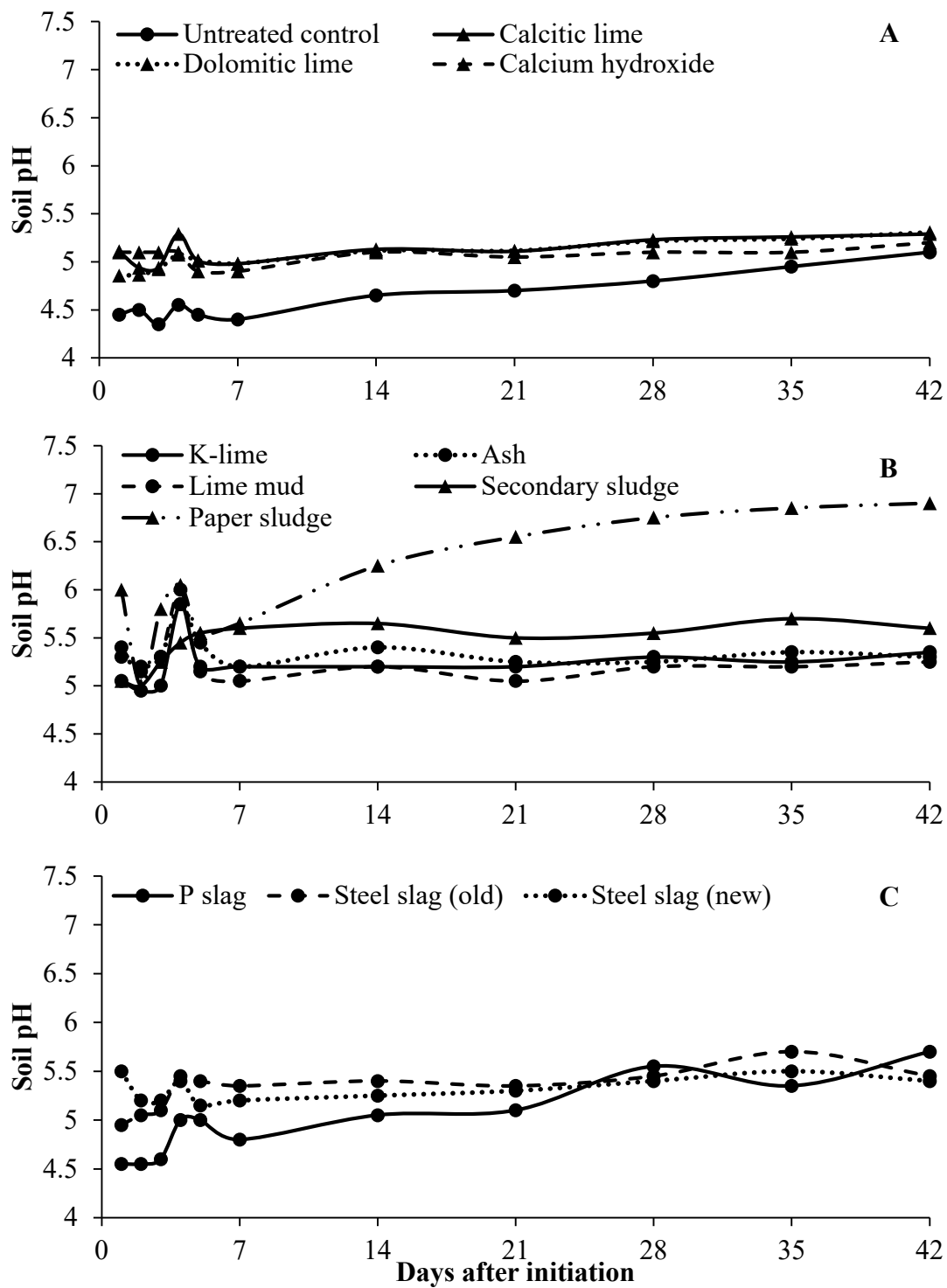


Figure 2.3. Soil pH of Marvyn loamy sand over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at 50% recommended rate according to the titration curve.

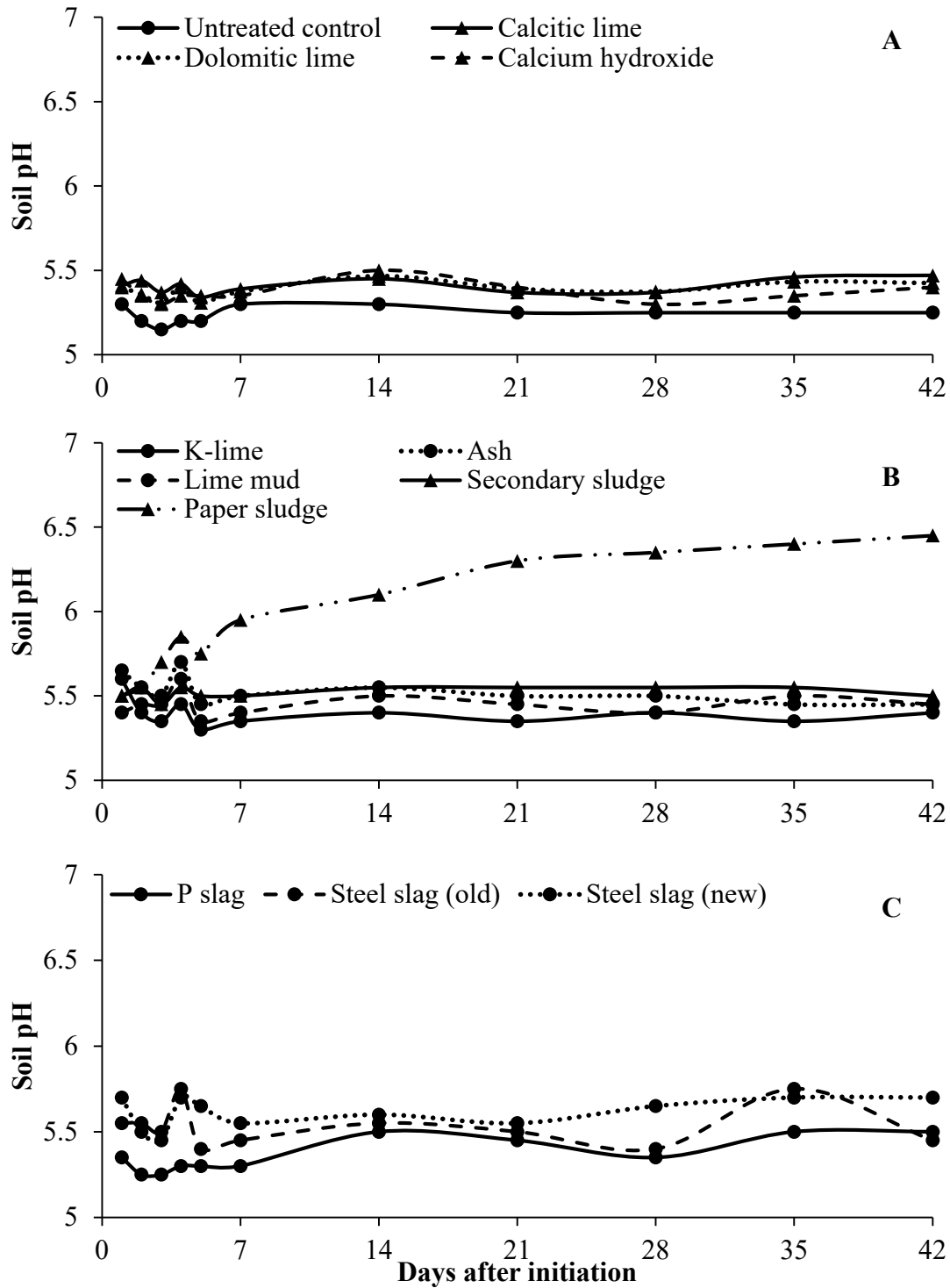


Figure 2.4. Soil pH of Lucedale loam over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at 50% recommended rate according to the titration curve.

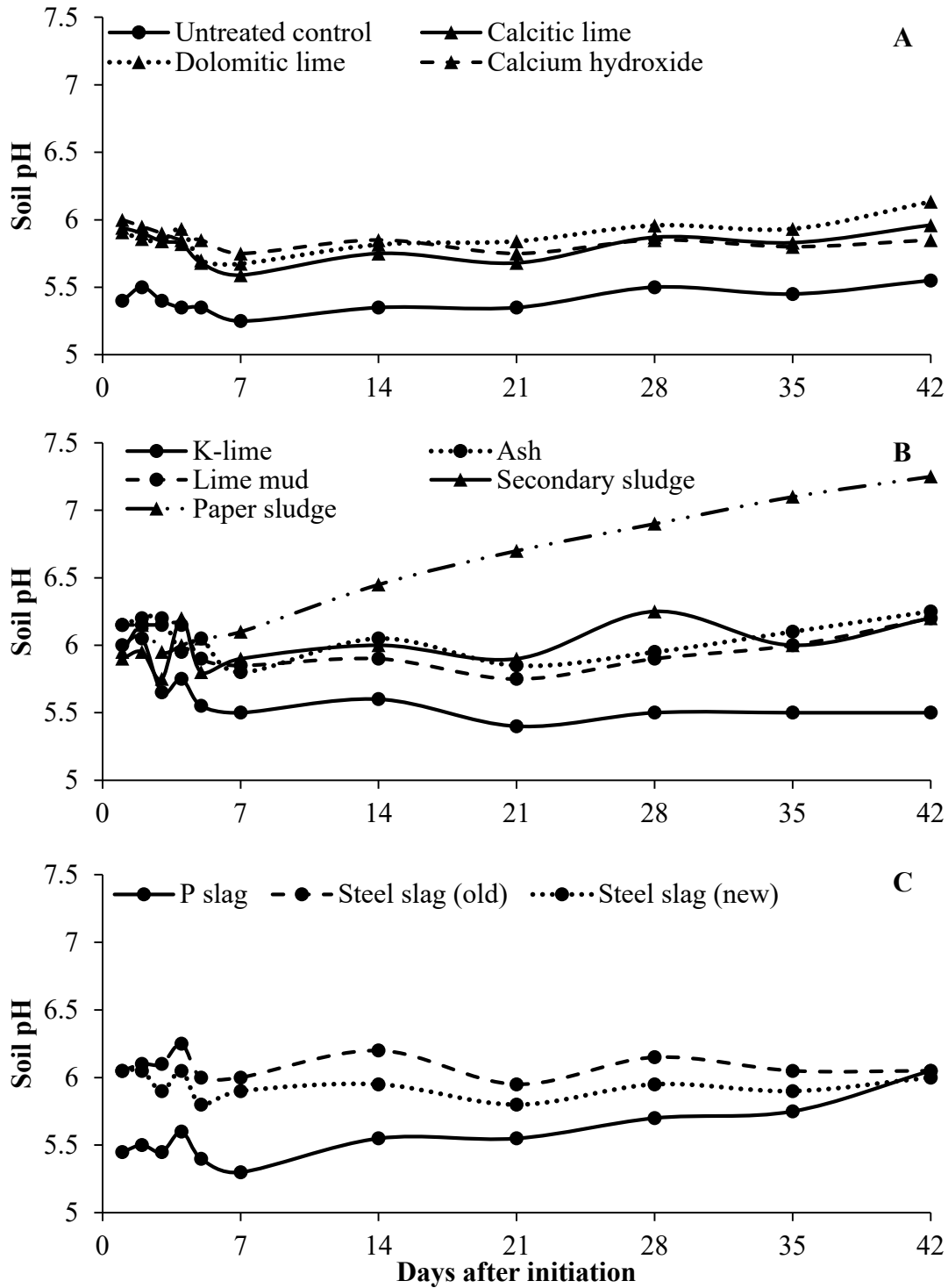


Figure 2.5. Soil pH of Benndale fine sandy loam over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at recommended rate according to the titration curve.

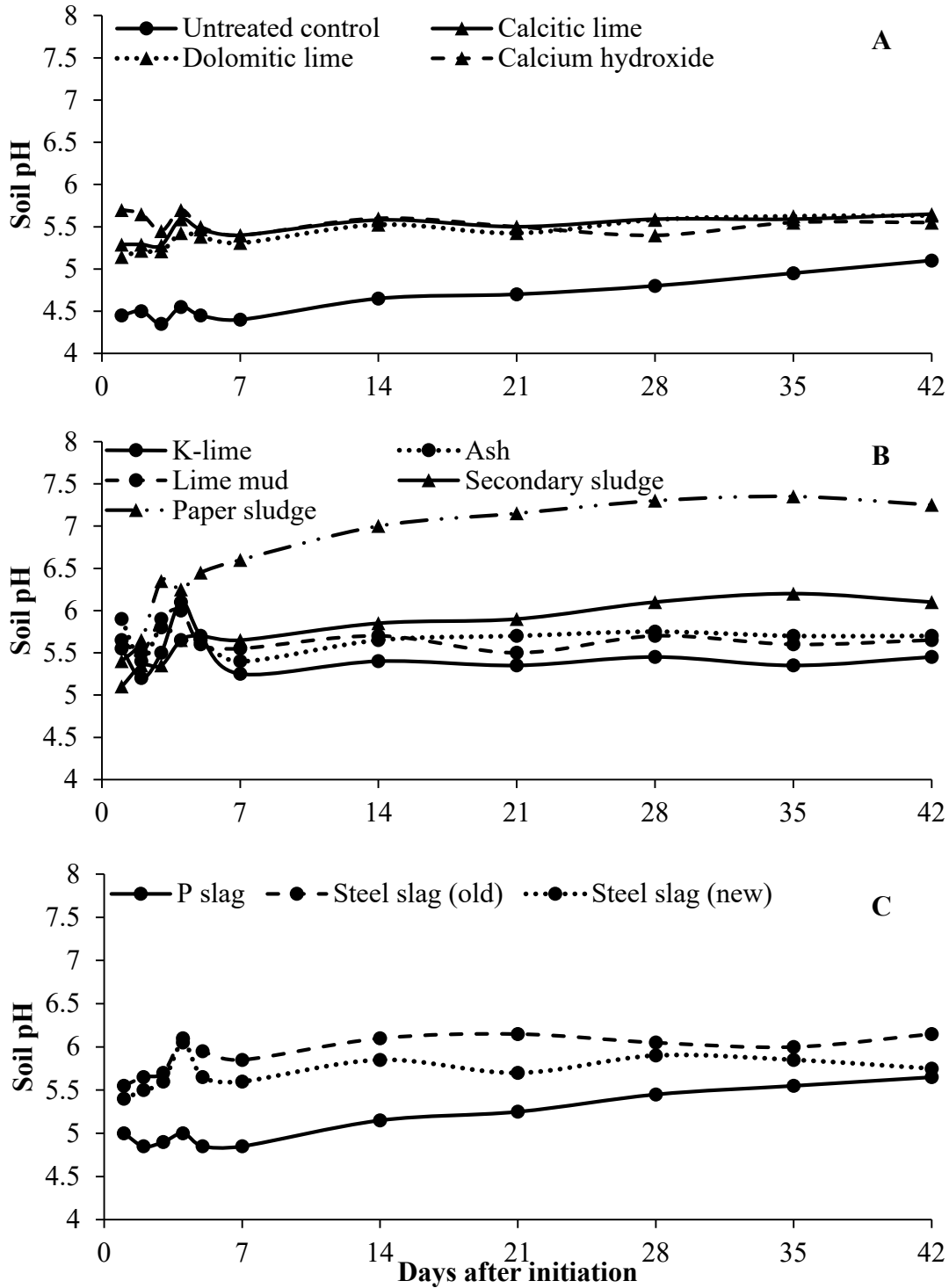


Figure 2.6. Soil pH of Marvyn loamy sand over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at recommended rate according to the titration curve.

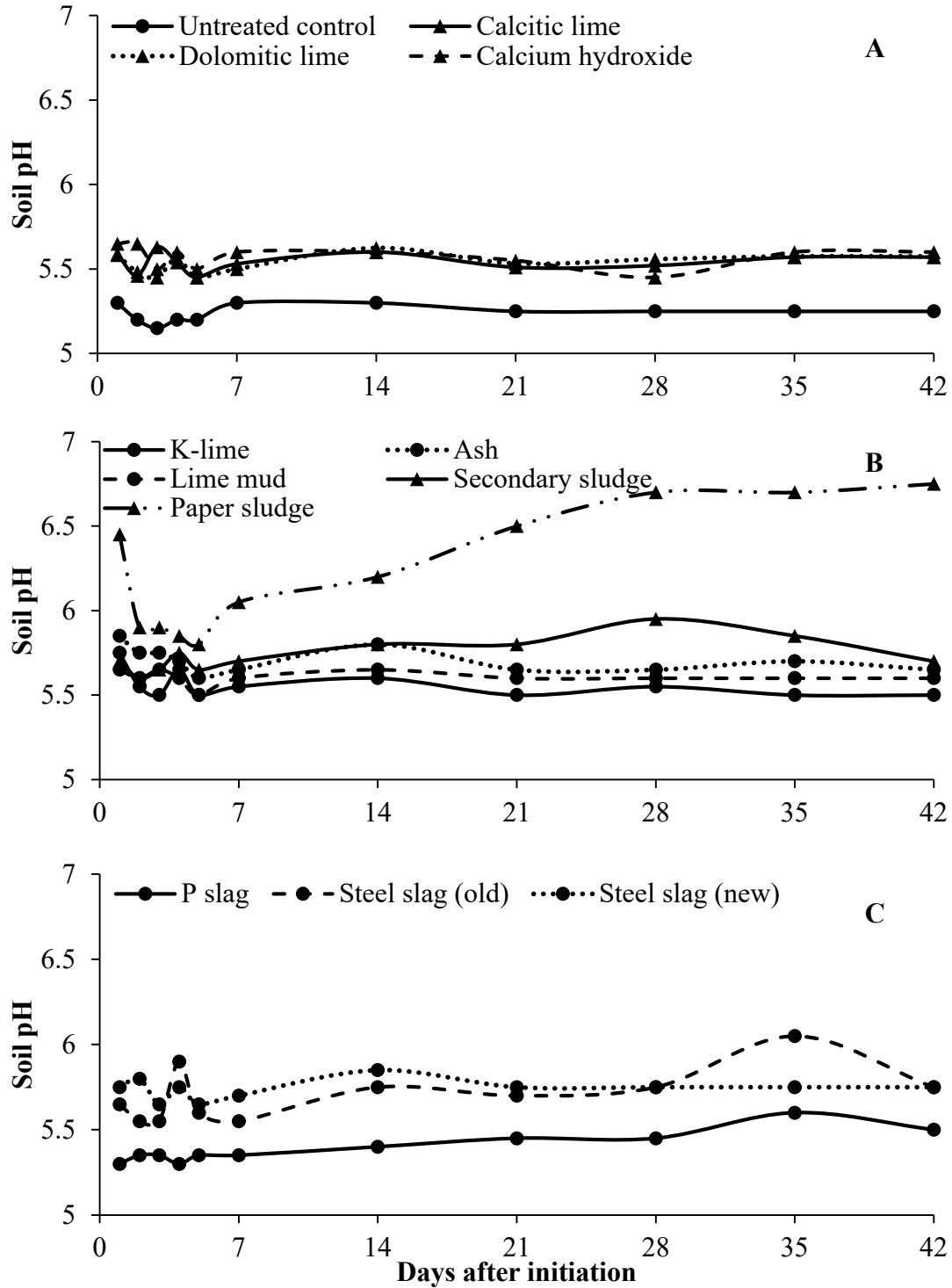


Figure 2.7. Soil pH of Lucedale loam over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at recommended rate according to the titration curve.

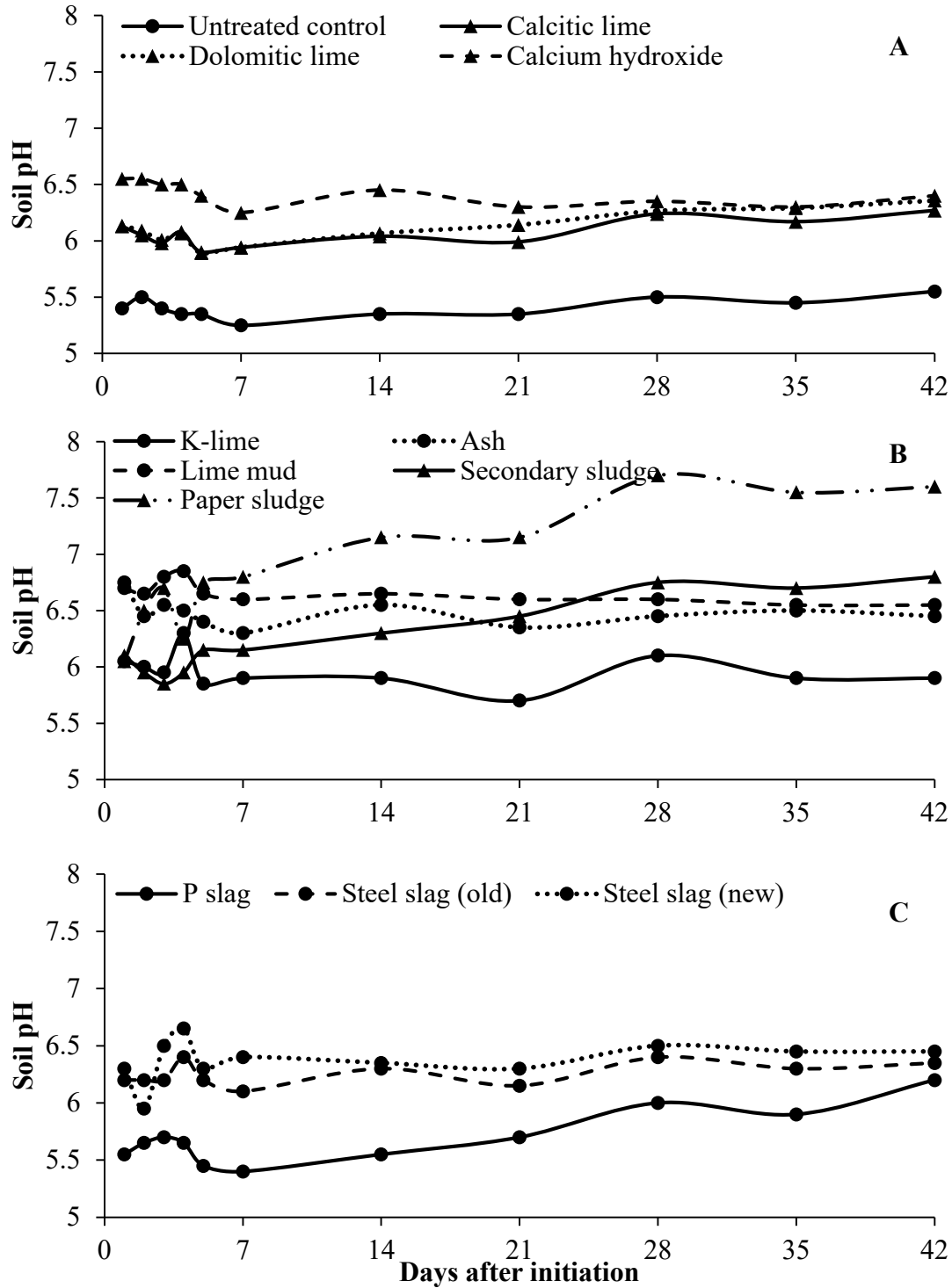


Figure 2.8. Soil pH of Benndale fine sandy loam over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at 200% recommended rate according to the titration curve.

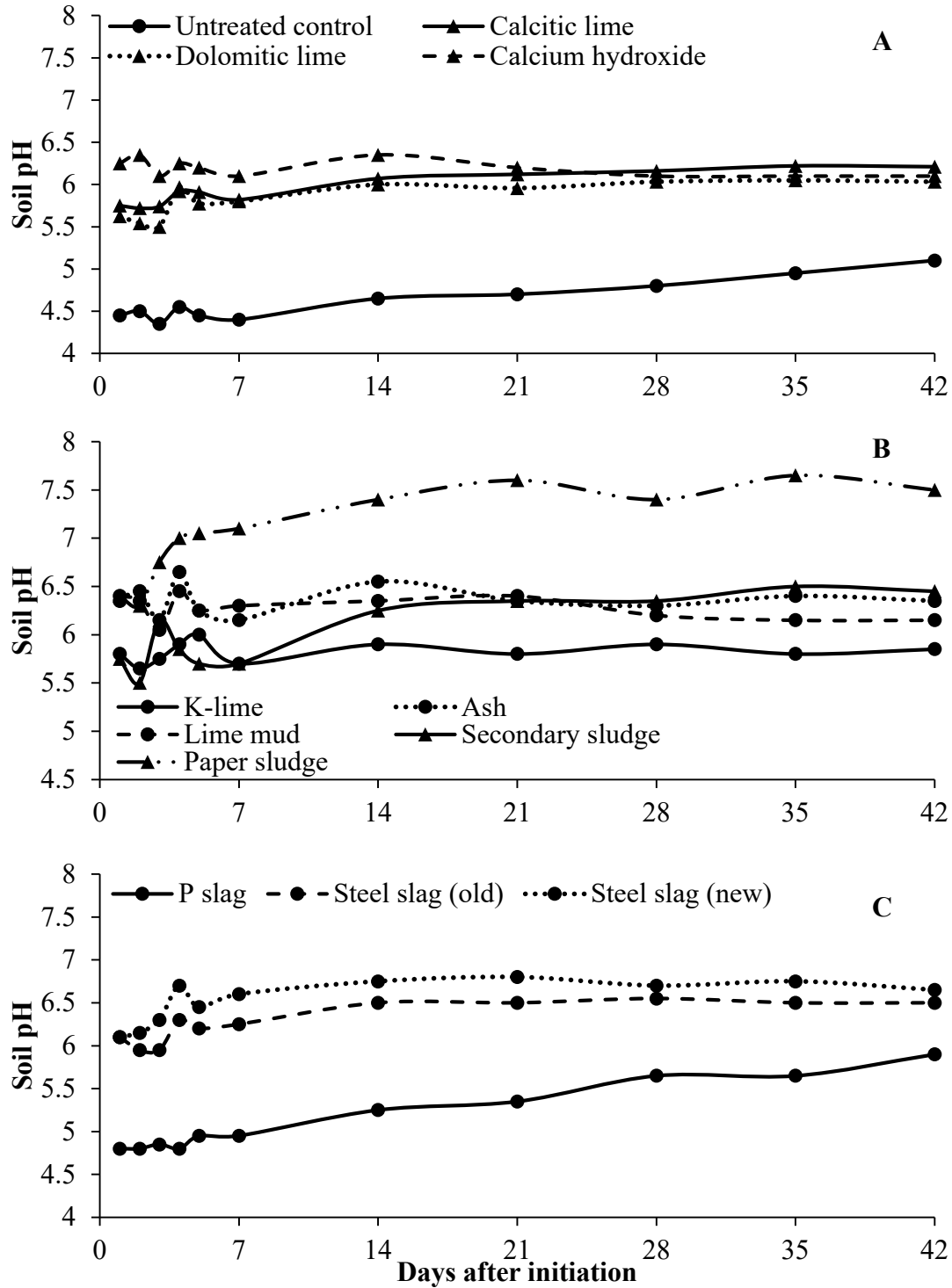


Figure 2.9. Soil pH of Marvyn loamy sand over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at 200% recommended rate according to the titration curve.

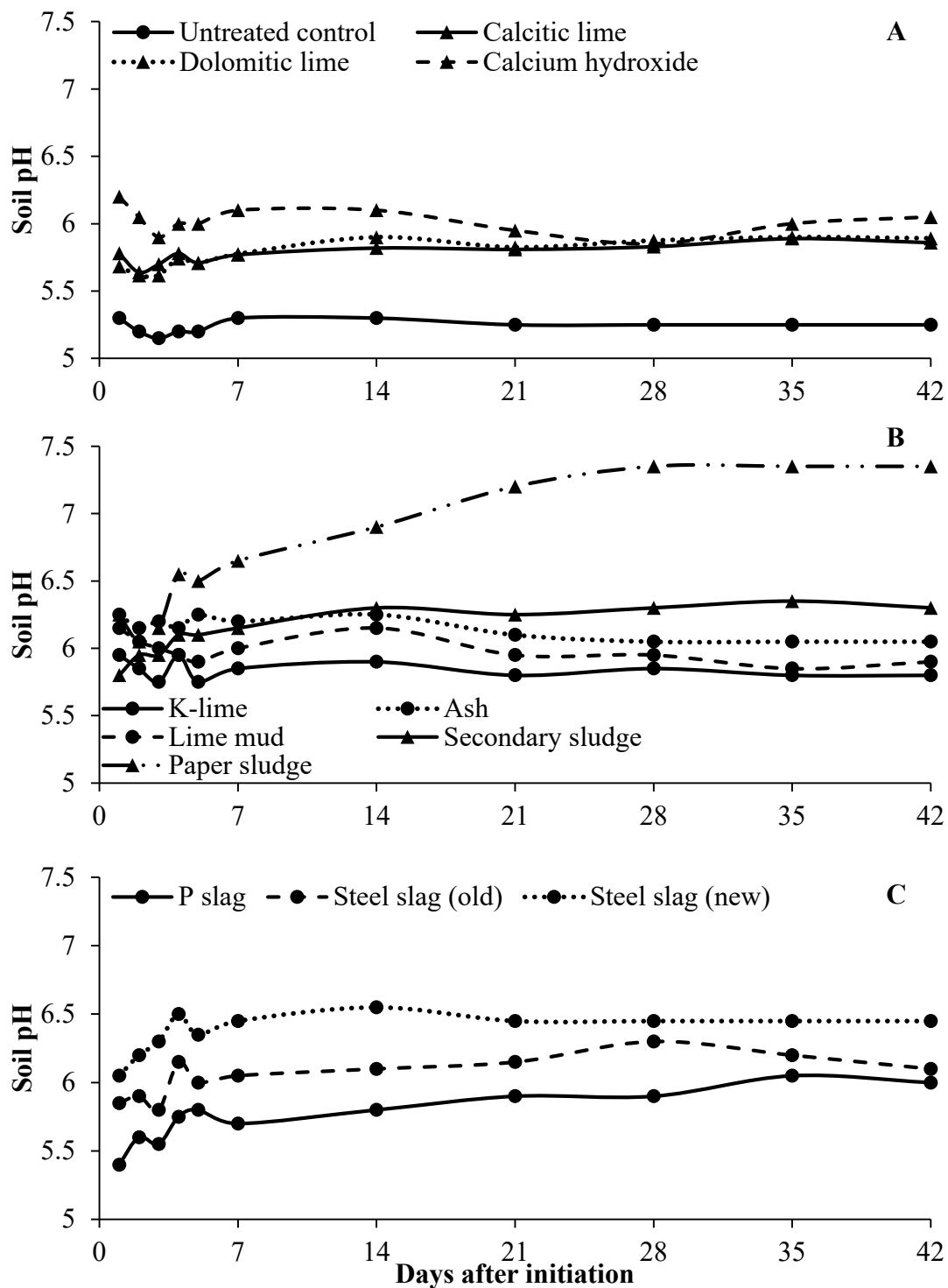


Figure 2.10. Soil pH of Lucedale loam over a 42-d incubation study. Ground limestone (A), papermill byproducts (B), and slags (C) were incorporated at 200% recommended rate according to the titration curve.

Table 2.7. Recommended rate of Ca(OH)₂ to achieve soil pH of 6.5 according to the titration curves and modified Adams-Evans buffer.

Soil series	Titration curve	Modified Adams-Evans buffer†
	-----mg Ca(OH) ₂ kg ⁻¹ -----	
Benndale fine sandy loam	149.3	206.5
Marvyn loamy sand†	494.0	873.4
Lucedale loam	362.2	950.7

† Estimation was based on an initial pH of 4.4 using the buffer method. Actual initial pH was slightly lower (3.9).

Table 2.8. Effectiveness of calculated relative neutralizing value (RNV) for each liming material compared to reagent grade Ca(OH)₂ after a 42-d incubation.

No.	Products	Benndale fine	Marvyn	Lucedale	Mean
		sandy loam	loamy sand	loam	
		-----%			
1	Lime 1	100	105	101	102
2	Lime 2	101	102	93	99
3	Lime 3	102	102	94	99
4	Lime 4	91	100	98	96
5	Lime 5	95	101	95	97
6	Lime 6	92	89	92	91
7	Lime 7	102	106	101	103
8	Lime 8	98	102	100	100
9	Lime 9	104	100	98	101
10	Lime 10	103	101	98	101
11	Lime 11	97	95	95	96
12	K-lime	92	96	96	95
13	Ash	101	104	100	102
14	Lime mud	102	101	98	100
16	Secondary sludge	106	106	104	105
17	Paper sludge	119	123	121	121
18	Steel slag (old)	99	107	101	102
19	Steel slag (new)	101	109	107	105
20	P slag	97	97	99	98
	Mean	100	102	100	101

III. Effect of calcium silicate slag on availability of silicon and trace elements

in rice (*Oryza sativa* L.) production

Abstract

Adequate Si supply is necessary for successful rice and sugarcane production. Calcium silicate slag from phosphate mining is potentially a good source of Si. However, this type of slag contains trace elements (e.g., Cd, Cr, Pb, ^{210}Po , ^{226}Ra , and ^{230}Th) that have the potential to contaminate the grains and straws from rice. Before this slag can be used as a supplement for crop production, it is necessary to determine its effect on solubility and bioavailability of trace elements, as well as its potential to supply Si to the plant. A greenhouse cultivation study was performed to evaluate this issue. Four application rates (0, 1000, 2000, 4000 mg kg⁻¹) of calcium silicate slag were surface applied or incorporated into an organic soil and a mineral soil used for rice/sugarcane culture. Applied slag increased soil pH by 0.2 to 0.8 units, increased plant available Si, and Si in rice straw. Small increases in rice biomass were also observed. Total concentration of trace elements in the soil was not affected by slag application. Plant available Mn and Ni decreased in the mineral soil, while extractable Cu increased in the organic soil. Total concentrations of Mn in the rice grain and Ca and Mg in the rice leaf decreased with increasing slag rate. Total radioactivity in soil and rice grain was not influenced by slag addition. These results indicate that Si in the slag is available to rice, and trace contaminants in this slag do not appear to be a concern for rice production or the environment due to the very low concentrations and low bioavailability of these elements.

Key words

Calcium silicate slag; Rice; Silicon; pH; Trace elements

Introduction

Silicon (Si) is the second most abundant element in the earth crust. Although all terrestrial plants contain Si in their tissues, it is not considered essential for most higher plants, except for the members of Equisetaceae (Epstein, 1994). Members of the Gramineae families (e.g., rice and sugarcane) are particularly high in Si accumulation (>4% Si, Hudson et al., 2005), and an inadequate supply of Si can cause various abnormalities with respect to plant growth, development, and reproduction. Based on modified definition of essentiality for higher plants, Si can be defined as a “quasi essential” element for higher plants (Epstein and Bloom, 2005). Silicon has also demonstrated a number of beneficial effects on growth and yield of several plant species (e.g., rice, wheat, sugarcane, barley, and sorghum), which include improvement of leaf exposure to light (Ma and Takahashi, 2002), resistance to lodging (Idris et al., 1975; Crusciol et al., 2009), decreased susceptibility to pathogens and root parasites (Gascho, 1977; Anderson et al., 1987; Menzies et al., 1991; Gascho and Korndorfer, 1999; Ma and Yamaji, 2006), and amelioration of abiotic stresses such as drought and salt stress (Ma, 2004,2005; Ma and Yamaji, 2006).

Calcium silicate slag, specifically slag produced as a byproduct from the refining of phosphate rocks for phosphorus fertilizers, is potentially a good source of Si for crops such as rice and sugarcane. Previous studies demonstrated that rice grown on organic soils amended with calcium silicate slag had greater height, plant biomass, and yield and were less susceptible to disease (Gascho, 1977; Elawad et al., 1982; Snyder et al., 1986). In a rice-sugarcane rotation, slag applications to a Histosol increased both rice straw Si and sugarcane leaf Si concentrations (Anderson et al., 1987). However, this type of slag also contains trace elements that have the potential to contaminate the grains and straw from rice. Elements of concern include chromium

(Cr), cadmium (Cd), lead (Pb), polonium (Po), radium (Ra), thorium (Th), and uranium (U) due to their potential toxicity and/or low level radioactivity. In addition, there are potential environmental concerns associated with solubilization and mobility of these trace elements to surface waters and groundwater.

The plant availability and environmental mobility of Si and trace elements in calcium silicate slag will largely depend on their solubility and on the effect of slag on soil properties such as pH. However, there are few studies that have evaluated trace element bioavailability from slag. Mortvedt (1986) conducted a greenhouse experiment and found that uptake of ^{226}Ra by fescue and wheat into aboveground tissue was not affected by calcium silicate slag application. The potential for trace elements contained in calcium silicate slag materials to accumulate in crops is still largely unknown. Because calcium silicate slag is primarily targeted for rice and sugarcane, results need to verify its use in these crops. Therefore, the objective of this study is to determine the effect of calcium silicate slag on soil pH, solubility, and bioavailability of trace elements, as well as its potential to supply Si to the plant.

Materials and Methods

A greenhouse study with rice, var. "CL151", was performed at Plant Science Research Center (32.59° N, 85.48° W) at Auburn University, AL, which was repeated in 2015 and 2016. The experiment design was a factorial design with 4 replications using randomized complete block arrangement. Treatments, including 4 slag rates (0, 1000, 2000, and 4000 mg kg⁻¹) that were either surface applied or incorporated, were evaluated on two soils typically used for rice/sugarcane culture: Sharkey clay (very-fine, smectitic, thermic Chromic Epiaquerts) from Stoneville, MS and Pahokee muck (Euic, hyperthermic Lithic Haplosaprists) from Belle Glade,

FL. Slag was dried at 65°C for 48 h, ground using a pulverizer to pass 2-mm sieve, and surface applied or incorporated immediately prior to planting.

Direct dry-seeded rice was grown in 700 cm³ soils (840 g Sharkey clay and 450 g Pahokee muck) in square pots (10.5 × 12.5 cm top and 8.5 × 12.5 bottom). In detail, 9 seeds were sowed to each pot at planting (29 June 2015 and 23 May 2016), and seedlings were thinned to 1 per pot at 21 days after planting (DAP). Soil was initially flooded for 24 h. Then, water was drained, and soil moisture was maintained at field capacity daily with supplied tap water using gravimetric method for 5 wk. Permanent flooding started at 35 DAP and was eliminated at 110 DAP. Flooded condition was maintained at a standing depth of 3 cm. Urea was surface applied to each pot at a rate of 160 kg N ha⁻¹ immediately prior to permanent flooding. Two weeks after permanent flooding, zinc sulfate solution was foliar applied at a rate of 1.12 kg Zn ha⁻¹. Rice was harvested at 120 DAP.

After harvest, rough rice (whole rice grain with hull) was threshed by hand. Brown rice (whole rice grain without hull), stem, leaf, and root were dried at 65°C for 48 h, weighed, and ground to fine powder using a coffee grinder (KRUPS F203, KRUPS company, Millville, NJ). Aboveground plant biomass was removed from each pot, then soils were dried at 65°C for 48 h, thoroughly mixed, ground using a mortar and pestle, and sieved to ensure soil passed a 2-mm screen. The slag, plant tissues, and soils were microwave digested using a Mars Xpress microwave (CEM Corp., Matthews, NC) using EPA-3051 procedure (USEPA, 1994) prior to total element determination by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Spectro Ciros CCD, side on plasma, SPECTRO Analytical Instruments Inc., Kleve, Germany). Soil pH was determined using a 1:2 ratio (w/v) of soil and deionized water (Hue and Evans, 1986). Total Si in rice leaf and stem was determined using molybdenum blue colorimetry

following oven-induced digestion (Kraska and Breitenbeck, 2010). Plant available Si was extracted using 0.5 M acetic acid (Korndorfer et al., 2001) and analyzed with ICP-AES. Plant available trace elements and metals in the slag and soils were extracted using DTPA soil test (Lindsay and Norvell, 1978) followed by ICP-AES analysis. Total radioactivity in brown rice and soils was analyzed by Auburn University Radiation Safety Department using liquid scintillation analyzer (Tri-Carb 1900 TR, PerkinElmer Inc., Waltham, MA).

Mixed model methodology as implemented in SAS PROC GLIMMIX were used to analyze the data (Littell et al., 2006). Year, soil series, slag rate, and application method were treated as fixed effects, whereas block was the random effect. To test for differences among main effects and their interactions, the Tukey adjustment was applied to the least square means (LSMEANS) statement of SAS 9.3 software (SAS Institute Inc., Cary, NC, USA).

Results and Discussion

Background information

Soil pH for Sharkey clay and Pahokee muck is 6.9 and 7.0, respectively. This slag is coarse-textured with only 22.1 and 0.6% passing 10 and 60 mesh (2 and 0.25 mm) screen. Calcium carbonate equivalent (CCE) of this slag is 58%, indicating it has moderate liming potential. Total Si in the slag is 198.3 g kg⁻¹. Plant available Si in the slag, Sharkey clay, and Pahokee muck soils is 139.4, 73.9, and 28.8 mg Si kg⁻¹, respectively. Plant available Si in the Sharkey clay was higher than the critical value (60 mg Si kg⁻¹) suggested by Korndorfer et al. (2001), thus no Si fertilization is recommended. Pahokee muck was lower in plant available Si than the critical value, which is expected for an organic soil containing <35% mineral matter

(Snyder, 2005). Therefore, supplemental Si is recommended for crop production in the Pahokee muck because it may have limited ability to supply adequate Si.

In addition to Si, the slag also contains plant essential nutrients, such as P, Ca, Mg, Fe, Mn, Cu, Zn, Co, and Ni (Table 3.1). Potentially hazardous contaminants in the slag include As, Cd, Cr, and Pb, but when applied at typical rate (4480 kg ha^{-1}), total amount of these contaminants are considerably below the maximum loading rate limit per year for sludge and biosolids applied to land in USEPA's Part 503 Rule (Table 3.2, USEPA, 1993). Concentrations of plant available elements in the slag are much lower than their total concentrations, indicating only a small proportion of the total elements are readily available to plant (Table 3.3). Total radioactivity in this slag is 4.0 Bq g^{-1} , which is higher than radioactivity in typical natural soils (0.5 Bq g^{-1} , National Research Council, 1999). Applying the slag at the highest rate used in this study (4000 mg kg^{-1}) would cause the radioactivity of the soil to increase by 0.016 Bq g^{-1} , which translates to only 3.2% of the background radioactivity.

Soil pH, plant available Si, Si in plant tissues, and biomass were analyzed for main effects and interactions due to year, soil series, slag rate, and application method (Table 4). The interaction of year \times soil series \times slag rate \times application method was significant for soil pH ($P = 0.003$) and plant available Si (0.026), but not for Si in plant tissues or biomass (Table 3.4). Data were combined for application method to interpret effect of interactions among year, soil series, slag rate on Si in plant tissue and biomass.

Soil pH

Soil pH of the Sharkey clay increased slightly relative to untreated control with surface-applied slag in 2016 and incorporated slag in both 2015 and 2016 (Table 3.5). This effect was

more evident in the soils with incorporated slag, where pH increased 0.5 to 0.8 units, compared to increases of 0.2 to 0.5 units with surface application from the untreated control to the highest slag rate. In contrast, soil pH of the Pahokee muck was not affected by slag addition (Table 3.5). Lack of effect on soil pH is possibly due to the higher buffer capacity of Pahokee muck soil, which is an organic soil in the Histosol soil order.

Due to the short duration of these experiments (i.e., 120 days), it is possible that the pH could continue to rise slowly over time as the slag material continues to slowly dissolve. This effect could be more pronounced in the original slag material in which only 22% passed the 2-mm sieve. Larger particles take longer to dissolve and increase pH; however, slow pH changes are often moderated by the slow natural soil acidification process that is common to most cropping systems.

Plant available Si and Si in plant tissues

Bioavailability of Si was evaluated by estimating plant available Si in the soil and measuring Si in plant tissue. Plant available Si in both Sharkey clay and Pahokee muck gradually increased with increasing slag rate under both application methods in both years. However, the increase relative to the untreated control was not significant except for surface-applied slag at 4000 mg kg⁻¹ in the Sharkey clay in 2016 (Table 3.6). The low solubility of the slag may cause very slow release of the Si similar to the slow effect of the slag's liming ability, essentially making it a slow-release Si fertilizer. This effect has been noted in the literature in rice and sugarcane production where a single slag application may have benefits for multiple cropping seasons (Anderson et al., 1987; Snyder et al., 1986).

Plant uptake of Si was estimated by concentrations of Si in the leaf and stem. Data were combined for years and application methods as there was no interaction for these variables (Table 3.4). Leaf and stem Si in unamended Sharkey clay was 46.5 and 27.5 g kg⁻¹, respectively. Addition of slag did not increase leaf or stem Si in this soil. In contrast, applied slag gradually increased leaf Si from 23.7 to 42.7 g kg⁻¹ and stem Si from 14.3 to 26.8 g kg⁻¹ in Pahokee muck, indicating that the Si in the applied slag was available to the plant and absorbed into plant tissues (Fig. 3.1). A commonly used criterion to evaluate Si sufficiency in harvested rice straw in the U.S. is 50 g Si kg⁻¹ (De Datta, 1981). Because leaf Si was near this level and because additional slag did not increase tissue Si in the mineral soil, it is likely that Si was sufficient. Increases in plant Si in the organic soil reflect active uptake of Si in the low Si soil. Of the total Si added to soil from slag, 19.2 to 25.7% accumulated in the rice straw in Pahokee muck, compared to 3.5 to 5.1% in Sharkey clay. A greater accumulation of Si from slag utilized by rice grown in the organic soil may explain why plant available Si was lower in this soil.

Rice biomass

Rice biomass was assessed on a leaf, stem, rough rice, and brown rice basis. Because there was a significant year × soil series × slag rate interaction for leaf, stem, rough rice, and brown rice, but not for application method (Table 3.4), the data for each application method was combined. Applied slag at 4000 mg kg⁻¹ in Sharkey clay increased leaf biomass in 2016 (Table 3.7). Except for this increase, slag supplementation showed no statistical effect on biomass of stem, rough rice, or brown rice in either soil in either year (Table 3.7). However, all biomass assessments tended to increase with increasing slag rate, and the greatest increase was observed in rough rice and brown rice in Pahokee muck, which increased by 13.4 and 15.3%, respectively, compared to the untreated control.

Korndorfer et al. (2001) suggested that a yield response to Si fertilization would occur when harvested rice straw contained $<34 \text{ g Si kg}^{-1}$. Rice grown in Sharkey clay contained $>45 \text{ mg Si kg}^{-1}$ in leaf; therefore, a yield response was not expected. In contrast, rice grown in Pahokee muck contained $23.7 \text{ mg Si kg}^{-1}$ in leaf (no slag application), which suggests a response in biomass could occur. In the current study, biomass indicators of leaf, stem, rough rice, and brown rice in the untreated controls were lower in plants grown in the organic soil compared to the mineral soil, and the greatest increases in biomass due to slag were observed in the organic soil. Previous studies have also demonstrated that application of Si to mineral soils does not consistently increase rice grain yields (Bollich et al., 1997; Lee et al., 2000). In the U.S., field research with Si-containing amendments has reported increased rice grain yield on Histosols in Florida Everglades agricultural area (Snyder et al., 1986; Anderson et al., 1987; Deren et al., 1994).

Total and plant available elements in soils

Year, soil series, slag rate, application method, and their interactions showed no significant effects on total concentrations of soil nutrients or contaminants (i.e., Ca, Mg, P, Fe, Mn, Co, Cu, Ni, As, Cr, Cd, Pb) analyzed in this study (Table 3.8). Thus, it is statistically impossible to determine which soil contained slag by total elemental concentrations.

Concentrations of DTPA extractable Fe, Co, Cr, Cd, and Pb were also not influenced by slag application (Table 3.9).

Plant available Cu was affected by a significant soil series \times slag rate interaction ($P = 0.002$). Copper availability decreases with increasing soil pH; however, plant available Cu did not decline with added slag in Sharkey clay, even though the liming effect of slag was significant in this mineral soil (Fig. 3.2). Soil organic matter, especially humic acid, has been reported to

have a high binding capacity for Cu (Logan et al., 1997), thus organic soils in the Histosol order usually have limited Cu availability. In the current study, applied slag increased extractable Cu in Pahokee muck soil by 0.5 mg kg^{-1} relative to untreated control, and differences among the slag rates were not significant (Fig. 3.2). Results indicate that applied slag may help maintain or improve Cu availability in soils regardless of its minor liming effect.

Plant available Ni ($P = 0.010$) and Mn ($P = 0.026$) exhibited a year \times soil series \times slag rate interaction, and thus data were combined for application methods. Plant available Ni and Mn gradually decreased with increasing slag rate in both years in Sharkey clay, but not Pahokee muck (Table 3.10). Availability of Mn in soils is dependent on pH and redox conditions (Kabata-Pendias, 2010). Because redox conditions were similar among the treatments and slag supplementation notably increased soil pH of Sharkey clay, it is likely that changes in Mn availability are due to the liming effect of the slag. This may have caused available Mn in soil solution to precipitate as Mn-oxides or Mn-hydroxides and thus become unavailable. Nickel tends to co-precipitate with Fe and Mn oxides (Kabata-Pendias, 2010). With increasing pH, surface charges on Fe and Mn oxides become more negative and NiOH^+ sorption may be enhanced (Siebielec and Chaney, 2006). Therefore, the availability of Ni is also negatively related to soil pH. Because pH was less affected by slag in the Pahokee muck and because organic matter is known to bind Mn and Ni strongly (Kabata-Pendias, 2010; Tejada et al., 2008), it is likely that the Mn and Ni remained available in Pahokee muck.

Total concentration of elements in brown rice

Total concentrations of Ni, As, and Cr were not detectable in brown rice. Concentrations of P, Ca, Mg, Ca, Co, Cu, Cd, and Pb were not affected by slag application, except for Mn (Table 3.11).

Slag supplementation gradually decreased concentration of Mn in brown rice produced in Sharkey clay (Fig. 3.3), which is likely due to decreased Mn availability in soils resulting from the liming effect of the slag. In addition, supplemental Si may have contributed to decreased Mn uptake. A previous study using hydroponics found that Si may enhance the oxidation power of rice roots by facilitating O₂ transport from shoot to root, and reduce solubility and availability of Mn in rhizosphere (Okuda and Takahashi, 1962).

Total concentration of elements in leaf and stem

Concentrations of Fe, P, Cu, Ni, As, Cr, Cd, and Pb were not significantly affected by slag application in either leaf or stem (Table 3.12). Significant year × soil series × slag rate interactions were observed for Mn in leaf (P = 0.008) and stem (P = 0.047). Leaf and stem Mn tended to decrease with increasing slag rate in both soils, but this trend was only significant for Mn in leaf in Sharkey clay in 2016 (Table 3.13). Results are consistent with the reduced plant available Mn results. Manganese deficiency in rice occurs when the Mn concentration in the plant tissue is < 20 mg kg⁻¹ (Wells et al., 1993). In the current study, even the lowest Mn concentrations in plant tissue in Pahokee muck and Sharkey clay were well above this critical value and no deficiency symptoms were observed, thus Mn deficiency induced by slag application was unlikely in these soils.

A soil series × slag rate interaction was significant for Ca (P = 0.001) and Mg (P < 0.001) in rice leaf. Slag addition significantly decreased Ca and Mg concentrations in Pahokee muck, but not in Sharkey clay (Fig. 3.4). This result was not expected as applied slag provided additional Ca and Mg. Similar results with rice grown in slag-amended Histosol in FL were previously reported and were attributed to the dilution effect of the higher biomass (Snyder et al., 1986). However, correlation between tissue concentration and total accumulation in plant in the

current study showed that total Ca and Mg accumulation in leaf decreased linearly with decreasing tissue concentration due to slag application, suggesting that decreased Ca and Mg concentrations cannot be explained by dilution effect (Fig. 3.5). The Pahokee muck soil developed on limestone bedrock, thus carbonates and bicarbonates are present. At slightly alkaline pH, Ca and Mg may precipitate with carbonate forming calcium and magnesium carbonates, which would decrease availability for plant uptake (Havlin et al., 2014). Further research may be necessary to better understand mechanisms.

Requirements of Ca and Mg for adequate rice growth are 1.5 g Ca kg⁻¹ and 1.0 g Mg kg⁻¹ in mature rice straw (De Datta, 1981). In this study, Ca and Mg concentrations in the leaf were above the critical values, thus deficiency is unlikely.

Total radioactivity in rice grain and soils

Total radioactivity in soils and brown rice was not significantly affected by main effects or interactions of year, soil series, slag rate, or application method, indicating radioactivity in the slag is not transferred to the soil or rice grain (Table 3.14). Background radioactivity of the two soils used in this study (≤ 0.05 Bq g⁻¹) is ~10-times lower than that in typical natural soils (0.5 Bq g⁻¹; National Research Council, 1999), and applied slag added minimal radioactivity to the soils. Compared to radioactivity in commercially produced and sold rice from different counties (0.34 to 0.81 Bq g⁻¹) reported by Najam et al. (2015), rice grain from the current study was 3 to 10 times lower in radioactivity.

Conclusions

Applied calcium silicate slag increased pH of the mineral soil by 0.2 to 0.8 unit in this study, indicating it has moderate liming potential and may be used as alternative liming material

if its particle size can be reduced to < 2 mm. The slag increased plant available Si in both soils and Si accumulation in rice straw of the organic soil, thus Si in this slag is available to plants. Applied slag also tended to improve plant biomass and yield.

Manganese in leaf, stem, and rice grain in the mineral soil, and Ca and Mg in leaf in the organic soil was decreased by slag application. However, concentrations of these elements were all above the range for adequate rice growth and no deficiency symptoms were observed, thus slag-induced Mn, Ca, and/or Mg deficiency in plant tissue was unlikely. However, application of slag to high pH mineral soils, especially those naturally low in Mn could result in Mn deficiency.

Applied slag maintained or slightly improved availability of Cu in the soils. Total and plant available concentrations of potential contaminants in soils, including As, Cr, Cd, Pb, Fe, and Co, were not affected by slag application. These elements were not accumulated in plant tissues either. Total radioactivity in both soils and rice grain were near detection limits and was much lower than commercially sold rice. Therefore, trace contaminants in this slag do not appear readily available to plant and should not have a detrimental effect on the environment or rice production.

Overall, calcium silicate slag from the phosphorus refining process has potential to provide Si and act as a weak liming agent in rice production. Trace contaminants do not appear to be problematic for land application; however, specific soils low in Mn or high in other trace elements or radioactivity may be of concern.

Table 3.1. Total concentration of elements determined by EPA 3051 method in the slag, Sharkey clay, and Pahokee muck soils

Elements	Ca	Mg	P	Fe	Mn	Co	Cu	Ni	Zn	As	Cd	Cr	Pb
	-----g kg ⁻¹ -----				-----mg kg ⁻¹ -----								
Slag	299.3	1.8	7.1	1.5	154.9	4.6	6.5	74.6	39.8	2.4	34.3	104.7	9.1
Sharkey clay	3.1	2.6	0.5	11.8	331.5	9.7	15.4	16.1	27.5	0.6	87.4	12.6	24.7
Pahokee muck	44.7	5.4	0.9	10.4	86.1	4.9	49.2	6.7	31.6	2.4	37.5	9.7	16.1

Table 3.2. Maximum loading rate limit per year allowed by USEPA’s Part 503 Rule and total amount of trace elements in 4480 kg calcium silicate slag

	As	Cd	Cr	Cu	Pb	Ni	Zn
	-----kg ha ⁻¹ -----						
Maximum loading rate limit per year	2.0	1.9	150	75	15	21	1.4
Typical slag rate (4480 kg ha⁻¹)	0.011	0.15	0.47	0.029	0.047	0.33	0.18

Table 3.3. Concentration of plant available elements determined by DTPA soil test in the slag, Sharkey clay, and Pahokee muck soils

Elements	Fe	Mn	Co	Cu	Ni	Zn	Cd	Cr	Pb	
	--mg kg ⁻¹ --		-----μg kg ⁻¹ -----							
Slag	128.7	9.2	13.8	8.8	108.1	258.5	6.0	33.5	46.0	
Sharkey clay	55.8	8.8	45.0	1873.3	515.2	998.2	156.2	ND†	1739.0	
Pahokee muck	324.4	2.7	137.4	1890.7	271.3	8610.8	59.7	ND†	751.1	

† ND indicates non-detectable by ICP-MS.

Table 3.4. Analysis of variance for effects of year (2015 or 2016), soil series (Sharkey clay or Pahokee muck), slag rate (0, 1000, 2000, or 4000 mg slag kg⁻¹), application method (surface applied or incorporated), and their interactions on soil pH, plant available Si in soil, Si in plant tissues, and biomass.

Source of variation	P value†							
	Soil pH	Plant available Si	Leaf Si	Stem Si	Leaf biomass	Stem biomass	Rough rice biomass	Brown rice biomass
Year	0.002	0.131	0.114	<0.001	<0.001	<0.001	<0.001	<0.001
Soil	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Slag rate	<0.001	<0.001	<0.001	<0.001	<0.001	0.046	0.293	0.286
Application method	0.105	0.029	0.091	0.013	<0.001	0.781	0.623	0.720
Year × soil	<0.001	0.003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Year × slag rate	0.059	0.843	0.122	0.789	0.514	0.940	0.908	0.861
Year × application method	0.412	0.911	0.342	0.849	0.187	0.708	0.149	0.153
Soil × slag rate	<0.001	0.229	<0.001	<0.001	0.353	0.939	0.889	0.946
Soil × application method	0.826	0.215	0.037	0.004	0.018	0.008	0.548	0.973
Slag rate × application method	0.290	0.483	0.026	0.307	0.417	0.856	0.561	0.410
Year × soil × slag rate	0.329	0.832	0.881	0.268	<0.001	0.005	0.022	0.018
Year × soil × application method	0.001	0.168	0.037	0.709	0.003	0.133	0.550	0.744
Year × slag rate × application method	0.027	0.764	0.066	0.982	0.011	0.065	0.032	0.078
Soil × slag rate × application method	0.003	0.535	0.144	0.924	0.102	0.566	0.597	0.432
Year × soil × slag rate × application method	0.003	0.026	0.727	0.956	0.001	0.195	0.077	0.056

† P value represents adjusted P value generated using Tukey-Kramer method. P value <0.05 indicates significant effect.

Table 3.5. Soil pH of Sharkey clay and Pahokee muck. For each soil, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	2015		2016	
	Surface applied	Incorporated	Surface applied	Incorporated
mg kg⁻¹				
Sharkey clay				
0	6.8 a	6.6 c	6.9 b	6.9 b
1000	6.9 a	7.0 b	7.1 b	7.0 b
2000	7.0 a	7.1 b	7.1 b	7.1 b
4000	7.0 a	7.4 a	7.4 a	7.4 a
Pahokee muck				
0	6.8 a	6.9 a	6.8 a	6.8 a
1000	6.9 a	7.0 a	6.9 a	7.0 a
2000	7.0 a	6.9 a	7.0 a	7.0 a
4000	7.0 a	6.9 a	7.0 a	7.0 a

Table 3.6. Plant available Si, in Sharkey clay and Pahokee muck. For each soil, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	2015		2016	
	Surface applied	Incorporated	Surface applied	Incorporated
	mg kg ⁻¹ -----mg kg ⁻¹ -----			
Sharkey clay				
0	75.3 a	72.4 a	90.9 b	84.2 a
1000	81.0 a	87.5 a	97.7 b	87.6 a
2000	98.9 a	76.4 a	99.1 ab	98.3 a
4000	106.1 a	102.6 a	134.3 a	103.1 a
Pahokee muck				
0	28.3 a	29.3 a	29.9 a	30.5 a
1000	47.2 a	30.9 a	33.5 a	36.0 a
2000	39.5 a	44.9 a	37.0 a	37.7 a
4000	60.3 a	44.8 a	43.2 a	44.9 a

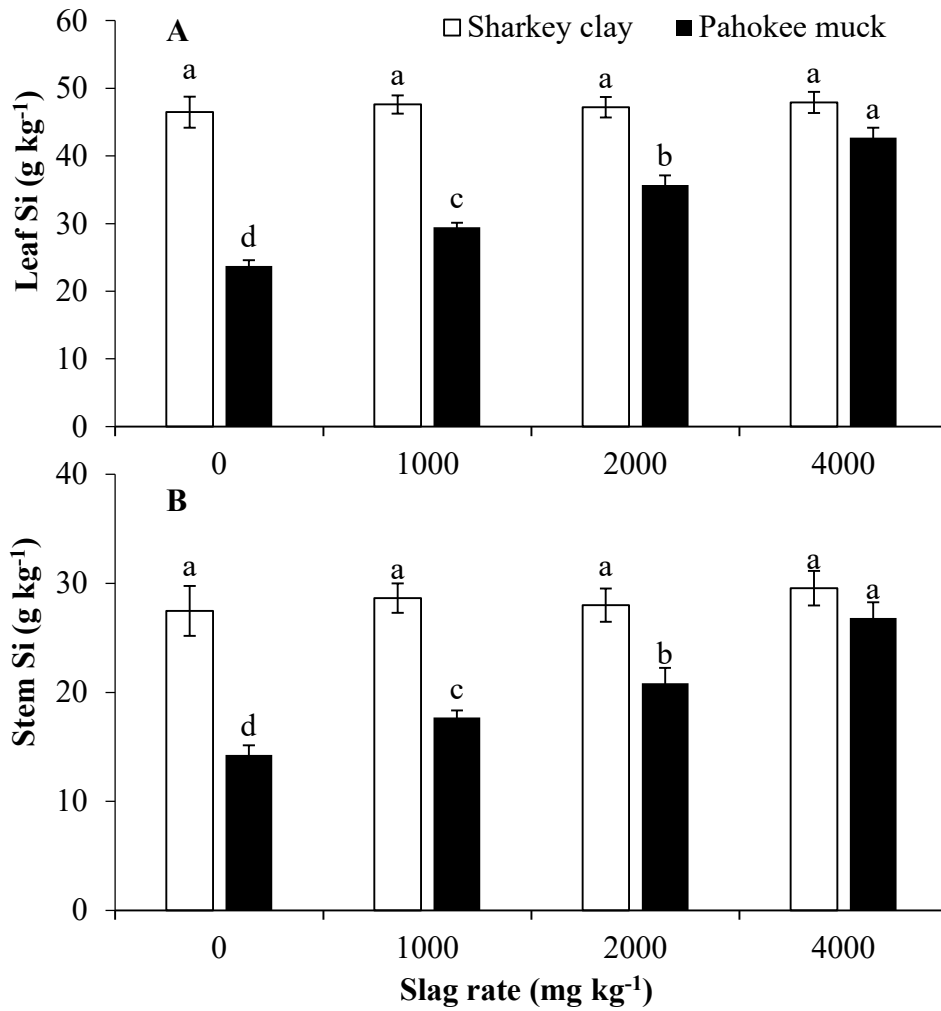


Figure 3.1. Silicon in rice leaf (A) and stem (B). Data were combined for year and application method due to lack of interaction. For each soil, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Table 3.7. Biomass of leaf, stem, rough rice, and brown rice at harvest. Data were combined for application methods due to lack of interaction. For each soil, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	2015				2016			
	Leaf	Stem	Rough rice	Brown rice	Leaf	Stem	Rough rice	Brown rice
mg kg⁻¹	-----g plant⁻¹-----							
Sharkey clay								
0	1.71 a	2.81 a	5.34 a	4.01 a	2.71 b	4.97 a	7.48 a	6.22 a
1000	1.80 a	2.85 a	4.87 a	3.74 a	2.86 ab	5.34 a	7.66 a	6.33 a
2000	1.87 a	3.02 a	4.87 a	3.75 a	2.91 ab	5.53 a	7.60 a	6.52 a
4000	1.90 a	3.09 a	5.19 a	4.16 a	3.04 a	5.76 a	7.90 a	6.26 a
Pahokee muck								
0	1.42 a	2.25 a	4.02 a	3.21 a	1.70 a	3.77 a	4.99 a	4.06 a
1000	1.44 a	2.45 a	4.14 a	3.31 a	1.77 a	3.59 a	5.10 a	4.22 a
2000	1.54 a	2.54 a	4.33 a	3.43 a	1.86 a	3.66 a	5.40 a	4.41 a
4000	1.54 a	2.97 a	4.34 a	3.39 a	1.89 a	3.80 a	5.64 a	4.68 a

Table 3.8. Total concentration of elements in soils at harvest. Data were combined for year and application methods due to lack of interaction. The “-slag” and “+slag” treatments represent untreated control and mean values of the three slag rates, respectively.

Treatment	Total concentration in soils											
	Ca	Mg	P	Fe	Mn	Co	Cu	Ni	As	Cr	Cd	Pb
	g kg ⁻¹				mg kg ⁻¹							
Sharkey clay												
-Slag	2.7	2.6	0.49	11.4	328.3	6.1	12.9	13.9		8.7	82.7	20.0
+Slag	3.3	2.7	0.53	11.5	355.2	6.4	13.8	14.1	ND [†]	8.4	84.5	19.8
Pahoee muck												
-Slag	38.5	5.5	0.91	10.5	81.8	2.2	46.8	4.7	ND	6.6	53.7	12.2
+Slag	38.9	5.3	0.93	10.4	89.2	2.3	47.1	4.7	ND	6.5	57.0	12.3
P value[‡]	0.88	0.75	0.10	0.61	0.20	0.37	0.80	0.29	--	0.93	0.80	0.92

[†] “ND” indicates non-detectable by ICP-AES.

[‡] P values <0.05 indicate significant difference between the “-slag” and “+slag” treatments in each soil.

Table 3.9. Concentration of plant available elements at harvest. Data were combined for year and application method due to lack of interaction. The “-slag” and “+slag” treatments represent untreated control and mean values of the three slag rates, respectively.

Treatment	Plant available concentration in soils					
	Fe	Co	Cu	Cr	Cd	Pb
	-----mg kg ⁻¹ -----					
Sharkey clay						
-Slag	148.7	0.08	3.7	ND†	0.37	20.0
+Slag	147.4	0.06	3.7	ND	0.37	19.8
Pahokee muck						
-Slag	422.4	0.38	2.1	ND	0.80	12.2
+Slag	418.7	0.37	2.6	ND	0.82	12.3
P value‡	0.41	0.55	0.002	--	0.85	0.18

† “ND” indicates non-detectable by ICP-AES.

‡ P values <0.05 indicate significant difference between the “-slag” and “+slag” treatments in each soil.

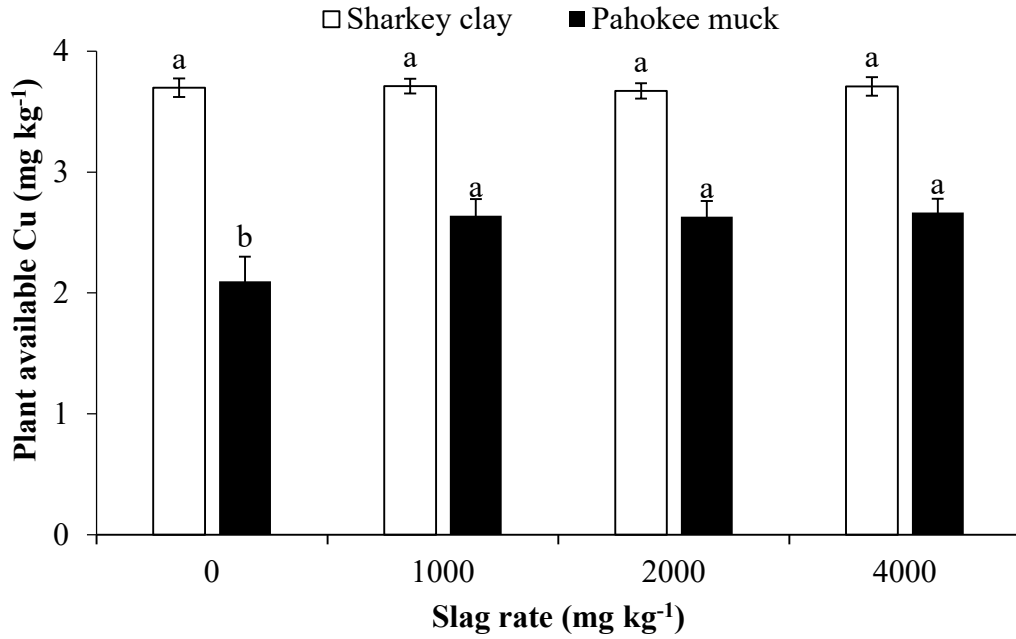


Figure 3.2. Plant available Cu at harvest. Data were combined for year and application method due to lack of interaction. For each soil, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Table 3.10. Plant available Ni and Mn at harvest. Data were combined for application method due to lack of interaction. For each soil, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	2015		2016	
	Ni	Mn	Ni	Mn
	mg kg ⁻¹ -----mg kg ⁻¹ -----			
Sharkey clay				
0	0.98 a	11.9 a	1.12 a	22.6 a
1000	0.84 ab	11.6 a	1.00 a	17.8 ab
2000	0.73 b	9.5 b	0.93 a	16.4 b
4000	0.75 b	9.4 b	0.64 b	11.8 c
Pahokee muck				
0	0.22 a	2.6 a	0.21 a	2.2 a
1000	0.31 a	3.9 a	0.27 a	3.7 a
2000	0.24 a	3.3 a	0.27 a	3.9 a
4000	0.24 a	3.3 a	0.27 a	3.5 a

Table 3.11. Total concentration of elements in brown rice. Data were combined for year and application method due to lack of interaction. The “-slag” and “+slag” treatments represent untreated control and mean values of the three slag rates, respectively.

Treatment	Total concentration in brown rice											
	P	Mg	Ca	Fe	Mn	Co	Cu	Ni	As	Cr	Cd	Pb
	---g kg ⁻¹ ---			-----mg kg ⁻¹ -----								
Sharkey clay												
-Slag	3.1	1.1	134.6	7.0	39.6	6.1	12.9		ND	ND	14.2	0.7
								ND [†]				
+Slag	3.1	1.1	132.9	7.4	32.7	6.4	13.8	ND	ND	ND	15.0	0.5
Pahoee muck												
-Slag	3.4	1.2	156.5	8.4	16.7	2.2	46.8	ND	ND	ND	17.8	0.9
+Slag	3.3	1.2	143.7	7.8	15.5	2.3	47.1	ND	ND	ND	12.2	0.6
P value[‡]	0.07	0.10	0.89	0.36	0.002	0.55	0.71	--	--	--	0.73	0.63

[†] “ND” indicates non-detectable by ICP-AES.

[‡] P values <0.05 indicate significant difference between the “-slag” and “+slag” treatments in each soil.

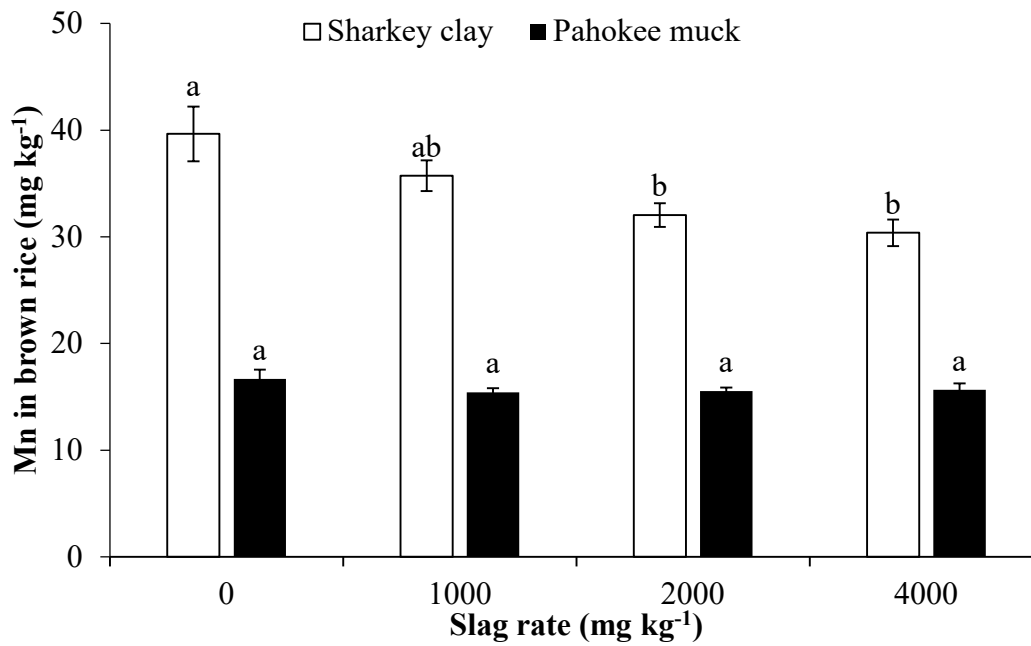


Figure 3.3. Concentration of Mn in brown rice. Data were combined for year and application method due to lack of interaction. For each soil, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Table 3.12. Total concentration of elements in leaf and stem. Data were combined for year and application method due to lack of interaction. The “-slag” and “+slag” treatments represent untreated control and mean values of the three slag rates, respectively.

Treatment	Total concentration in leaf and stem										
	Ca	Mg	P	Fe	Co	Cu	Ni	As	Cr	Cd	Pb
	---g kg ⁻¹ ---		-----mg kg ⁻¹ -----								
Leaf											
Sharkey clay											
-Slag	7.4	3.4	400.9	111.3	ND	2.3	3.8	10.7	6.4	1.1	1.1
+Slag	7.6	3.4	401.0	101.9	ND	2.3	3.0	10.8	5.4	1.5	0.6
Pahokee muck											
-Slag	11.0	4.9	540.5	94.1	ND	2.2	2.6	ND	4.9	3.9	0.6
+Slag	9.6	4.0	509.5	83.3	ND	2.3	2.3	ND	3.7	3.9	0.7
P value [‡]	0.001	0.001	0.67	0.66	0.79	0.86	0.14	0.26	0.35	0.54	0.68
Stem											
Sharkey clay											
-Slag	2.0	2.1	563.5	119.5	ND	5.3	1.4	6.9	1.4	7.5	0.9
+Slag	2.4	2.1	557.6	100.8	ND	5.0	1.4	6.2	1.3	5.6	0.6
Pahokee muck											
-Slag	2.3	2.5	671.2	68.9	ND	4.3	0.8	ND	0.7	6.4	0.9
+Slag	2.2	2.2	628.5	63.1	ND	5.4	1.3	ND	1.2	5.8	0.7
P value [‡]	0.62	0.17	0.92	0.91	0.82	0.58	0.39	0.23	0.71	0.97	0.84

† “ND” indicates non-detectable by ICP-AES.

‡ P values <0.05 indicate significant difference between the “-slag” and “+slag” treatments in each soil.

Table 3.13. Concentration of Mn in leaf and stem. Data were combined for application method due to lack of interaction. For each soil, different letters within each column among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	2015		2016	
	Leaf	Stem	Leaf	Stem
mg kg ⁻¹ -----mg kg ⁻¹ -----				
Sharkey clay				
0	1396.6 a	416.6 a	2222.7 a	585.7 a
1000	1355.9 a	361.5 a	2057.2 a	605.5 a
2000	1160.9 a	390.0 a	1586.5 b	483.2 a
4000	1204.1 a	361.9 a	1330.2 b	489.3 a
Pahokee muck				
0	214.4 a	74.2 a	196.3 a	73.4 a
1000	173.7 a	66.7 a	159.0 a	62.9 a
2000	160.8 a	59.9 a	141.5 a	57.0 a
4000	142.2 a	69.7 a	115.9 a	49.7 a

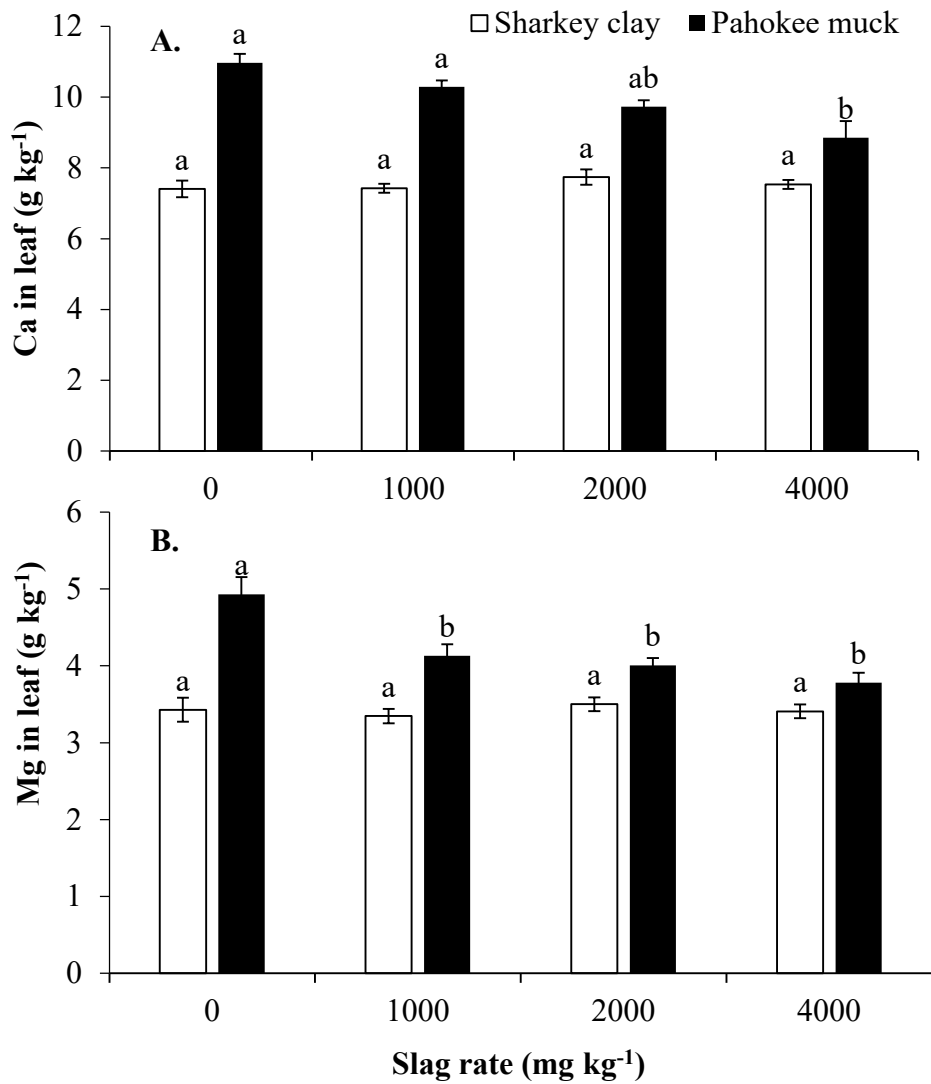


Figure 3.4. Concentration of Ca (A) and Mg (B) in leaf. Data were combined for year and application method due to lack of interaction. For each soil, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

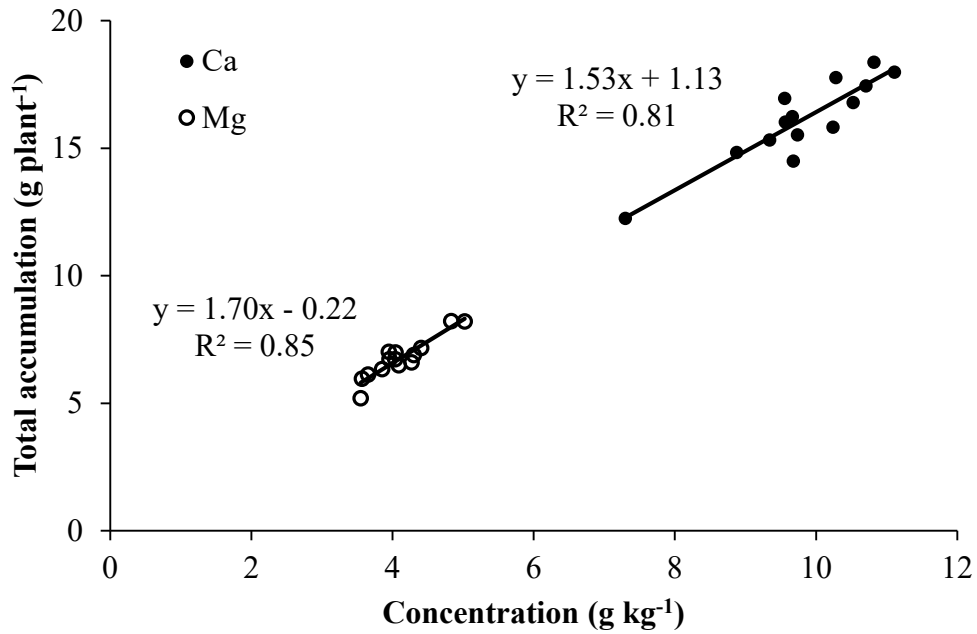


Figure 3.5. Correlation between Ca and Mg concentration and their total accumulation in leaf of rice grown in Pahokee muck. Data were combined for year and application method due to lack of interaction.

Table 3.14. Total radioactivity in soil and brown rice. Data were combined for year and application method due to lack of interaction. The “-slag” and “+slag” treatments represent untreated control and mean values of the three slag rates, respectively.

Treatment	Total radioactivity	
	Soil	Brown rice
mg kg⁻¹	-----Bq g ⁻¹ -----	
Sharkey clay		
-Slag	0.05	0.05
+Slag	0.06	0.06
Pahokee muck		
-Slag	0.04	0.11
+Slag	0.05	0.07
P value†	0.82	0.92

† P values <0.05 indicate significant difference between the “-slag” and “+slag” treatments in each soil.

IV. Effect of calcium silicate slag on drought stress in rice (*Oryza sativa* L.) production

Abstract

Silicon (Si) has been reported to reduce drought stress on many agricultural and horticulture crops. However, limited studies have evaluated this effect with rice. Calcium silicate slag is a good source of Si when applied to rice. In order to determine the role of calcium silicate slag on drought stress in rice production, a greenhouse study was performed. Two moisture regimes (flooding and 50% field capacity), 4 slag rates (0, 1000, 2000, 4000 mg kg⁻¹), and 2 application methods (surface application and incorporation) were evaluated on Sharkey clay, a typical soil for rice cultivation. Results showed that applied slag increased soil pH by 0.1 to 0.5 unit. Plant available Si in the soil and total Si in rice leaf and stem gradually increased with increasing slag rate. Applied slag at the highest rate tended to improve fresh and dry biomass of rice compared to untreated control. When subject to prolonged drought stress, added slag did not affect stomatal conductance or intercellular CO₂, but tended to increase transpiration and photosynthetic rate. Drought stress resulted in higher accumulation of proline, glucose, and fructose in leaf, but sucrose was not affected. Increased carbon isotope discrimination ($\Delta^{13}\text{C}$) suggested better water status of rice subjected to drought stress with supplemental slag, possibly due to Si-induced sugar and proline accumulation in leaf. These results indicate that Si in the slag is available to rice and may help reduce drought stress in rice production.

Key words

Calcium silicate slag; Drought stress; Rice; Proline; Sugar; Carbon isotope discrimination

Introduction

Rice (*Oryza sativa* L.) is an annual grass that has been adapted and bred for flooded culture. An adequate supply of water and timely flooding events are essential for optimum rice production. Drought stress is considered one of the major factors limiting rice productivity. Even mild drought stress can result in significant yield reduction in rice (Centritto et al., 2009). More than 20% of the total rice production area in the world, especially rainfed upland and lowland rice, suffers from drought of different intensities (Pandey, and Bhandari. 2008). Climate change, especially global warming, has exacerbated water shortage and drought, making it an increasingly severe constraint limiting rice production worldwide (Wassmann et al., 2009). Rice produced in the U.S. is almost exclusively grown in a flooded culture. The Mississippi River Valley Alluvial Aquifer is an indispensable water sources for major rice-producing states (e.g., Arkansas and Mississippi) in the U.S. However, water table of this aquifer has been continuously dropping in the past 30 years (Schrader, 2015). Erratic distribution of rainfall in rice growing season as well as declining water table may make rice production in this area more susceptible to drought stress. Due to the unpredictability of drought, improving plant resistance to drought is an important strategy to overcome this problem.

Despite its abundance in the soil, silicon fails to meet the universally adopted definition of essentiality for higher plants as established by Arnon and Stout (1939), except members in the Equisetaceae family (Chen and Lewin, 1969). However, Si has been proved to be beneficial for the healthy growth and development of many plant species, and severe deficiency in Si can cause abnormalities in growth, development or reproduction in many higher plants, particularly rice (*Oryza sativa* L.) and sugarcane (*Saccharum officinarum* L.) in the Gramineae family. Therefore, Si may be considered “quasi-essential” based on the modified definition of essentiality for higher

plants proposed by Epstein and Bloom (2005). In rice, Si has been found to enhance growth and yield (Gascho, 1977; Elawad et al., 1982; Snyder et al., 1986; Anderson et al., 1987), improve light interception of leaf (Ma and Takahashi, 2002), reduce lodging (Idris et al., 1975), and increase resistance to disease and pest (Datnoff et al., 1997; Savant et al., 1997).

Silicon has also been demonstrated to alleviate drought stress in many agriculture and horticulture crops, such as wheat (Gong et al., 2003; Gong et al., 2005), sorghum (Hattori et al., 2005), maize (Kaya et al., 2006), potato (Crusciol et al., 2009), sunflower (Gunes et al., 2008), and rice (Chen et al., 2011). Commonly used sources of Si in these studies include reagent grade silicic acid and potassium/sodium/calcium silicate, which are not usually practical for field-scale delivery.

Calcium silicate slag, which is a byproduct from the refining of phosphate rocks for phosphorus fertilizers, is a potential liming material and a source of Si. Rice and sugarcane grown on organic soils in Florida had greater yield and were less susceptible to disease following pre-plant application of calcium silicate slag (Gascho, 1977; Elawad et al., 1982; Snyder et al., 1986). Few studies have evaluated calcium silicate slag as a source of Si with rice for alleviating drought stress. Therefore, the objectives of this study are to evaluate the potential of using calcium silicate slag to reduce drought stress in rice production and evaluate appropriate slag rates and application methods.

Materials and Methods

A greenhouse study with rice (var. "CL151") was performed at Plant Science Research Center (32.59° N, 85.48° W) at Auburn University, AL. The experiment design was a factorial design with 4 replications using randomized complete block arrangement. Moisture regimes

included flooding, which is typical growth condition for rice, and 50% field capacity, which is considered drought stress. Treatments, including 4 slag rates (0, 1000, 2000, and 4000 mg kg⁻¹) that were either surface applied or incorporated, were evaluated under both moisture regimes on Sharkey clay (very-fine, smectitic, thermic Chromic Epiaquerts), a typical soil for rice culture from Stoneville, MS.

Calcium carbonate equivalent (CCE) of the calcium silicate slag was 58%, indicating it had moderate liming potential. Total Si and plant available Si (i.e., soil test Si) in the slag were 198.3 g Si kg⁻¹ and 139.4 mg Si kg⁻¹, respectively. Soil pH of the Sharkey clay was 7.0. Plant available Si was 73.9 mg Si kg⁻¹, which exceeded the critical value (60 mg Si kg⁻¹) for rice suggested by Korndorfer et al. (2001). Field capacity and permanent wilting point of the Sharkey soil were 39 and 12% water by volume determined using a moisture retention curve (Fig. 1). The drought stress treatment in this study was maintained at 50% field capacity, which was 19.5% volumetric water content in the soil (Fig. 4.1).

Rice was grown in 700 cm³ soil in 10-cm square pot (10.5 × 12.5 cm top and 8.5 × 12.5 cm bottom). Slag was dried at 65°C for 48 h, ground using a pulverizer to pass 2-mm sieve and applied immediately prior to planting. Nine seeds were sown in each pot at planting, and seedlings were thinned to 2 per pot at 21 days after planting (DAP). Soil was initially flooded for 24 h. Then, water was drained, and soil moisture was maintained at field capacity daily using gravimetric method for 4 wk. Permanent flooding and drought stress started at 28 DAP. Flooding was maintained at a standing depth of 3 cm. Urea was surface applied to each pot at a rate of 160 kg N ha⁻¹ immediately before moisture treatments. Zinc sulfate solution was foliar applied at a rate of 1.12 kg Zn ha⁻¹ at 35 DAP. Rice was harvested at 56 DAP. This study was

replicated twice. Planting and harvest occurred on 9 Jun 2016 and 4 Aug 2016 for the 1st replication and 1 Sep 2016 and 27 Oct 2016 for the 2nd replication.

Foliage density, stomatal conductance, intercellular CO₂, transpiration, and photosynthetic rate were measured immediately prior to the moisture treatment and weekly afterward. Foliage density was measured using LAI-2200 plant canopy analyzer (LI-COR Inc., Lincoln, NE). Stomatal conductance, intercellular CO₂, transpiration, and photosynthetic rate were measured on the youngest fully-expanded leaf using LI-6400 portable photosynthesis system (LI-COR Inc., Lincoln, NE).

After harvest, fresh biomass of leaf and stem was recorded, and tissues were collected for Si, proline, neutral sugars, and carbon isotopic composition analysis. Leaf and stem were then dried for 48 h in FreeZone Plus freeze dry system (Labconco Corp, Kansas City, MO), weighed, and ground to fine powder using a coffee grinder (KRUPS Company, Millville, NJ). Proline in fresh leaf was analyzed according to Shabnam et al. (2015). Total Si in rice leaf and stem was determined using molybdenum blue colorimetry following oven-induced digestion (Kraska and Breitenbeck, 2010b). Leaf sugars, including glucose, fructose, sucrose, arabinose, mannose, galactose, and cellobiose, were extracted according to Shanmugavelan et al. (2013) and analyzed using ultra-high performance liquid chromatography with an evaporative light scattering detector (UPLC-ELSD, Waters Corp, Milford, MA). Carbon isotopic composition in dry leaf was analyzed by UC Davis Stable Isotope Facility using PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Carbon isotope discrimination ($\Delta^{13}\text{C}$) was calculated assuming an isotopic composition in ambient air of -8.0‰, using the following equation as defined by Farquhar et al. (1989).

$$\Delta^{13}\text{C}(\text{‰}) = \frac{\delta_a - \delta_p}{1 + \delta_p} \times 1000$$

Where δ_a and δ_p are the isotopic compositions of atmospheric CO₂ and plant, respectively, expressed relative to international standard Pee Dee Belemnite (PDB).

After harvest, soils from each pot were mixed well, dried at 65°C for 48 h, ground using a mortar and pestle, and sieved to pass a 2-mm screen. Soil pH was determined using a 1:2 ratio (w/v) of soil and deionized water (Hue and Evans, 1986). Plant available Si was estimated by extracting with 0.5 M acetic acid (Korndorfer et al., 2001) prior to analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Spectro Ciros CCD, side on plasma, SPECTRO Analytical Instruments Inc., Kleve, Germany).

Mixed model methodology as implemented in SAS PROC GLIMMIX were used to analyze the data (Littell et al., 2006). Replication, moisture regime, slag rate, and application method were treated as fixed effects. Sampling time for foliage density and photosynthetic parameters was treated as repeated measurement. Block was the random effect. To test for differences among main effects and their interactions, the Tukey-Kramer adjustment was applied to the least square means (LSMEANS) statement of SAS 9.4 software (SAS Institute Inc., Cary, NC, USA).

Results and discussion

Main effect of replication and its interactions with other factors (i.e., moisture regime, slag rate, application method, and sampling time) in this study were not significant. Therefore, data were combined for the two replications in the following analysis.

Soil pH

Soil pH has strong influence on availability of many essential plant nutrients; therefore, effect of slag supplementation on soil pH was first evaluated. Slag rate \times application method interaction was significant ($P = 0.009$). Soil pH gradually increased with increasing slag rate for both application methods, and the trend was more evident for incorporated slag (Fig. 2), which was expected. Although the pH increase was significant for these treatments, the maximum pH increases (i.e., between control and highest slag rate) were 0.1 to 0.3 unit for surface-applied slag and 0.2 to 0.5 units for incorporated slag (Fig. 4.2).

Plant available Si and Si in plant tissue

Bioavailability of Si was evaluated by estimating plant available Si in the soil and measuring Si in plant tissue. There was a significant moisture regime \times slag rate \times application method interaction for plant available Si ($P = 0.001$). Slag supplementation gradually increased plant available Si under both moisture regimes, and the strongest trend occurred under drought stress when slag was surface applied (Fig. 4.3A). Plant available Si was greater in soils amended with surface-applied slag than incorporated slag at higher slag rates (i.e., 2000 and 4000 mg kg⁻¹) under drought stress (Fig. 4.3B). Since water was supplied daily during this study, surface-applied slag may be gradually dissolving and leaching into the soil with each watering event, resulting a higher plant available Si in the soil. In contrast, leaching away from slag particles during dissolution is minimal under flooding and slag incorporation.

Significant moisture regime \times slag rate interaction was observed for both leaf ($P = 0.022$) and stem Si ($P = 0.045$). Rice subjected to drought stress accumulated 64 and 49% less Si in leaf and stem relative to flooded rice (Fig. 4.4), indicating drought stress severely restricted Si

availability to rice. With supplemental slag, Si in rice leaf tended to increase under both flooded and drought stress (Fig. 4.4A). Silicon in water-deficient rice stem also tended to increase (Fig. 4.4B). When exposed to drought stress, supplemental slag at 4000 mg kg⁻¹ increased leaf and stem Si by 25 and 23% relative to untreated control. Similar results were reported by Chen et al. (2011) in rice. In the U.S., a commonly used criterion to evaluate Si sufficiency in harvested rice straw is 50 g Si kg⁻¹ (De Datta, 1981), but a critical value for early season sampling has not been established. A survey by Kraska and Breitenbeck (2010a) showed that low early season Si assimilation was common, and average Si in mature straw was ~79% higher than in the youngest fully expanded leaf at mid-tillering. According to this study, estimated Si in mature straw of flooded rice in the current study would be 65 to 72 g Si kg⁻¹, indicating sufficient Si supply by this mineral soil. When exposed to drought stress, Si in mature straw would be estimated at 23 to 28 g Si kg⁻¹, which is ~50% lower than the critical level. Higher slag rates may be necessary to ensure adequate Si supply when water supply is deficient. Release of Si from the slag is dependent on the water available for slag dissolution; thus complete amelioration of drought stress with slag is unlikely.

Plant biomass

Significant moisture regime × slag rate interactions were observed for both fresh and dry biomass ($P < 0.05$). Under flooded condition, slag applied at 4000 mg kg⁻¹ significantly increased fresh and dry biomass of leaf and stem compared to untreated control (Table 1). Typically, shoot growth tends to be retarded when plants are exposed to drought stress. This was observed as control plants were 38 and 53% lower in fresh leaf and stem biomass, and 43, 40, and 37% lower in dry leaf, stem, and root biomass. Under flooded condition, both fresh and dry biomass of leaf and stem increased with applied slag at 4000 mg kg⁻¹. Although there was a trend

of increasing fresh leaf and stem biomass with supplemental slag under drought stress, no significant increase was observed, except for leaf dry biomass (Table 4.1). Slag amendments also tended to increase root biomass of rice grown under drought stress. Chen et al. (2011) also found that supplemental Si improved anatomical traits of rice root (e.g., length and volume) under drought stress. Improved root traits may help improve water and nutrients accessibility under drought stress.

In general, plants tend to inhibit shoot growth and improve root growth at suboptimal water availability and thus have a lower shoot/root ratio. In this study, shoot/root ratio was significantly lower for drought-stressed rice. However, shoot/root ratio was not affected by slag application, regardless of moisture regime. This is possibly resulting from continued shoot growth and enhanced root growth with slag application (Table 4.1). Similar result was reported by Sonobe et al. (2010) in sorghum.

Foliage density and photosynthesis

Foliage density and photosynthetic indicators (i.e., stomatal conductance and intercellular CO₂) were used to further evaluate the response of the plant to drought over the various slag rates. A moisture regime × slag rate interaction ($P = 0.046$) was noted for foliage density, thus data were combined for application methods and sampling times. Under flooded condition, foliage density was not affected by slag rate. Applied slag tended to increase foliage density of drought-stressed rice, but significant increase from the control only occurred at the highest slag rate (Fig. 4.5). Similar observation in rice was reported by Idris et al. (1975). This may be attributed to increased leaf erectness resulting from increased leaf Si under drought stress condition.

Drought stress significantly decreased stomatal conductance (75 to 83%) and intercellular CO₂ (10 to 12%) compared to flooding, regardless of Si application ($P < 0.01$). Supplemental slag showed no pronounced effect on stomatal conductance or intercellular CO₂ of drought-stressed or flooded rice (Table 4.2). Moisture regime \times slag rate \times sampling time interaction was significant for transpiration ($P < 0.001$) and photosynthetic rate ($P = 0.018$), thus data were interpreted separately by sampling time. Drought stress resulted in reduced transpiration and photosynthetic rates relative to flooding for all slag treatments (Table 4.3 and 4.4). When water supply was adequate, transpiration and photosynthetic rate were not influenced by slag application. Under drought stress, transpiration and photosynthetic rate were not affected by slag supplementation initially, but as drought stress prolonged (i.e., 3 and 4 wk), rice grown in slag-amended soils tended to have higher transpiration and photosynthetic rate (Table 4.3 and 4.4).

Previous research showed that the transpiration and photosynthetic rate of drought-stressed rice decreased with supplemental Si, possibly due to stomata closure resulting from deposited Si beneath the cuticle of the leaves (Agarie et al., 1998; Ma et al., 2001). In contrast, other studies found that supplemental Si increased transpiration and photosynthetic rate in rice (Chen et al., 2011), sorghum (Hattori et al., 2005, 2007), and wheat (Gong et al., 2003) under water-deficient condition. Inconsistent results of these studies indicate that the mechanism underlying positive impacts of Si on plants under drought stress condition are poorly understood. Hattori et al. (2008) suggested that the Si-induced reduction of drought stress was independent of leaf water status.

Carbon isotope discrimination ($\Delta^{13}\text{C}$), proline, and sugars in leaf

The correlation between water use efficiency and $\Delta^{13}\text{C}$ has been extensively studied in many crops, especially C3 crops such as wheat (Farquhar and Richards, 1984; Condon et al.,

1990), peanut (Hubick et al., 1986; Wright et al., 1994), cowpea (Ismail and Hall, 1993), and rice (Impa et al., 2005). Plants subjected to drought stress have lower $\Delta^{13}\text{C}$ (Farquhar et al., 1989). The $\Delta^{13}\text{C}$ in leaf tissue of flooded rice was not significantly affected by slag application. Rice exposed to water deficit tended to have lower $\Delta^{13}\text{C}$ in leaf tissue than those under flooding; however, $\Delta^{13}\text{C}$ increased with increasing slag rate, suggesting that drought stress was less evident with supplemental slag (Table 4.5).

Compatible solutes, such as proline, a non-protein amino acid, and sugars, act as osmotic regulators and tend to accumulate in leaf when plants are subjected to drought stress (Greenway and Munns, 1980). Water deficit resulted in higher proline concentrations in rice leaves than those under flooded conditions, regardless of slag application (Fig. 4.6), which suggests plants were under drought stress. Proline in fresh leaf showed no response to slag application under flooded condition. Decreased proline with increasing slag rate was observed in fresh leaf of rice exposed to drought stress (Fig. 4.66), suggesting a reduction in drought stress due to applied slag. Supplemental Si was found to produce higher leaf proline concentration in potato (Crusciol et al., 2009), chickpea (Gunes et al., 2007), and sunflower (Gunes et al., 2008) under drought stress, which is inconsistent with the current study.

Among all seven sugars analyzed in this study, only glucose, fructose, and sucrose were detectable in leaf. When exposed to drought stress, more glucose ($P < 0.01$) and fructose ($P < 0.01$) were accumulated in rice leaf, but sucrose was not affected relative to flooded rice ($P = 0.29$; Table 4.6). This result is consistent with previous research on wheat (Xue et al., 2008). Other studies using sunflower (Fulda et al., 2011) and peanut (Uppala et al., 2013) found increased sucrose in addition to glucose and fructose in leaf when exposed to drought stress. Without supplemental Si (i.e., the control plants), drought-stressed leaf tended to accumulate less

sucrose and more glucose and fructose than flooded leaf (Table 4.6). Application of slag did not affect the sugar composition of the leaves in the flooded treatment. Under drought conditions, sugar concentrations increased, although only the highest slag rate was significantly higher than the control (Table 4.6). Applied slag increased sucrose concentration in drought-stressed leaf to a comparable level in flooded leaf.

Crusciol et al. (2009) observed higher proline but lower total sugars in potato leaves that received Si than those did not, when exposed to water deficit. Possible explanation for the opposite trend of proline and sugar is that they compete for carbon skeletons. In the current study, sugars may play a dominant role in osmotic adjustment, as their total concentration was higher than the proline. Negative effect of decreased proline with increasing slag rate may be offset by increased sugars; therefore, overall water status in slag-amended rice was still improved relative to untreated control under drought stress condition. The mechanisms of Si-induced sugar and proline accumulation in leaves are still largely unknown and are worthy of further study.

Conclusion

Applied calcium silicate slag slightly increased soil pH (≤ 0.5 unit) under both flooded and drought conditions, indicating it has minimum liming ability. Calcium silicate slag provided Si available for rice uptake under flooded and water-deficit conditions. When exposed to drought stress, rice amended with the slag showed better water status, suggesting calcium silicate slag may help reduce drought stress in rice production. In this study, significant different results typically occurred at the highest slag rate, which was equivalent to 8960 kg ha^{-1} in field production. Since surface applied slag was found to be more effective on increasing plant available Si in the soil than incorporated slag, calcium silicate slag may be broadcasted prior to

planting at a rate of 8960 kg ha⁻¹ in field production to ensure adequate Si supply and prevent drought stress.

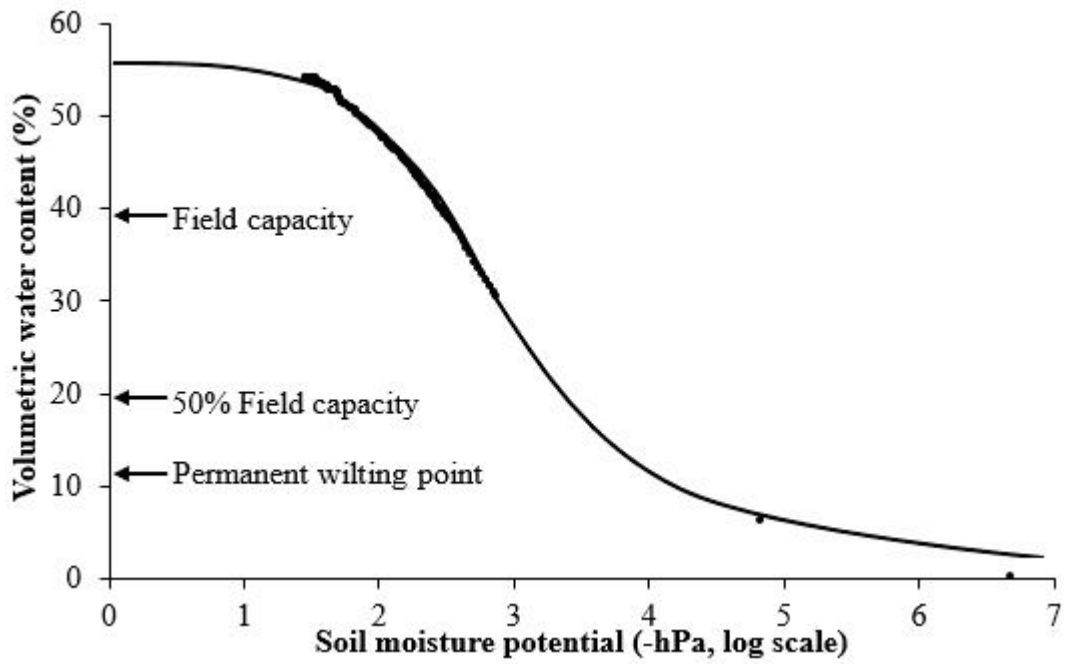


Figure 4.1. Water retention curve of Sharkey clay using Van Genuchten model

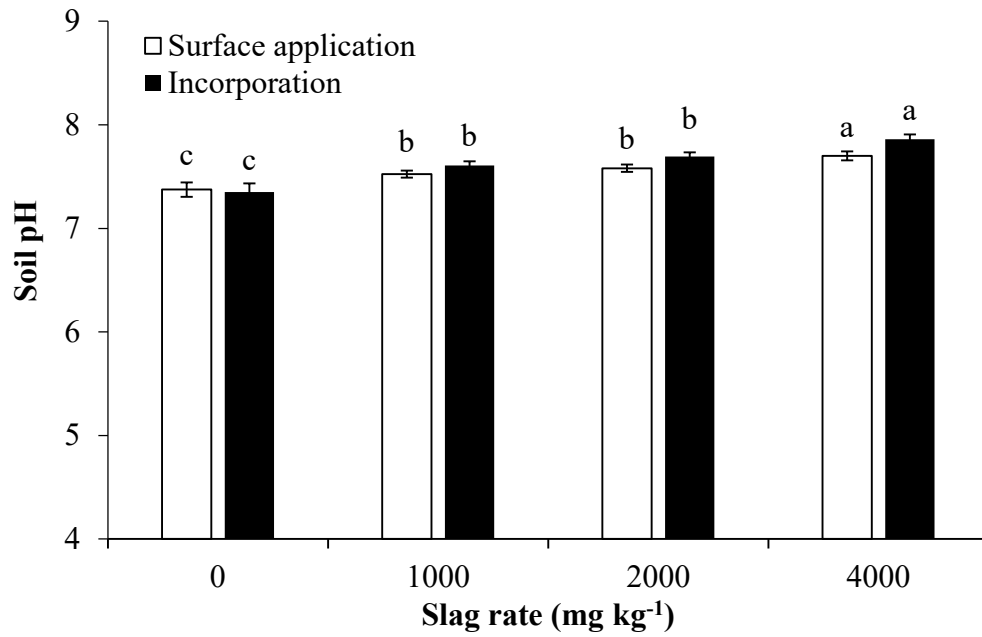


Figure 4.2. Soil pH at harvest. Data were combined for replications and moisture regimes due to lack of interaction. For each application method, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

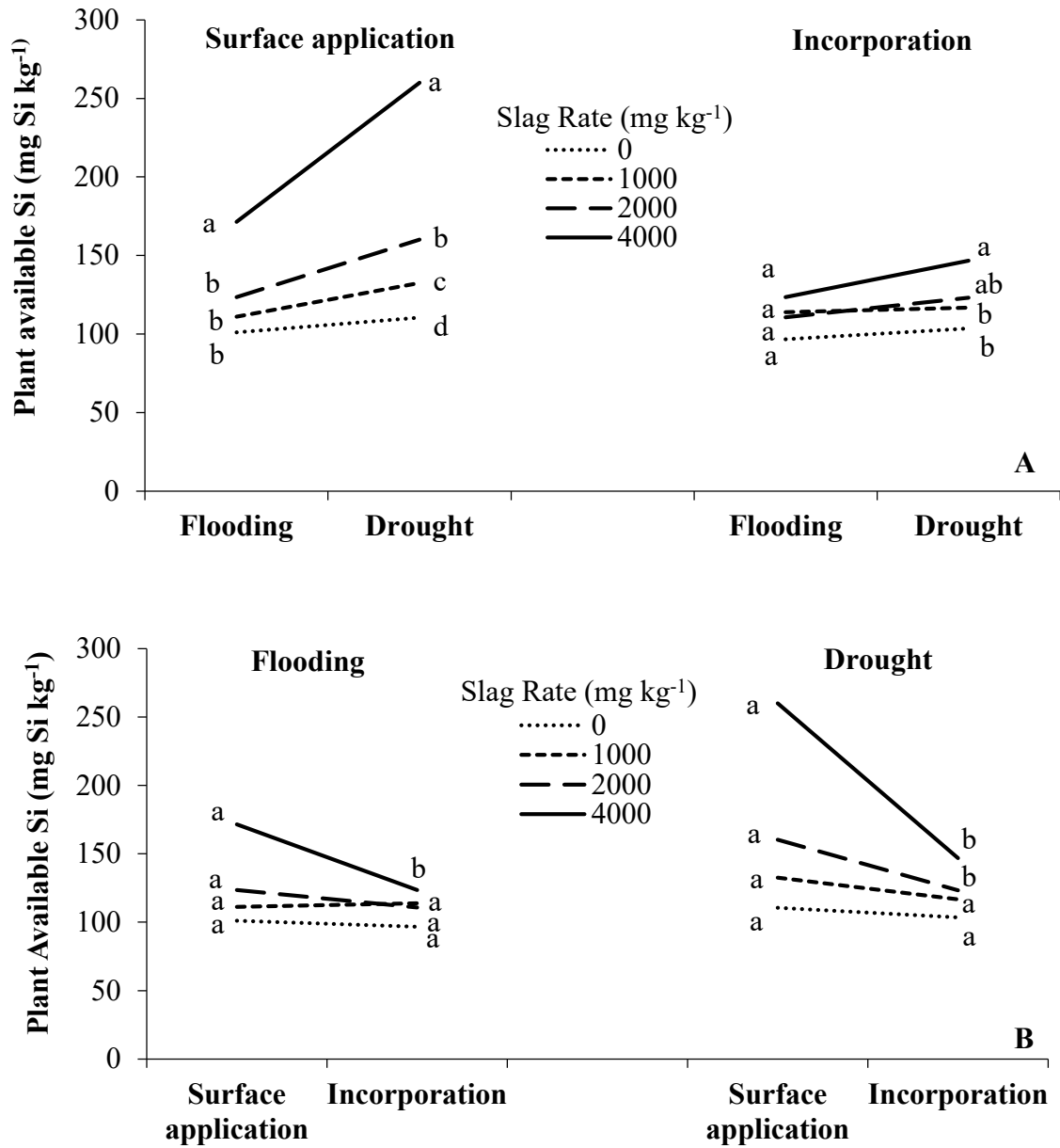


Figure 4.3. Plant available Si (0.5 M acetic acid soil extract) at harvest. Data were combined for replications due to lack of interaction. Different letters among slag rates (A) and between application methods (B) indicate significant difference at $\alpha=0.05$ level.

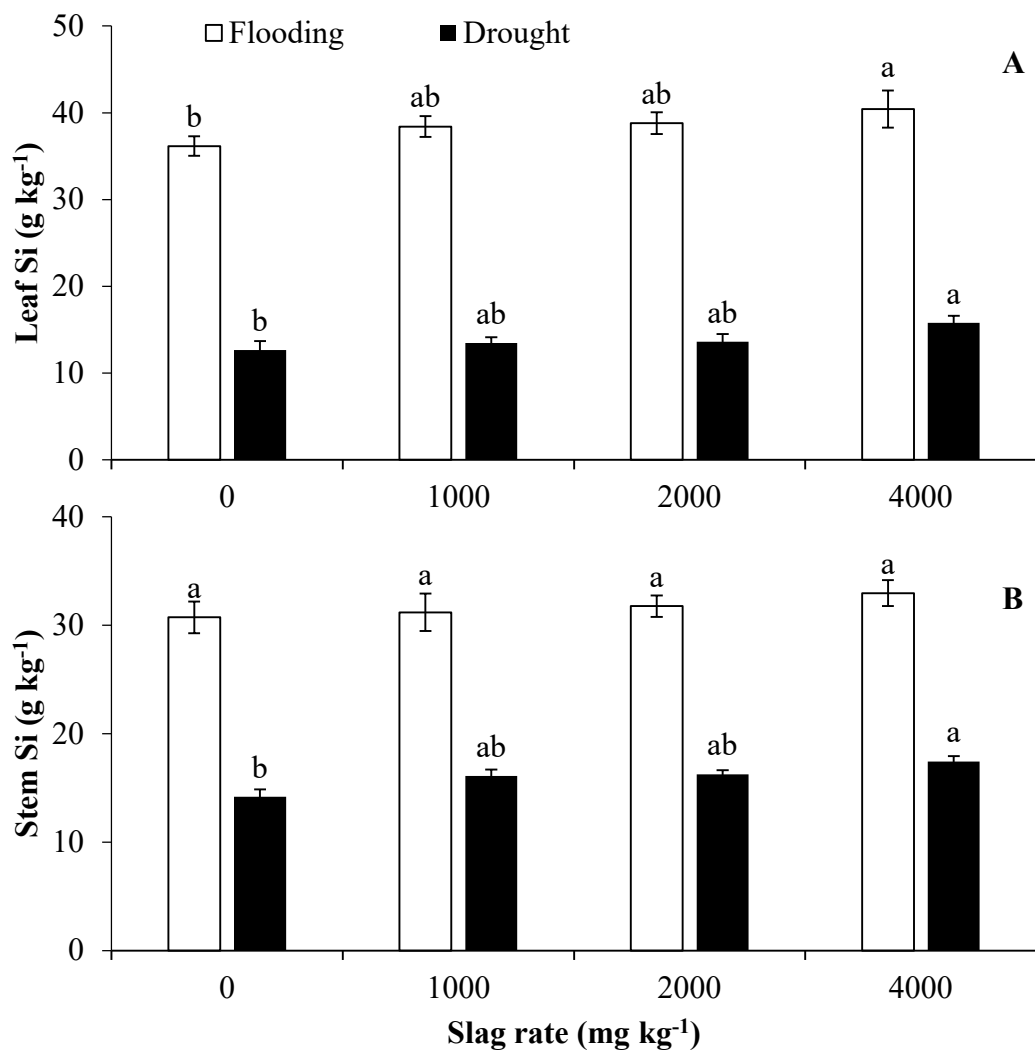


Figure 4.4. Leaf (A) and stem (B) Si at harvest under flooded and drought stress conditions. Data were combined for replications and application methods due to lack of interaction. For each moisture regime, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Table 4.1. Fresh and dry biomass of rice at harvest. Data were combined for replications and application methods due to lack of interaction. For each moisture regime, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	Fresh biomass		Dry biomass			
	Leaf	Stem	Leaf	Stem	Root	Shoot/root
mg kg⁻¹	----g plant ⁻¹ ----		-----g plant ⁻¹ -----			
Flooding						
0	2.79 b	6.26 b	0.63 b	1.36 b	0.60 ab	3.37 a
1000	2.73 b	6.15 b	0.60 b	1.30 b	0.57 b	3.36 a
2000	2.95 ab	6.34 b	0.62 b	1.36 b	0.56 b	3.57 a
4000	3.10 a	6.97 a	0.72 a	1.51 a	0.69 a	3.33 a
Drought						
0	1.74 a	2.92 a	0.36 b	0.81 a	0.38 b	3.19 a
1000	1.70 a	2.91 a	0.36 b	0.82 a	0.42 ab	2.76 a
2000	1.81 a	3.03 a	0.37 b	0.87 a	0.45 a	2.77 a
4000	1.91 a	3.31 a	0.47 a	0.94 a	0.44 ab	3.16 a

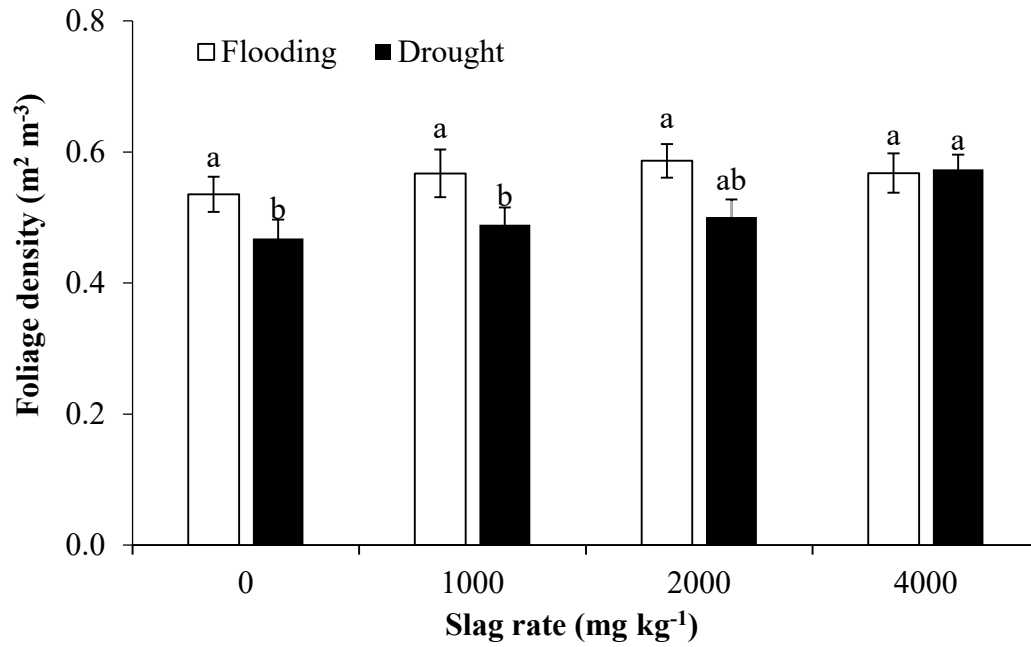


Figure 4.5. Foliage density of rice plant. Data were combined for application methods and sampling times due to lack of interaction. For each moisture regime, different letters among slag rate indicate significant difference at $\alpha=0.05$ level.

Table 4.2. Stomatal conductance and intercellular CO₂ of rice leaf. Data were combined for application method and sampling time due to lack of interaction. Different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	Stomatal conductance		Intercellular CO₂	
	Flooding	Drought	Flooding	Drought
mg kg⁻¹	--mmol H₂O m⁻² s⁻¹--		--μmol CO₂ mol⁻¹--	
0	0.87 a	0.22 a	415.1 a	369.3 a
1000	0.83 a	0.17 a	425.6 a	378.2 a
2000	0.87 a	0.15 a	414.4 a	366.3 a
4000	0.83 a	0.17 a	410.6 a	369.5 a

Table 4.3. Transpiration of rice leaf at different sampling time. Data were combined for replications and application methods due to lack of interaction. For each moisture regime, different letters among slag rates indicate significant differences at $\alpha=0.05$ level.

Slag rate	Transpiration rate				
	0 wk [†]	1 wk	2 wk	3 wk	4 wk
mg kg⁻¹	-----mmol H ₂ O m ⁻² s ⁻¹ -----				
Flooding					
0	5.85 a	7.77 a	13.13 a	8.85 a	11.33 a
1000	5.93 a	7.54 a	12.92 a	9.22 a	11.54 a
2000	5.84 a	7.41 a	13.07 a	8.57 a	11.14 a
4000	5.49 a	7.94 a	14.86 a	8.89 a	11.30 a
Drought					
0	4.71 a	1.49 a	7.62 a	3.00 b	5.36 b
1000	5.18 a	1.73 a	7.33 a	3.66 ab	5.28 b
2000	5.11 a	1.82 a	7.41 a	4.73 a	5.81 ab
4000	5.13 a	2.11 a	7.82 a	5.28 a	6.53 a

[†] “0 wk” indicates immediately prior to moisture treatments.

Table 4.4. Photosynthetic rate of rice leaf at different sampling time. Data were combined for replication and application method to lack of interaction. For each moisture regime, different letters among slag rates indicate significant differences at $\alpha=0.05$ level.

Slag rate	Photosynthetic rate				
	0 wk [†]	1 wk	2 wk	3 wk	4 wk
mg kg ⁻¹	----- $\mu\text{mol CO}_2 \text{ mol}^{-1} \text{ s}^{-1}$ -----				
Flooding					
0	28.46 a	44.86 a	51.00 a	34.21 a	39.93 a
1000	27.84 a	40.94 a	49.76 a	35.01 a	35.77 a
2000	33.64 a	42.68 a	52.39 a	33.57 a	36.08 a
4000	29.11 a	45.85 a	54.83 a	33.12 a	36.52 a
Drought					
0	33.11 a	31.15 a	41.04 a	24.18 b	25.51 b
1000	29.59 a	31.46 a	43.12 a	25.95 ab	26.37 b
2000	32.22 a	30.77 a	44.83 a	28.18 ab	27.78 b
4000	29.72 a	29.15 a	45.40 a	30.51 a	33.57 a

[†] “0 wk” indicates immediately prior to moisture treatments.

Table 4.5. Carbon isotope discrimination ($\Delta^{13}\text{C}$) in rice leaf. Data were combined for replication and application method due to lack of interaction. Different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	Flooding	Drought
mg kg⁻¹	-----‰-----	
0	23.334 a	22.269 b
1000	23.311 a	22.467 ab
2000	23.192 a	22.542 a
4000	23.224 a	22.620 a

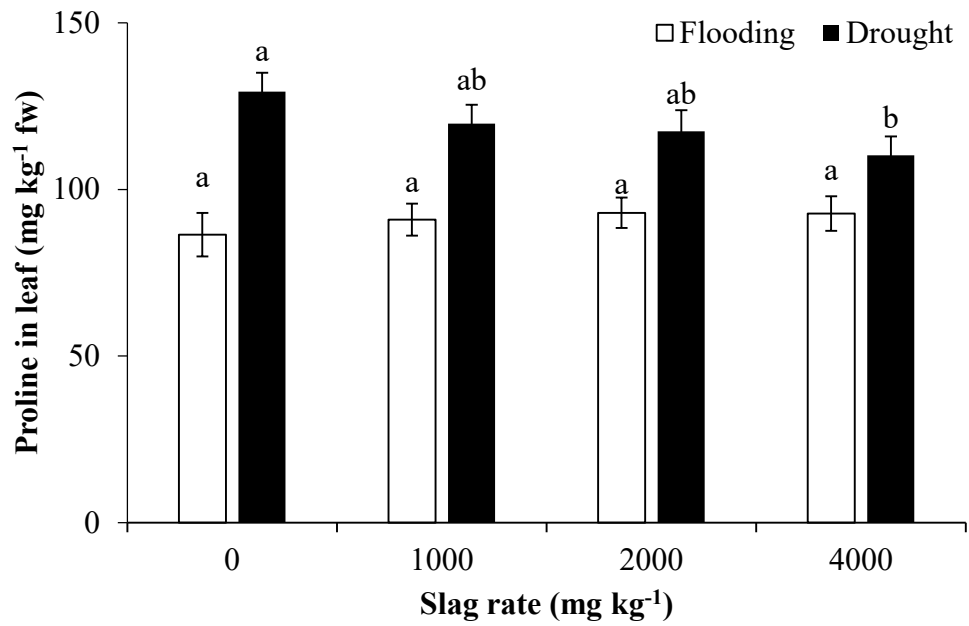


Figure 4.6. Proline in rice fresh leaf. Data were combined for application method due to lack of interaction. For each moisture regime, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Table 4.6. Sugars in rice leaf. Data were combined for replication and application method due to lack of interaction. For each moisture regime, different letters among slag rates indicate significant difference at $\alpha=0.05$ level.

Slag rate	Glucose		Fructose		Sucrose	
	Flooding	Drought	Flooding	Drought	Flooding	Drought
mg kg ⁻¹	-----g kg ⁻¹ dw-----					
0	10.6 a	13.5 b	9.7 a	12.5 b	55.9 a	43.2 b
1000	12.2 a	15.2 ab	10.8 a	13.5 ab	54.0 a	51.7 b
2000	13.2 a	15.4 ab	11.4 a	14.6 ab	60.8 a	54.9 ab
4000	13.0 a	17.7 a	12.6 a	15.9 a	59.6 a	60.7 a

V. Conclusion

Industrial byproducts have substantial values in agriculture as liming amendments. The RNV does a good job estimating the effectiveness of ground limestone and industrial byproducts provided that the particle size estimates are accurate. Assuming the moisture content was reduced, the papermill lime mud has calcium carbonate equivalent (CCE) and particle size that is superior to conventional ground limestone and could be a suitable substitutional liming material. The calcium silicate slag from phosphorus fertilizer industry (P slag) also has the potential to be a good liming agent, provided the particle size can be reduced to < 2 mm. Other byproducts have restrictions (e.g., low liming ability and/or high trace metals) likely limiting their usage as liming material.

The P slag can also be used as a source of Si for rice production. The trace contaminants (e.g., heavy metals and radioactive elements) in the slag are unlikely to cause environmental risks or polluted food due to their low content in slag and minimal uptake by the plant. The P slag also provides beneficial effects on mitigating drought stress in rice production. The typical rate for the slag, 4480 kg ha^{-1} , is possibly an adequate rate to reduce drought stress in rice production. The surface-applied and incorporated slag showed similar performance, except that surface application is more effective in increasing plant available Si. Therefore, the P slag may be broadcasted at planting to ensure adequate Si supply and prevent drought stress in field production.

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