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A Review of Silicon in Soils and Plants and Its Role in US Agriculture: History and Future Perspectives

Brenda S. Tubana,[1] Tapasya Babu,[2] and Lawrence E. Datnoff[3]

Abstract: Silicon (Si) is the second most abundant element in the earth's crust and plays a number of important roles in the mineral nutrition of plants. In the past 20 years, the scientific documentation on the benefits of Si to crops has helped establish Si fertilization as an agronomic practice in many agricultural lands worldwide. However, very little information has been consolidated on the use of Si specifically for US agriculture. Consequently, the objectives of this review are to provide (1) information on the dynamics of Si in soil, use, and sources; (2) a history and up-to-date documentation on Si-related research in many areas of US production agriculture; and (3) perspectives on Si as a plant beneficial nutrient and the potential of Si fertilization as an agronomic practice in US crop production systems. The Si-driven mechanisms enhancing the productivity of a wide array of crops under stressed conditions are discussed in this review. Based on the recent 10-year average production level and published shoot Si content, the principal crops grown in the United States can collectively take up 9.55 million tons of Si annually, whereas the annual Si removal rate for the entire US cropland area is estimated at 21.1 million tons. On the basis of this projected annual Si removal rate, adoption of continuous intensive farming systems in the country, low solubility of soil Si, and complex chemical dynamics of Si in soil, increasing plant-available Si levels through fertilization is therefore foreseen a logical agronomic practice for US agriculture.

Key Words: Crop production, fertilizer, monosilicic acid, nutrient, silicon, soil fertility

(*Soil Sci* 2016;181: 00–00)

Silicon (Si) is the second most abundant element in the earth's crust, almost exclusively found in the form of silicon dioxide (SiO_2) in association with a wide array of Si-bearing minerals in crystalline, poorly crystalline, and amorphous phases (Sommer et al., 2006). In the early 1900s, Si was recognized as one of the 15 elements needed for plant life (Halligan, 1912). However, to date, the essentiality of Si is only known for diatoms, scouring rushes, and other members of the yellow-brown or golden algae (Epstein, 1999). Its essentiality for higher plants remains questionable because of the lack of evidence showing Si's direct role in plant metabolism and production of Si-bearing organic compounds (Ma et al., 2001; Knight and Kinrade, 2001; Ma and Takahashi, 2002; Richmond and Sussman, 2003). Nevertheless, because of the logically flawed definition of essentiality of nutrients (Epstein, 1999), Si being a major inorganic constituent in higher plants, and the significant amount of evidence showing the value of Si in improving crop productivity (Epstein, 1994; Keeping et al., 2009; Meyer and Keeping, 2005; Snyder et al., 2007), the application of Si fertilizers today is very common in many crop production systems worldwide.

The importance of Si as a nutrient in crop production is among the most valued roles of Si to humans. According to FAOSTAT (2014), the most produced crops in the world in 2012 included grain crops (wheat, *Triticum aestivum* and rice, *Oryza sativa*) and sugarcane (*Saccharum officinarum*) (Fig. 1). Based on the estimated Si content of these crops (Hodson et al., 2005), seven are classified as Si accumulators—plant species that accumulate more than 1.0% Si on dry matter basis. Crops can remove as much as 210 to 224 million tons Si per year worldwide (Bazilevich et al., 1975; Reimers, 1990; Savant et al., 1997a).

The only place in the United States where Si fertilization is an established agronomic practice is in the Everglades Agricultural Area (EAA) in south Florida, used mainly in the production of sugarcane and rice. Many agricultural-based research studies involving Si started decades ago in this region. Currently, a large number of research projects on Si are happening in many parts of the United States because of the vast amount of research demonstrating the element's benefits to plant development and performance. In addition, the progress of Si research was recently highlighted by the Association of American Plant Food Control Officials officially designating Si as a plant "beneficial substance" followed by recognition of the official method (5-Day Na_2CO_3-NH_4NO_3–soluble Si extraction method) for quantifying soluble Si in solid fertilizer products (Sebastian, 2012; Sebastian et al., 2013). Now, Si may be sold as a fertilizer in the United States. Recently, the International Plant Nutrition Institute included Si in their fact sheet series—Nutri-Facts, further highlighting the importance of Si in plant nutrition especially under stressful conditions (http://www.ipni.net/nutrifacts-northamerican).

The documentation on the progress of Si research in agriculture has been assembled to view its value on a global perspective; however, no work has been done so far to consolidate Si research findings for US agriculture. This review contains information on the dynamics of Si in plant and soil, its uses, and sources along with a comprehensive history and up-to-date documentation on past and current Si research in US agriculture. In addition, the principal types of crops and soils of US lands, perspectives on Si as a plant-beneficial nutrient in US crop production systems, and the potential of Si fertilization as a viable, environment-friendly, and profitable agronomic practice are discussed in this review.

Abundance, Occurrence, and Dynamics of Si in Soil

The pedosphere of the earth's crust consists on average of 28% Si by weight ranging from 0.52% to 47%: traces of Si are

[1]Soil Science, School of Plant, Environmental, and Soil Sciences, Louisiana State University Agricultural Center, Baton Rouge, LA.
[2]Soil Science, Department of Soil and Crop Sciences, Cornell University, Ithaca, NY.
[3]Plant Pathology, Department of Plant Pathology and Crop Physiology, Louisiana State University Agricultural Center, Baton Rouge, LA.
Address for correspondence: Brenda S. Tubana, PhD, Soil Science, School of Plant, Environmental, and Soil Sciences, Louisiana State University Agricultural Center, 104 Sturgis Hall, Baton Rouge, LA 70803. E-mail: btubana@agcenter.lsu.edu
Financial Disclosures/Conflicts of Interest: *This review article was partially funded by Edward C. Levy Co. Received 06-08-2016.*
Received June 8, 2016.
Accepted for publication September 18, 2016.

ISSN: 0038-075X
DOI: 10.1097/SS.0000000000000179

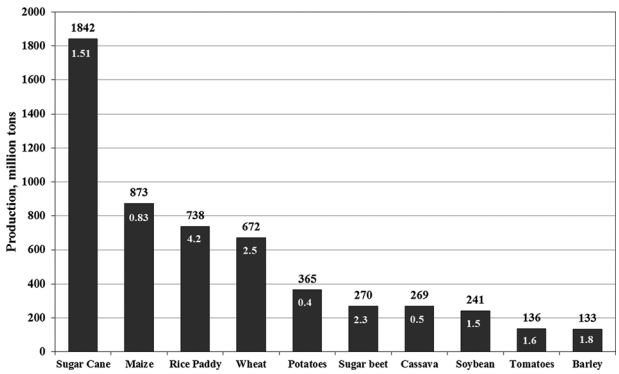

FIG. 1. Top 10 produced crops in the world in 2012. Seven of these crops are classified as Si accumulators (>1.0% Si in dry matter). The values inside the bar are the reported shoot Si content by Hodson et al. (2005).

commonly present in carbonaceous rocks such as limestones and carbonites, whereas rocks such as basalt and orthoquartzite contain high concentrations of Si (23%–47%) (McKeague and Cline, 1963; Wedepohl, 1995; Monger and Kelly, 2002). The chemical weathering of silicate-containing minerals is the ultimate source of dissolved Si (as monosilicic acid, H_4SiO_4), which contributes to continental soil formation through linked biogeochemical reactions (Basile-Doelsch et al., 2005). Silicon release to soil solution from weathering of silicate-containing minerals is rather slow and is governed by precipitation and neoformation of authigenic Si constituents, Si adsorption/desorption on various solid phases, uptake and assimilation by vegetation and microorganisms, preservation of stable Si forms in the profile, and addition from external atmospheric inputs (Cornelis et al., 2011). These are linked processes, and the largest interpool Si transfer takes place between biomass (biogenic silica from phytoliths and microorganisms) and soil solution (dissolved Si in the form of H_4SiO_4) at rates ranging from 1.7 to 5.6 $\times$ 10^{12} kg Si y^{-1} (Conley, 2002). In the ocean, the largest interpool Si transfer is between biogenic silica from diatoms and dissolved Si at 6.7 $\times$ 10^{12} kg Si y^{-1} (Tréguer et al., 1995; Matichencov and Bocharnikova, 2001). Laruelle et al. (2009) estimated that the amount Si transformed into biogenic silica averages 2.5 $\times$ 10^{12} kg y^{-1}.

Silicon in soils is grouped into liquid, adsorbed, and solid phase fractions. The composition of these fractions of Si compounds in the soil is presented in Fig. 2 (Matichencov and Bocharnikova, 2001; Sauer et al., 2006). The solid Si phase consists of poorly crystalline and microcrystalline, amorphous, and crystalline forms of Si. The largest solid phase fraction of Si occurs in crystalline forms, mainly as primary and secondary silicates, and silica materials. Amorphous solid phase Si originates from either as biogenic (originating from plant residues and remains of microorganisms) or litho/pedogenic (Si complexes with Al, Fe, heavy metals, and soil organic matter) materials (Matichencov and Bocharnikova, 2001). The amount of amorphous Si typically ranges from less than 1 to 30 mg g^{-1} on a total soil basis (Jones, 1969; Drees et al., 1989). The solubility of Si in the solid phase significantly affects the concentration of Si in the liquid phase. Larger contribution is expected from amorphous silica than quartz, a crystalline silicate material. The solubility of amorphous Si ranges between 1.8 and 2 mM compared with quartz's 0.10 to 0.25 mM Si (Drees et al., 1989; Monger and Kelly, 2002). Biogenic silica also contributes to the concentration of Si in soil solution, and with solubility 17 times higher than quartz, this contribution to the dynamics of plant-available Si in soil solution is rather significant (Fraysse et al., 2006). Both the liquid and adsorbed phase fractions of Si consist of H_4SiO_4, as well as polysilicic acids, and those dissolved Si complex with inorganic and organic compounds. The silicic acid occurring as monomeric (H_4SiO_4) is the plant-available form of soil Si. Polymerization, a process by which monomeric units of silicic acid form a chain, results in the formation of polymeric silica or high-molecular-weight silica (Williams and Crerar, 1985). Unlike H_4SiO_4, polysilicic acid has not been shown to be plant-available; however, it can link soil particles through the creation of silica bridges, which improve soil aggregation and water-holding capacity (Norton et al., 1984). The liquid Si and adsorbed Si, along with

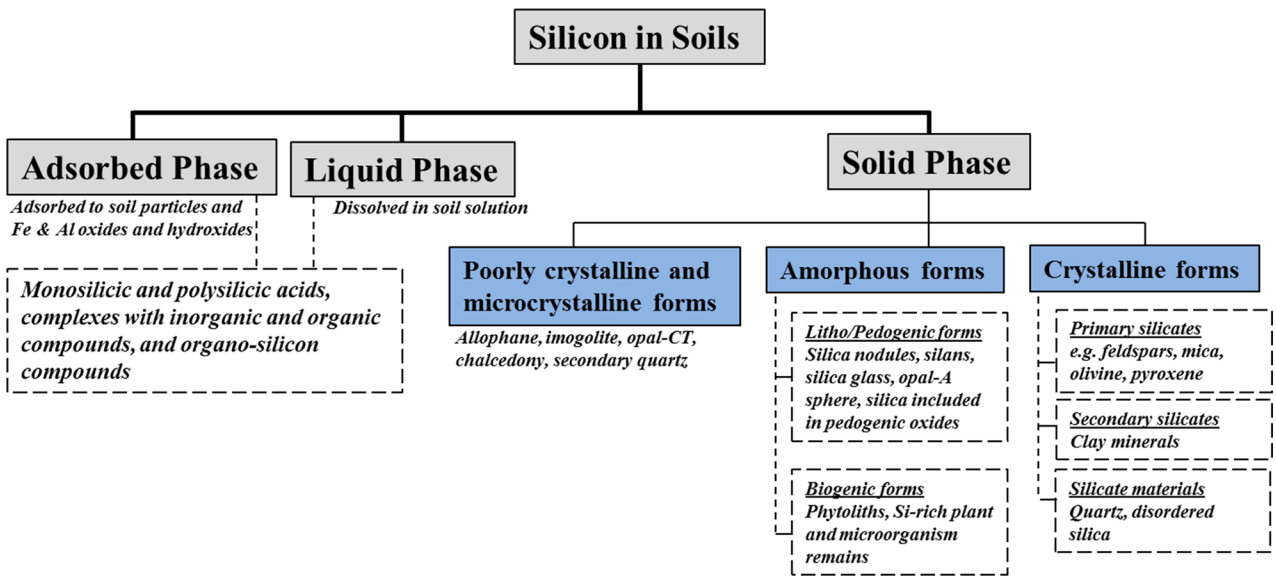

FIG. 2. Different fractions of Si in soils. Adapted from Tubana and Heckman (2015). Adaptations are themselves works protected by copyright. So in order to publish this adaptation, authorization must be obtained both from the owner of the copyright in the original work and from the owner of copyright in the translation or adaptation. A color version of this figure is available in the online version of this article.

amorphous forms of solid phase Si, play an important role in the dynamics of plant-available forms of Si in the soil.

Essentially, the sufficiency or deficiency in soil Si is determined by the rate of replenishment of Si in soil solution and the rate of Si uptake during plant growth (Marschner, 1995). Soil solution is an open system wherein leaching and diffusion affect dissolution products produced during the weathering process of silicate minerals (Harley and Gilkes, 2000). White (1995) evaluated published data on natural dissolution rates of several soil minerals during weathering process. According to this summary, the weathering rate constant for silicate minerals (including plagioclase, K-feldspar, and hornblende) in natural environments (i.e., soil, soil solution, catchment, and aquifer) ranged from $10^{-20.5}$ to $10^{-15.2}$ mol cm^{-2} s^{-1}. Weathering rates can also be estimated in laboratory experiments; however, values are known to be 1 to 3 orders of magnitude higher than natural systems (Paces, 1983; Velvel, 1986; Sverdrup, 1990). Faimon (1998) provided an overview of the release of Si from feldspar (66% SiO_2), granodiorite (72% SiO_2), and amphibolite (47% SiO_2) based on long-term laboratory batch experiments. In this work, both the rates of constant Si fluxes into soil solution from these primary rock minerals and Si fluxes out of solution into secondary solids were estimated. The amounts of Si released from feldspar, granodiorite, and amphibolite were 1.35, 2.18, and 5.57 mmol m^{-2} d^{-1}, respectively, whereas estimated fluxes of Si out of solution into secondary solids were 3.6×10^{-3}, 7.4×10^{-3}, and 2.3×10^{-2} μmol L^{-1} d^{-1}, respectively. It is important to take note that in an open soil system the amount of plant-available Si release to soil solution from weathering of minerals is highly dependent on the composition of the soil solution, the reactions taking place at mineral surfaces, fractions of primary minerals, and secondary phases along with the processes taking place in the rhizosphere (Colman and Dethier, 1986).

Source and Uses

Wollastonite, a naturally occurring mineral rich in Si, is mined for production of ceramics, friction products, metallurgy, paints, and plastics (Virta, 2004). It has an ideal composition of 34.3% calcium (Ca), 24.3% Si, and some minor amounts of aluminum (Al), iron (Fe), manganese (Mn), magnesium (Mg), potassium (K), sodium (Na), and minerals such as calcite, diopside, garnet, idocrase, and quartz (Virta, 2004; Maxim, 2008). In 2004, the world production of wollastonite ore was estimated to be between 550,000 and 600,000 metric tons (Moore, 2003). China is considered to be the leading producer, with an estimated production of 300,000 metric tons. Deposits of wollastonite have been found in the United States, specifically in Arizona, California, Idaho, Nevada, New Mexico, New York, and Utah (Virta, 2004). It was mined commercially in California and New York between 1930 and 1970. The US production was rather limited, ranging between 115,000 and 127,000 metric tons y^{-1} in 2003 (Hawley, 2004).

Vasanthi et al. (2012a) provided a review of Si occurrence and its role in anthropogenic activity, including usages in households, construction and architecture, industrial applications, and others. For example, pure Si, produced from the reduction of SiO_2 with carbon, is the principal and cheap component of most semiconductor devices such as integrated circuits or computer chips. Silicon is one of the principal materials in the photovoltaic and integrated circuits industries. It is also used for manufacturing of Al-Si alloys to produce cast parts for the car industry. Silicon dioxide is mined for these industries, as well as for construction materials to produce glass, concrete, and cement. In 1999, the US sales of wollastonite were allocated mainly for production of plastics (37%) and ceramics (28%); smaller fractions were allocated for metallurgical applications (10%), paint (10%), friction products (9%), and miscellaneous (6%) (Industrial Minerals, 1999).

In agriculture, Si-based compounds have many uses in crop production. For example, Si fluid is used as a spreading agent for agrochemicals (Vasanthi et al., 2012a). Silicon (R_2SiO, where R is an organic group) is safe to use and has good wetting properties. More importantly, it spreads quickly and evenly, thus is used as an agricultural adjuvant (spreading agent). Silicate materials are useful carriers of bioproducts. Organic farming systems utilize non–synthetic-based pesticides such as talc and phytosil to address the growing issues of pesticide residues on food commodities and environmental pollution (Vasanthi et al., 2012b).

Uptake, Assimilation, and Si-Induced Mechanisms of Plant Resistance to Stress

Plants absorb Si as H_4SiO_4. At the pH levels of most agricultural soils, H_4SiO_4 concentration in soil solution ranges from 0.1 to 0.6 mM (Knight and Kinrade, 2001). Absorption of H_4SiO_4 takes place at the lateral roots via active, passive, and rejective mechanisms (Cornelis et al., 2011). It is believed that in high Si accumulators the amount of H_4SiO_4 taken up by active mechanism is greater than concentrations taken by mass flow because of the high density of Si transporters in roots and shoots facilitating H_4SiO_4 movement across root cell membranes (Mitani and Ma, 2005). In rice, both radial transport and xylem loading of H_4SiO_4 are mediated by transporters *Lsi1* and *Lsi2* in roots and *Lsi6* in shoots (Mitani and Ma, 2005; Ma et al., 2006, 2007). Takahashi et al. (1990) categorized plants as high accumulator, intermediate accumulator, or nonaccumulator relying on active, passive, and rejective uptake mechanisms, respectively. However, when Takahashi and his colleagues developed this category, it was based solely on measuring Si in the foliage and did not routinely measure this element in other plant organs. Some plant species such as Chinese cabbage (*Brassica rapa*), crimson clover (*Trifolum incarnatum*), coffee (*Coffea*), green onions (*Allium cepa*), peppers (Capsicum), radishes (*Raphanus sativus*), and tomatoes (*Solanum lycopersicum*) are now known to concentrate more Si in their roots than in their shoots (Lewin and Reimann 1969; Carre-Missio et al., 2009; French-Monar et al., 2010; Huang et al., 2011).

So, it may be assumed that all plants rooting in soil will contain Si in their plant tissue and that Si concentrations may exceed those of many essential mineral elements. For this reason, it is unlikely that there are non–Si-accumulator plants. Many researchers continue to note that plants classified as high accumulators contain 10 to 100 g kg^{-1} Si in dry weight, and most are monocotyledons, such as wheat, sugarcane, rice, and barley (*Hordeum vulgare*) (Liang et al., 2007; Ma et al., 2001; Ma and Takahashi, 2002). Intermediate–Si-accumulation plants contain between 5 and 10 g kg^{-1} dry weight and are mainly monocotyledons, whereas dicot plants with less than 5 g kg^{-1} Si in dry matter are low Si accumulators. The H_4SiO_4 absorbed by root's cells is deposited into leaf epidermal cells. After water removal, the accumulated leaf H_4SiO_4 becomes condensed into a hard polymerized silica gel ($SiO_2.nH_2O$) known as phytoliths (Yoshida et al., 1962; Jones and Handreck, 1965, 1967; Raven, 1983). Silica deposited in leaf epidermal cells is immobile and cannot be translocated to new growing leaves.

TABLE 1. Proposed Si Mechanisms Associated With Plants' Improved Tolerance to Biotic and Abiotic Stresses

Mechanisms	Specific Actions
External or involved in soil and root in preventing excessive uptake of metal	High [H_4SiO_4] increases soil pH—precipitates metal, e.g., Al, Cd, Fe, Mn (Lindsay, 1979)
	H_4SiO_4 adsorbs Al hydroxides diminishing the activity of Al in solution (Baylis et al., 1994)
	Mobile Al is strongly adsorbed on surfaces of silica (Schulthess and Tokunda, 1996)
	Si induces oxidizing capacity of roots facilitating the conversion of plant-available Fe^{2+} to a less plant-preferred Fe^{3+} (Ma and Takahashi, 2002)
	Si induces release of OH^- by roots which raises soil pH (Wallace, 1993)
Reinforces plant's protective layer and mechanical structure	Silica in shoots enhances plant's structural component and creates a hard outer layer (Belanger et al., 2003)
	Improve overall mechanical strength and protective layer of plant (Epstein and Bloom, 2005; Hayasaka et al., 2008)
Mediated/primed mechanisms of defense	Increased production of glucanses, phytoalexins, and PR-1 proteins (Rodrigues et al., 2003, 2004, 2005)
	Enhanced deposition of phenolic-based compounds (Dann and Muir, 2002; Belanger et al., 2003; Rodrigues et al., 2003)
	Up- and down-regulation of a number of unique defensive and metabolic genes (Brunings et al., 2009; Chain et al., 2009; Fauteux et al., 2005; Ghareeb et al., 2011)
	Interferes with the synthesis and/or action of fungal ethylene (van Bochaven et al., 2014)
	Sequestration of cations and enhancing activity of some protein molecules (Fauteux et al., 2005)
Internal or *in planta*	Enhances plants antioxidant systems (Gong et al., 2005; Liang et al., 2006; Inal et al., 2009)
	Silica deposits in cell wall react (coprecipitate) to heavy metals impairing their translocation inside the plants (Richmond and Sussman, 2003; Ma et al., 2004)
	Prevents accumulation of Na of salt-stressed plants through Si-induced reduction in transpiration (Yeo et al., 1999)

The amount of literature documenting the benefits of Si on plants is vast and primarily highlights the value of Si fertilization in maintaining plant productivity under stressed conditions (Epstein, 1999; Li et al., 2007). The established Si-induced mechanisms to improve plants' resistance to biotic and abiotic stresses take place in the soil, the root system, and inside the plant. Table 1 summarizes some of the known current mechanisms and actions involved externally and internally to induce plants' resistance to a wide array of stresses. The codeposition of silica and metals (e.g., Al, Mn, Cd) in solution (in soil and the root system) and in the plant results in reduced concentrations of free, toxic level of metal ions in plants. The silica-precipitated metal ions are not easily translocated, reducing their potential toxic effects on the plant (Richmond and Sussman, 2003; Ma et al., 2004). Silicon deposition of silica in shoots and leaf epidermis, also known as the mechanical barrier hypothesis (Bélanger et al., 2003; Epstein and Bloom, 2005; Rodrigues et al., 2015), enhances the plant's mechanical strength and protective layer. This barrier is believed to help promote the plant's resistance to pathogens, reduce damage caused by insect feeding and grazing animals, improve plants' tolerance to lack-of-moisture stress through reduction in water loss via transpiration, improve root resistance to dry soils, increase photosynthetic rates, and reduce lodging rate (Savant et al., 1997b; Eneji et al., 2005; Hattori et al., 2005; Cotterill et al., 2007; Ma et al., 2006; Datnoff et al., 2009; Rizwan et al., 2012).

As mentioned previously, the mechanical barrier formed from Si polymerization (silica opals or phytoliths) below the cuticle and in the cell walls was the first proposed hypothesis to explain how Si reduced or impeded fungal penetration (Wagner, 1940; Heath and Stumpf, 1986; Carver et al., 1987). However, new insights suggest Si's effect on plant resistance may also occur through mediated host plant resistance mechanisms against pathogen infection (Rodrigues et al., 2015). They explained that in such mechanisms an R gene of the plant forms products, such as proteins, or activates a defense mechanism (s) that transfers resistance to specific plant pathogens. Silicon has been shown to up- and down-regulate certain genes and their defensive products in a number of host-pathogen interactions that include rice (*Magnaporthe oryzae*), tomato (*Ralstonia solanacearum*), and wheat (*Blumeria graminis* f. sp. *tritici*) (Brunings et al., 2009; Chain et al., 2009; Ghareeb et al., 2011). Chérif and his colleagues (1992a, 1992b, 1994) in Canada were the first to show that the activities of pathogenesis-related proteins (peroxidase, polyphenol oxidase, and chitinase) were significantly stimulated by Si in cucumber (*Cucumis sativus*) infected with *Pythium* species. Bélanger et al. (2003, 2003) (Fawe et al., 1998, 2001) provided some direct evidence showing that Si played more than a mechanical role. Silicon stimulated phytoalexin production within the plant, which was associated with cucumber resistance to *Podosphaera xanthii*. Based on these findings, Si was hypothesized to be actively involved in triggering defense mechanisms in response to fungal attack. This hypothesis was further supported by Datnoff et al. (1992), who reported that the fungitoxic compounds identified as momilactones (rice phytoalexins) were detected in Si-amended plants infected by the rice blast pathogen, *Magnaporthe oryzae* (Rodrigues et al., 2003, 2004). They further demonstrated that a differential accumulation of glucanase, peroxidase, and PR-1 transcripts was associated with limited fungal colonization in the epidermal cells, strongly associated with reduced rice blast development (Rodrigues et al., 2005). Fauteux et al. (2005) suggested that Si might act as a potentiator of plant defense responses or as an activator of specific signaling proteins that interact with several key components of plant stress signaling systems, ultimately leading to induced resistance against pathogenic fungi. Although the molecular mechanisms of how such priming is associated with Si are not well understood, a growing body of research evidence suggests that Si may be influencing plant's endogenous defensive hormone balances (Rodrigues et al., 2015). Higher levels of salicylic acid, jasmonic acid, and ethylene have been reported to be induced by Si supplements in a number of host-pathogen interactions and confirmed by microarray analysis

(Rodrigues et al., 2015). Genome-wide studies for tomato, rice, and wheat grown in soils amended with Si and inoculated by specific plant pathogens have shown a differential and unique expression of a large number of genes involved in host plant defense mechanisms or metabolism compared with control plants grown in non–Si-amended soil. The association between Si and priming in plant-pathogen interactions was corroborated by Vivancos et al. (2015), but their findings also implied that other mechanisms may also be involved besides the Si-dependent plant defense priming. Clearly, more research is warranted to determine how Si potentiates host plant resistance against both biotic and abiotic stress.

Silicon in Perspective: History and Documented Benefits in US Crop Production Systems

In 1964, Clements published a chapter in the *Annual Review of Plant Physiology* entitled "Interaction of Factors Affecting Yield." He reported several instances where not only sugarcane and other crops showed yield responses to application of silicates. Other articles were later published on Si (Bollard and Butler, 1966; Jones and Handreck, 1967; Lewin and Reimann, 1969; Foy et al., 1978), which focused on aspects of Si in relation to soil-plant interactions, Si uptake and transport, and the mechanism by which Si enhances plant ability to withstand biotic (herbivory and pathogen) and abiotic (metal toxicity) stresses. Among these publications, the review by Jones and Handreck (1967) provided a turning point in Si research. They included a lengthy list of references highlighting the value of Si from agricultural, crop science, plant pathology, and plant physiology perspectives. In later work, Carpita (1996) described Si in the structure and biosynthesis of the cell walls of grasses.

In the United States, Maxwell (1989) produced the first analysis that estimated plant-available Si in soils from the Hawaiian Islands. Research pursuing the role of Si as a nutrient for different crops began in the early 1900s (Conner, 1921; Sommer, 1926; Lipman, 1938; Raleigh, 1939). In the study conducted by Conner (1921) on soybean (*Glycine max*), Ca silicate slag application outperformed lime, potash, and phosphate treatments by completely precipitating toxic Al salts, producing a 21% higher grain yield. Growth of rice and millet (*Pennisetum glaucum*) was improved with Si addition (Sommer, 1926), and seed heads of millet grown without Si were severely infected by plant pathogenic fungi. Lipman (1938) made similar observations regarding the effects of Si on growth and found seed production was enhanced in sunflower (*Helianthus annuus*) and barley. Raleigh (1939) documented a 44% increase in beet (*Beta vulgaris*) production in acid soils with high Al salts with the addition of Ca silicate slag compared with Ca hydroxide as a liming agent. He also observed that roots became necrotic and were covered by an organismal growth, fungal, or fungal-like mass, when sugar beet was grown in a nutrient solution without Si. The role of Si was evaluated on solution-cultured tomato (Woolley, 1957) and barley (Williams and Vlamis, 1957, 1967), further confirming the potential benefits of Si in plants.

The first direct use of Si as a fertilizer rather than as a liming agent was tested for sugarcane production in Hawaii (Clements, 1965a). The initiation of this study was instigated by the increasing incidence of leaf freckling (small rust-colored or brownish spots on the leaf surfaces) in cane plants. These cane plants were suspected to be suffering from a Si deficiency. A series of field experiments demonstrated that the application of Ca silicate slag not only reduced or completely eliminated leaf freckling but also resulted in significant increases in cane tonnage and stalk sucrose content (Clements, 1965b). These positive returns from Ca silicate slag application were also accompanied by a drastic reduction in the ratio of Mn and silica content in cane leaves. Later studies also showed Si precipitated Al and Mn, which alleviated injuries to roots and tops of sugarcane grown on soils with low pH and toxic concentrations of metals (Clements et al., 1974). On similar soils, Ayres (1966) showed increases of 9% to 18% in cane yield and 11% to 22% in sucrose content following the application of 6.2 Mg ha^{-1} electric furnace slag. While Ayres (1966) agreed that highly soluble Si depressed Al and Mn uptake by sugarcane, the amount of soluble Si in the soil was inherently low, expressing the view that there was a certain concentration of plant-available Si below which it would not be sufficient for normal growth of sugarcane, regardless of the supply of other available nutrients. Silicon was later recognized as "agronomically essential" for sugarcane production (Chen and Lewin, 1969; Fox and Silva, 1978; Lux et al., 1999; Pilon-Smits et al., 2009).

Similar Si benefits in sugarcane production as those reported in Hawaii in the 1960s were documented in the EAA of south Florida as earlier reported in Hawaii in the 1960s (Elawad et al., 1982). The majority of soils in this region are classified as organic soils or Histosols. These soils have a relatively small mineral fraction, approximately 20%, with correspondingly low bulk density. Snyder et al. (1986) noted that fields in this region when farmed to irrigated rice showed Si deficiency and that the application of 1 Mg ha^{-1} Ca silicate slag increased rice grain yields by greater than 30% while reducing the incidence of grain discoloration. Because of the low plant-available Si content of Histosols, the benefits of Si fertilization to sugarcane, rice, and citrus production are commonly observed in this region (Elawad and Green, 1979; Elawad et al., 1982; Deren et al., 1994; Matichenkov et al., 1999). Sugar yields, depending on crop age, increased by 25% to 129% in response to application of Ca silicate slag (Anderson et al., 1987; Elawad et al., 1982). For both sugarcane and rice crops, Si fertilization has become an established practice on commercial production fields in this region.

Several field and greenhouse studies in Florida demonstrated that Si will influence many components of host resistance, including incubation period, latent period, lesion number, and lesion size; Si also augments susceptible and partial resistance almost at the same level as complete genetic resistance and suppresses plant disease as effectively as do fungicides (Datnoff et al., 1992; Datnoff and Snyder, 1994; Datnoff et al., 1997; Rodrigues et al., 2001; Seebold et al., 2001; Brecht et al., 2004). A 1-year residual Si application was also effective in reducing blast and brown spot development in rice while enhancing yields more effectively than fungicides alone (Datnoff et al., 1991; Datnoff et al., 1997). Consequently, growers may save initial or additional application costs for either fungicides or Si fertilizer while providing positive environmental benefits (Alvarez and Datnoff, 2001).

Silicon research in the areas of plant physiology, soil fertility, and agronomy began to expand in other regions of the United States. In Louisiana, a series of field trials were established in 2000 to evaluate the impact of silicate slag application to sugarcane (Viator et al., 2004). Sugar yield increased by a total of 3,700 kg ha^{-1} ($P < 0.05$) for the whole crop cycle (three harvestings) of cane variety LCP 85-384 with a one-time application of 4.5 Mg ha^{-1} Ca silicate slag at planting (Viator et al., 2004). Tubana et al. (2012) showed that this Ca silicate application rate increased sugar yield by 1,450 kg ha^{-1} ($P < 0.01$). The potential of Si fertilization in disease management was also evaluated in rice production systems in Louisiana (Bollich et al., 2001). In Kansas, the deposition pattern of Si in tissues of a mature corn (*Zea mays* L.) was studied by Lanning et al. (1980). In Delaware, the potential of Si to reduce As uptake by rice was documented by Seyfferth and Fendorf (2012). They attributed the reduction in grain and straw As uptake

to competition between H_4SiO_4 and H_3AsO_3 (form of As taken up by plant) for adsorption sites on soil colloids and subsequent plant uptake. The effect of Si on growth and drought stress tolerance of corn, rice, soybean, and wheat was the central focus of a series of studies conducted by Janislampi (2012) in Utah. Under drought and salt stress conditions, both corn and wheat biomass at vegetative stage increased by 18% and 17%, respectively ($P < 0.05$) because of Si fertilization. Silicon also improved water use efficiency of corn by as much as 36% ($P < 0.05$).

In New Jersey, research plots to study Si nutrition were first established in 2000 at the Rutgers Snyder Research and Extension Farm in Pittstown (Heckman, 2012). Responses of crops/plants such as pumpkin (*Cucurbita maxima*), cabbage (*Brassica oleracea*), winter wheat, corn, oats (*Avena sativa*), and grasses to Ca silicate slag applications were documented. After more than a decade of research, enough data to justify Ca silicate slag as an effective liming material and Si fertilizer were collected. Increases in yields observed in these crops had corresponding increases in Si uptake and reduced insect damage (e.g., European corn borer) and disease development (e.g., powdery mildew). One of the highlights of these studies was the residual benefit of Ca silicate slag extending up to 3 to 4 years after the last application, economically justifying the value of this agronomic practice not only in field crops but also in forages and horticultural crops. The value of Si fertilization was also pursued in horticulture and floriculture involving scientists from Illinois, Maine, Oklahoma, and Ohio (Kamenidou, 2002; Frantz et al., 2008; Kamenidou et al., 2009; Hogendorp et al., 2012).

Several studies also evaluated the value of integrating Si fertilization in rice insect management in Louisiana (Sidhu et al., 2013) and horticultural crops in Kansas (Cloyd, 2009) and Illinois (Hogendorp et al., 2012). The augmentation of soil using Si-containing fertilizer resulted in increased rice Si uptake by as much as 32%, leading to a significant reduction in both relative growth rate and the boring success of *Diatraea saccharalis* larvae on Si-treated rice plants (Sidhu et al., 2013). Conversely, greenhouse studies by Cloyd (2009) and Hogendorp et al. (2012) demonstrated that the application of Si-based fertilizers did not raise Si uptake of fiddle-leaf fig (*Ficus lyrata*), nor did Si inhibit insect pest feeding and outbreaks. They attributed the lack of response to the inherent inability of horticultural crops such as fiddle-leaf fig plant to accumulate Si. However, Frantz et al. (2008) noted that there are several new floriculture species (*Zinnia elegans*, *Impatiens hawkeri*, verbena, and calibrachoa), which take up and accumulate significant concentrations of Si; this challenges the earlier phylogenetic studies suggesting that Si uptake is limited to only a few plant species. Similar studies in Oklahoma (Kamenidou, 2002; Kamenidou et al., 2009) revealed that the application of Si improved several horticultural traits of selected cut flowers.

Crop Removal Rates and Soil Si Status

Crop production removes large quantities of Si from soil. On a global perspective, the estimated amount of Si removed annually by different agricultural crops is between 210 and 224 million tons (Bazilevich et al., 1975; Reimers, 1990; Savant et al., 1997a). Larger removal rates are estimated from high–Si-accumulator crops such as wheat, sugarcane, and rice. Sugarcane removes approximately 300 kg ha^{-1} y^{-1}, whereas rice is as much as 500 kg Si ha^{-1} y^{-1} (Meyer and Keeping, 2001; Blecker et al., 2006; Makabe et al., 2009). These amounts are much higher than the removal rates of primary essential nutrients such as nitrogen (N),

TABLE 2. Estimated Shoot Si Uptake Based on 10-Year Average (2004–2013) of Harvested Area, Production Level of Principal Crops in the United States, and Their Reported Biomass/Harvested Portion Ratio and Shoot Si Content

Crops	Harvest Area Million Ha	Production* Million Tons	B/H Ratio‡	Authors	Shoot Biomass£ Million tons	Shoot Si[β] g kg^{-1}	Estimated Annual Shoot Si Uptake§ Tons	Shoot Si Uptake[ϵ] kg ha^{-1}
Barley	1.278	4.62	1.5	Brown, 2003	6.93	18.2	126,059	99
Maize	32.555	307.81	1.0	Renard et al., 1997	307.81	13.6[a]	4,209,964	129
Oats	0.556	1.26	1.4	Brown, 2003	1.764	15.1	26, 683	48
Rice	1.203	9.48	1.0	Summer et al., 2003	9.48	41.7	395,173	329
Sorghum	2.307	9.33	1.0	Renard et al., 1997	9.33	15.4	143,648	62
Soybeans	29.841	84.69	1.5	Renard et al., 1997	127.04	13.9	1,765,738	59
Sugar beet	0.485	29.18	1.0	Dadkhah and Grifiths, 2006 Shaw et al., 2002	29.18	23.4†	682,886	1408
Sugarcane	0.362	27.42	0.14	Hassuani et al., 2005	3.84	15.1	57,966	160
Wheat	19.865	58.35	1.5	Renard et al., 1997	87.53	24.5	2,144,278	108
Total	88.452						9,552,395	107[b]

*Harvested portion of the crops (e.g., stalk in cane;, grain in rice, roots for beets etc.).

‡Biomass ratio to harvested parts of the plant; harvested = grain, stalks, roots.

¶Citations for the B/H ratio.

£Estimated biomass (e.g., straw in rice, stover in corn, leaves in sugarcane) production computed as the product of production and B/H ratio.

§Computed as the product of production level, B/H ratio and shoot Si.

βSi content in shoot reported by Hodson et al. (2005).

ϵComputed as estimated shoot Si uptake divided by the 10-year average harvested area.

aLatshaw (1924) (stover—leaves, stems, and cobs).

†Draycott (2006).

bAverage shoot Si uptake estimated as total annual shoot Si uptake divided by the total harvest area.

phosphorus (P), and K. After years of continuous cropping, harvesting of crops for human consumption can eventually result in reduction of plant-available Si in soils (Meunier, 2003; Meunier et al., 2008). To put this in perspective, for rice production entirely relying on release of H_4SiO_4 from amorphous silica as its Si source, the supply of plant-available Si is expected to be exhausted after 5 years of continuous cultivation (Desplanques et al., 2006). A review by Savant et al. (1997b) suggested that the decline in yields of rice grown in many areas of the world was associated with soil depletion of plant-available Si. This may pose further problems in soils with large fractions of quartz sand, high organic matter content, and characterized as highly weathered, leached, acidic, and low in base saturation (Foy, 1992; Datnoff et al., 1997).

The US produces a diverse group of crops that are used for fiber, grains and hay, legumes, oilseeds, root crops, sugar crops, and vegetables. In 2014, the total production of corn reached 361 million tons harvested from more than 33.6 million hectares of land; this production level represented approximately 35% of world production (USDA-NASS, 2015). Based on the average harvested area and production level of principal US crops in the last 10 years, corn and soybean have been the nation's most important crops (Table 2). According to Takahashi et al. (1990), high–Si-accumulator plants have 10 to 100 g kg^{-1} Si content in shoots. Therefore, with the exception of corn, the principal crops grown in the United States are high Si accumulators. While corn is not classified as a Si accumulator by this standard, its high production level translates into a large amount of Si removal through plant uptake. To present an overview of Si uptake by these crops, several published data were consolidated to estimate shoot Si uptake, which is defined as the total amount of Si contained in the entire crop at maturity (e.g., in the straw, grain, roots, and husk of rice). However, there is limited information on Si content of the harvested portion of crops (e.g., grains for cereal, stalks for sugarcane, roots for sugar beets). While there are some known values, they are not yet published (Tubana, unpublished data). For example, the averaged Si content for corn grain is 2.6 g kg^{-1} (n = 64 samples), whereas rice panicles (grain + husk) contain an average of 23 g kg^{-1} (n = 256), and shredded unpressed cane stalks average 4.9 g kg^{-1} Si (n = 192). The Si contained in the harvested portions of these crops is lower than the shoot Si content reported by Hodson et al. (2005) and Draycott (2006) (Table 2). The published average biomass to harvested portion (B/H) ratio of these crops was then utilized to estimate the biomass or residue of the given production level in the past 10 years. The annual estimated shoot Si uptake annually by these principal crops was computed by multiplying shoot biomass estimate by the shoot Si level and then further dividing this value by the average 10-year harvested area to obtain shoot Si uptake per hectare by these crops.

$$\text{Shoot Si}_{\text{Biomass}}\ \text{uptake}\ (\text{kg ha}^{-1}) = \frac{\text{Average annual production}_{\text{Harvested portion}}\ \text{x B/H ratio x shoot Si content}}{\text{10-year Average harvested area}}$$

The high US corn production level in the last 10 years produced the highest annual shoot Si uptake at 4.21 million tons even with an intermediate Si content of 13.6 g kg^{-1} (Table 2). Wheat followed with 2.14 million tons, followed by soybean, a dicot plant species, estimated at 1.77 million tons. The actual removal rate by plant uptake is certainly higher than these estimates as the harvested parts of these crops were not accounted. Even so, the estimated shoot Si uptake per hectare of these crops almost consistently exceeded uptake of primary nutrients such as N, P, and K. Most notable are rice, sugar beet, sugarcane, and wheat with an estimated shoot Si removal of 329, 1,408, 160, and 108 kg Si ha^{-1}, respectively. The extremely high shoot Si uptake estimate for sugar beet can be attributed to the high Si content reported by Draycott (2006) at 23.4 g Si kg^{-1}. In fact, the sugar beet dry matter (tops) contained approximately 115 g Si kg^{-1}, which could explain the observed reduction in digestibility and metabolizable energy content of tops. Including all field crops on this list, the total estimated annual shoot Si uptake is 9.55 million tons, and the average shoot Si uptake is 107 kg ha^{-1}. On the other hand, there were reports of the Si removal rate of rice, sugarcane, and wheat being at 500, 300, and 50 to 150 kg ha^{-1}, respectively (Meyer and Keeping, 2001; Makabe et al., 2009; Bazilevich, 1993). Bazilevich (1993) also reported plant average Si uptake ranging from 50 to 200 kg ha^{-1}. Using the 10-year average

TABLE 3. Estimated Annual Si Removed from Soil per Area Basis by Principal Crops in the United States Based on 10-Year Average Harvested Area and Published Si Removal Rate by Crop per Hectare

	Harvest Area	Silicon Removal Rate			Estimated Si Annual Removal Rate‡
Crop	Million ha	Range, kg ha^{-1}	Median,[b] kg ha^{-1}	Author†	tons
Barley	1.278	50–200	125	Bazilevich, 1993	159,766
Maize	32.555	50–200	125	Bazilevich, 1993	4,069,371
Oats	0.556	50–200	125	Bazilevich, 1993	69,475
Rice	1.203	500	500	Makabe et al., 2009	601,287
Sorghum	2.307	50–200	125	Bazilevich, 1993	288,347
Soybeans	29.841	50–200	125	Bazilevich, 1993	3,730,068
Sugar beet	0.485	50–200	125	Bazilevich, 1993	60,604
Sugarcane	0.362	300	300	Meyer and Keeping, 2001	108,569
Wheat	19.865	50–150	100	Bazilevich, 1993	1,986,480
Total					11,073,967
Cropland[a]	168.810	50–200	125	Bazilevich, 1993	21,101,250

[a]US total land in 2007 planted to food crops (e.g., wheat, rice, sweet potatoes, beans), feed crops (e.g., corn-all, barley, hay), and other crops (e.g., cotton, flaxseed) (USDA-NASS, 2007).

[b]For Si content in range values, determined by adding the maximum and minimum values then divide by 2.

†Citation for the Si removal rate.

‡Computed as the product of 10-year average harvest area and average Si removal rate for each crop.

harvested area and these removal rate estimates, US production of rice, sugarcane, wheat, and the rest of these principal crops can remove a total of 11.07 million tons Si from the soil every year (Table 3). If this plant-Si average is used to estimate Si removal from the 168.81 million hectares of cropland (USDA-NASS, 2007), this translates to approximately 21.1 million tons of Si removed annually. The estimated area planted to these 10 principal crops is approximately 50% of the total US cropland.

The Si in shoots can be returned to the soil (recycling) through plant residue incorporation. There are conflicting reports on the turnover rates of plant-available Si from decomposition of plant materials. Ma and Takahashi (2002) noted that the positive effect of rice straw incorporation on plant-available soil Si is long term in nature and is not fully realized immediately after straw incorporation. However, Marxen et al. (2016) reported that phytoliths from fresh rice straw are soluble at a rate of 2% to 2.5% per day during the first 33 days of their experiment; this was followed by decreasing Si release rates, suggesting that phytolith solubility decreases over time in soil. The findings of Fraysee et al. (2009) were similar wherein phytoliths extracted from horsetail had a dissolution rate of approximately 0.6% and 3% phytolith-Si d^{-1} at pH 6 and 8.6, respectively. Most Si in the soil is in an inert form, and only a small fraction is soluble and available for plant uptake, whereas most Si in mineral soils is held in the crystalline structure of sand, silt, and clay particles, a Si form unavailable for plant uptake. Soils vary significantly in their ability to supply plant-available Si. In general, soils in which Si fertilization will likely result in increases in crop yields are typically highly weathered, leached tropical soils with low pH, base saturation, and silica-sesquioxide ratios (Silva, 1973). These soils are classified as Ultisols and Oxisols. Their clay minerals are predominantly hydrated Al and Fe oxides and kaolite, characterized as high P-fixing soils. Soils that are less weathered or geologically young have the capacity to supply higher amounts of plant-available Si than highly weathered soils.

Soils known to have limiting plant-available Si content found in the United States generally belong to the following soils orders: Histosols, Ultisols, Spodosols, Inceptisols, and Entisols. Ultisols are common in the Eastern United States, occupying approximately 9.2% of the total US land area (Fig. 3). These are acidic soils characterized by having a low amount of plant-available Ca, Mg, and K. These soils have undergone intense weathering and leaching as is commonly found in warm, humid regions of the United States with high average annual rainfall and are not suited for continuous crop production unless treated with fertilizer and lime. Accumulated clay and the presence of Fe oxides are common in the subsurface horizon of these soils. Plant-available Si in Ultisols is generally low in contrast to the Mollisols that are common in the US Great Plains. Histosols of the EAA of south Florida are composed mainly of organic materials (20%–30% by weight) and are known to have low quantities of plant-available Si. Production areas in this region are known to respond significantly to Si fertilization. Histosols occupy approximately 1.6% of the United States' land area (Fig. 3). Spodosols are acid soils characterized by a subsurface accumulation of Al- and Fe-humus complex. Similar to Ultisols, these soils require liming in order to be agriculturally productive. These soils are typically formed from coarse-textured parent material and occupy approximately 3.5% of the US land area (Fig. 4). Many regions in the United States have soils belonging to the weakly developed Entisols and Inceptisols that are believed to have low levels of plant-available Si as well (Fig. 5). Entisols generally have little or no evidence of pedogenic horizons development; many are sandy or very shallow (Soil Survey Staff, 1999). This is the most extensive soil

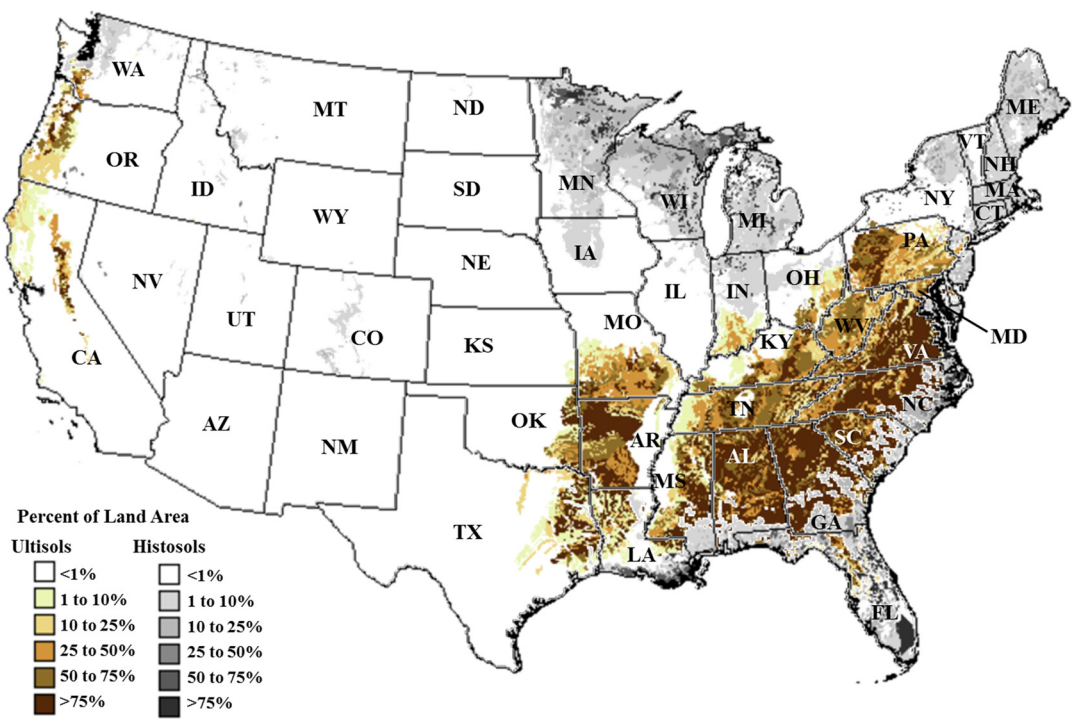

FIG. 3. Distribution of Ultisols and Histosols in US land area. Adapted from Soil Survey Staff (1999b). Adaptations are themselves works protected by copyright. So in order to publish this adaptation, authorization must be obtained both from the owner of the copyright in the original work and from the owner of copyright in the translation or adaptation. A color version of this figure is available in the online version of this article.

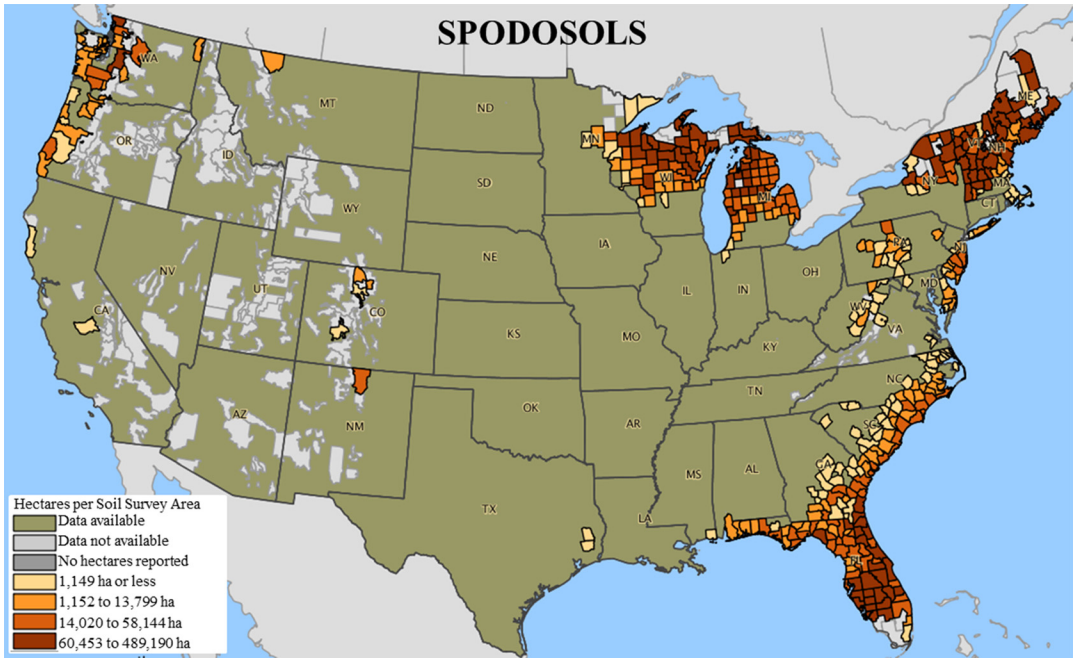

FIG. 4. Distribution of Spodosols in US land area. Adapted from the National Resources Conservation Service, 2014. Adaptations are themselves works protected by copyright. So in order to publish this adaptation, authorization must be obtained both from the owner of the copyright in the original work and from the owner of copyright in the translation or adaptation. A color version of this figure is available in the online version of this article. full color online

order occupying approximately 12.3% of the US land area. Soils belonging to Inceptisols are commonly found in humid and subhumid regions, widely distributed in the US land area (approximately 9.7%), often found on fairly steep slopes, young geomorphic surfaces, and on resistant parent materials. Horizons of these soils are altered and known to have many diagnostic horizons. Soil texture and the duration of cropping systems are criteria other than soil order, which can provide an overview of plant-available Si status. Soils with large fractions of quartz sand that have been farmed for many decades are likely to have low quantities of plant-available Si (Datnoff et al., 1997).

Silicon Fertilization Guidelines—Where Do We Stand?

Soil: Extraction Procedure and Critical Levels

The most common method to quantify the concentration of Si in water, soil extracts, and plant digest samples is via the molybdenum blue colorimetry (Hallmark et al., 1982). Monosilicic is the only form of silicic acid that is molybdate reactive, forming an intense blue color in solution, which increases with H_4SiO_4 concentration. The presence of other forms of Si (e.g., polysilicic acid) does not affect the formation of Si-molybdate blue complex. Silicon in solution can be measured by inductively coupled plasma-optical emission spectrometry, which can also measure all other forms of Si in solution including those that are not plant available. Thus, this limitation should be considered when estimating plant-available soil Si. Conversely, for quantifying total Si content in plant samples, inductively coupled plasma-optical emission spectrometry analysis may not pose any complications (Frantz et al., 2008).

From the vast amount of literature in the last 50 years, many procedures have been established and standardized for extracting different Si forms, not only plant-available forms, but also Si from amorphous silica and allophane in soils and sediments (Sauer et al., 2006). However, the abundance of Si in soil is interpreted differently when it comes to fertilization guidelines, where the most important fraction of Si is the form available for plant uptake. Plant-available Si is composed of H_4SiO_4 both in liquid (soil solution) and adsorbed phase (to soil particles). Tubana and Heckman (2015) summarized solutions, which have been used to extract and estimate plant-available Si, including water, calcium chloride ($CaCl_2$), acetate, acetic acid, sulfuric acid (H_2SO_4), and citric acid (Table 4). The extraction procedures associated with these solutions have undergone a series of modifications, which generally resulted in shorter extraction time requirements. The choice of solution is critical because the amount of plant-available Si estimated by these extraction procedures differs, and so would be the interpretation of results and fertilizer recommendation. For example, Fox et al. (1967) used H_2SO_4, acetic acid, water, and $Ca(H_2PO_4)_2$ to extract Si from soils of Hawaii. Water consistently extracted the least amount of Si, whereas those soils dominated by montomorillonite, kaolinite, goethite, and gibbsite contained the highest amount of Si based on the $Ca(H_2PO_4)_2$ procedure. The H_2SO_4 procedure extracted the highest Si content from soils, which contained large fractions of allophane, whereas the Si content of soils determined by the acetic acid procedure fell between water and $Ca(H_2PO_4)_2/H_2SO_4$. Recent works by Tubana et al. (2012) and Babu et al. (2013) have also demonstrated that the amounts of Si determined using different extractors for Midwest and southern US soils varied significantly. According to Babu et al. (2013), the amount of extractable Si was in the order of citric acid > acetic acid (24-h rest + 2-h shaking > 1-h shaking) > Na acetate > ammonium acetate > $CaCl_2$ > water for soils representing some 130 mineral soils of Louisiana currently farmed to different field crops. The soil Si determined by 0.5 M acetic acid solution ranged from 3 to 300 mg kg^{-1}. Similar study was done by Wang et al. (2004) except that they included Mehlich-3 solution. The amount of extracted Si was in the order of Mehlich-3 > citric acid > 0.1 M

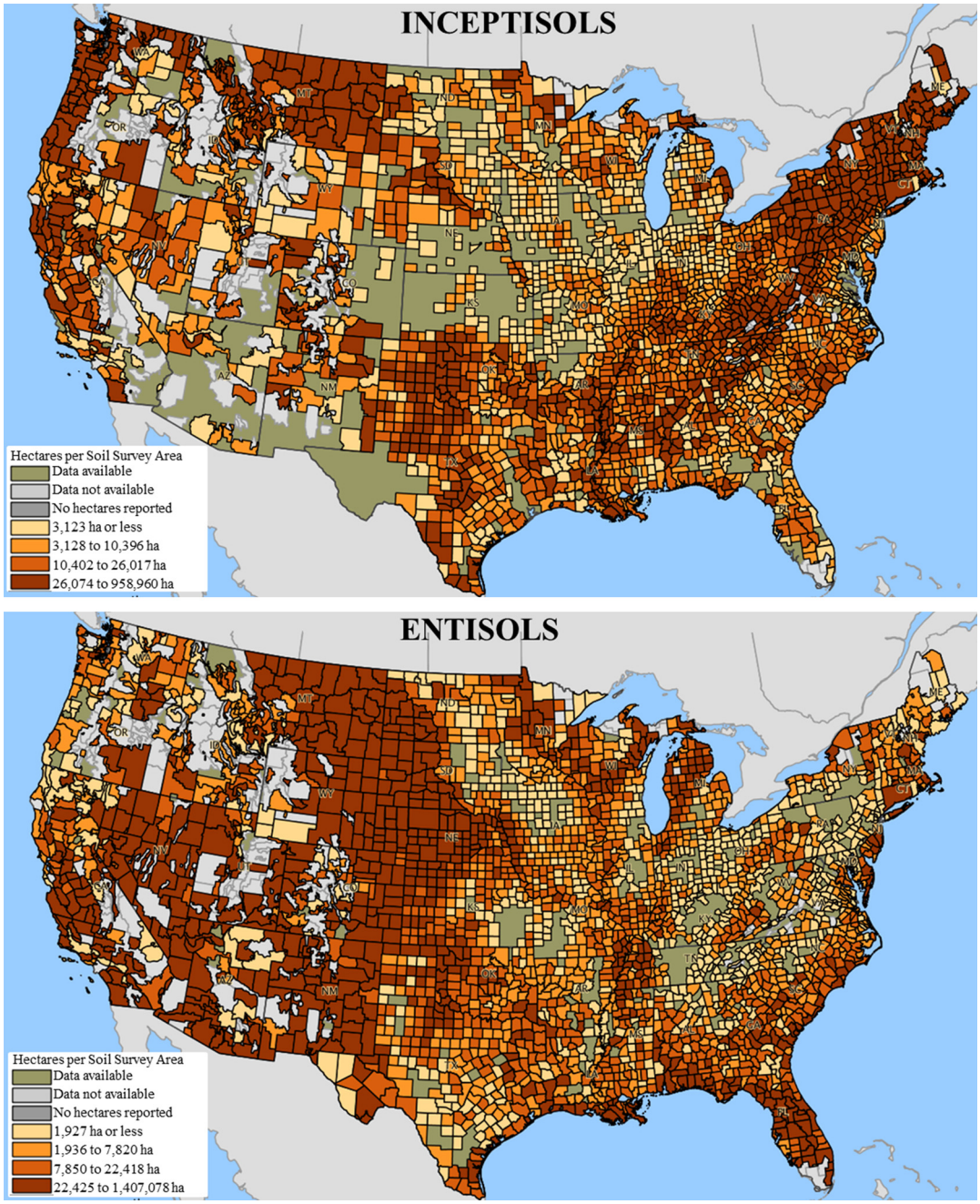

FIG. 5. Distribution of weakly-developed Inceptisols and Entisols in US land area. Adapted from the National Resources Conservation Service, 2014. Adaptations are themselves works protected by copyright. So in order to publish this adaptation, authorization must be obtained both from the owner of the copyright in the original work and from the owner of copyright in the translation or adaptation. A color version of this figure is available in the online version of this article.

HCl > acetic acid > acetate buffer > ammonium acetate > water, suggesting that Mehlich-3 solution likely extracts solution, exchangeable, and adsorbed Si fractions.

Establishment of soil Si test interpretation and fertilization guidelines require knowledge of the critical Si concentrations in the soil, defined as the point on an economic crop response curve corresponding to plant-available soil Si concentrations at which maximum crop yield is attainable. Beyond this critical Si concentration, it is expected that crop response to Si fertilization will not result in further significant yield increases, whereas below this concentration there is the likelihood of a crop significantly responding to Si fertilization. It is expected that critical Si concentrations, just like any other plant-essential nutrients, will vary with soil type, crop species, and soil testing procedure. The critical Si level established for the organic and mineral soils in south Florida (characterized by having low clay, Al, and Fe contents) was based on 0.5 M acetic acid procedure (1-h shaking). Using sugarcane as a test crop, the critical Si level was determined to be 32 g m^{-3} (McCray et al., 2011) and 19 mg Si kg^{-1} for a rice crop (Korndorfer et al., 2001). Elsewhere in the world, depending

TABLE 4. Extraction Procedures for Estimating Plant-Available Si Both in Soil Solution and Adsorbed Phase

Solution	Procedure	Silicon Fractions	References
H_2O	10 g in 50 mL + 0.1% NaN_3 to reduce biological activity; incubate 21 d at room temperature with manual shaking 2 times a day	Water soluble	Schachtschabel and Heinemann, 1967
	10 g in 100 mL; 4-h shaking	Water soluble	Fox et al., 1967; Khalid et al., 1978
	10 g in 60 mL; incubate at 40°C for 2 wk	Water soluble	Nonaka and Takahashi, 1988, 1990
	10 g in 100 mL; 1-h shaking	Water soluble	Korndörfer et al., 1999
$CaCl_2$	0.01 M $CaCl_2$; 1-g sample in 20-mL solution; 16-h shaking	Liquid phase; readily available	Haysom and Chapman, 1975
	0.01 M $CaCl_2$; 10-g sample in 100 mL solution; 1-h shaking	Liquid phase; readily available	Korndörfer et al., 1999
Na acetate + acetic acid	0.18 N Na acetate + 0.87 M acetic acid, adjusted to pH 4; 10-g sample in 100 mL solution; 5-h occasional shaking at 40°C	Soluble, some exchangeable	Imaizumi and Yoshida, 1958
	0.18 N Na acetate + 0.87 M acetic acid, adjusted to pH 4; 10-g sample in 100-mL solution; 1-h shaking	Soluble, some exchangeable	Korndörfer et al., 1999
NH_4 acetate	5% (0.5 M) NH_4 acetate, adjusted to pH 4.5–4.8 with 0.1 M acetic acid; 1-g sample in 20-mL solution; 1-h shaking	Soluble, some exchangeable	Ayre, 1966; Cheong and Halais, 1970
	5% (0.5 M) NH_4 acetate, adjusted to pH 4.8 with 0.1 M acetic acid; 1-g sample in 10-mL solution; 1-h shaking	Soluble, some exchangeable	Korndörfer et al., 1999
Acetic acid	0.5 M acetic acid; 1-g sample in 10-mL solution; 1-h shaking with 12 h resting	Soluble, some exchangeable	Snyder, 1991
	0.5 M acetic acid; 1-g sample in 10-mL solution; 1-h shaking	Soluble, some exchangeable	Korndörfer et al., 1999
	0.5 M acetic acid; 10-g sample in 25-mL solution; overnight resting + 2-h shaking	Soluble, some exchangeable	Snyder, 2001
Citric acid	0.1 M citric acid; 1-g sample in 50-mL solution; 2-h shaking, resting overnight + 1-h shaking	Soluble, exchangeable, adsorbed	Acquaye and Tinsley, 1964
Na citrate + $NaHCO_3$	80% 0.3 M Na citrate + 20% 1 M $NaHCO_3$; 2-g sample in 50-mL solution; 5 min at 80°C	Soluble, exchangeable, adsorbed to sesquioxide surfaces	Breuer, 1994
NH_4 citrate	1 M NH_4 citrate; 10-g sample in 25-mL solution; 80-h shaking	Soluble, exchangeable, adsorbed	Sauer and Burghardt, 2000, 2006
H_2SO_4	0.005 M H_2SO_4; 1-g sample in 200-mL solution; 16-h shaking	Soluble, exchangeable, adsorbed	Hurney, 1973
Mehlich-3	2 g soil in 10 mL Mehlich-3 solution; 5-min shaking	Soluble, exchangeable, adsorbed	Mehlich, 1984

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on soil type and extraction procedure, the critical Si concentration varied significantly. For example, the critical level ranged between 71 and 181 mg kg^{-1} for wheat grown on calcareous soils using Na acetate–acetic acid as the extracting solution, (Liang et al., 1994; Xu et al., 2001). Narayanaswamy and Prakash (2009) showed large differences in critical Si concentrations for rice grown on acidic soils in India because of extracting solutions: 54 versus 207 mg Si $kg^{-1}$for 0.5 M acetic acid (1-h shaking) versus 0.005 M H_2SO_4, respectively. For select mineral soils from the Midwest and southern United States Tubana et al. (2012) suggested that critical Si concentrations ranged between 120 and 150 mg Si kg^{-1} when using ryegrass biomass as the plant response variable.

Plant Tissue—Testing Procedure and Critical Level

Standardization of procedures in plant tissue Si testing has not encountered as many challenges as the standardization of soil Si testing. Only a few procedures are established for determining total Si content in plant tissue: gravimetric method, hydrofluoric acid solubilization, autoclave-induced digestion with strong NaOH solution, or microwave digestion assisted with nitric acid–hydrofluoric acid (Yoshida et al., 1976; Novozamsky et al., 1984; Elliot and Snyder, 1991; Feng et al., 1999). The most widely used method was the autoclave-induced digestion method developed by Elliot and Snyder (1991) because it is relatively rapid and does not require costly, specialized instrumentation. However, there were many reports regarding low precision of the method and at times underestimation of Si value in the plant (Taber et al., 2002; Haysom and Ostatek-Boczynski, 2006). Excessive foaming caused some undigested samples to adhere to the walls of plastic tubes, and during autoclaving, the sample particles had lower or no contact at all with the NaOH and H_2O_2, which resulted in incomplete digestion. This was later addressed by Kraska and Breitenbeck (2010a) with the addition of octyl-alcohol, which eliminates the excessive foaming caused by H_2O_2 addition. The stability of color development was prolonged as well with the addition of 1 mL of 5 mM ammonium fluoride, and the method was simplified by using a bench-top oven (95°C) over an autoclave. After these modifications, the procedure is now called the oven-induced digestion procedure (Kraska and Breitenbeck, 2010a). Recently, nondestructive, accurate, and high-throughput methods in assessing Si in plants were evaluated. Reidinger et al. (2012) assessed Si in plants using a portable x-ray fluorescence spectrometer with a detection limit of 0.014% Si. Smis et al. (2014) calibrated plant Si extracted by wet alkaline (0.1 M Na_2CO_3) solution according to Meunier et al. (2013), with the values near-infrared reflectance spectroscopy technique.

Silicon content of plant tissue is an accepted parameter for evaluating plant-Si status. Currently, there are few published plant tissue critical Si concentrations, not only in the United States, but also elsewhere in the world. The published concentrations are mainly for rice and sugarcane. The critical Si level established by Snyder et al. (1986) for rice grown on organic soils of the EAA of south Florida using straw was 3.0%. Recent work by Korndörfer et al. (2001) established critical concentrations for rice (between 1.7% and 3.7%) using similar straw sampling material. Using the most recent fully expanded leaf in rice (Y-leaf) at mid-tillering, Kraska and Breitenbeck (2010b) noted 5.0% as a concentration used to indicate sufficient Si for rice in Louisiana. Using sugarcane top visible dewlap leaf as sampling material, Anderson and Bowen (1990) identified the critical Si content was 1.0%, whereas McCray and Mylavarapu (2010) set a lower value of 0.5%. To maximize sugarcane yield, the Si content in leaf tissue should be more than the reported critical Si concentration (Snyder et al., 1986). It is important to note that the critical Si concentrations are very specific to crop species, location, and sampling material, underscoring the need to establish site-specific plant-Si content interpretations.

Sources of Silicon Fertilizer

The reduction of H_4SiO_4 in soil solution triggers several processes in the soil system as a means to replenish the lost Si until equilibrium is reached between the liquid and solid Si phases. There are soils capable of immediately replenishing lost Si in soil solution (e.g., crop removal), but certain types of soil may take some time to replace lost Si even under accelerated mineral weathering, depolymerization, and dissolutions of silicate complexes with heavy metals, hydroxides, and organic matter. Consequently, fertilization using different sources rich in Si becomes a logical approach.

The first patent for using Si-rich slag as fertilizer was obtained in the United States in 1881 (Zippicotte, 1881). While the naturally occurring wollastonite Ca silicate is more soluble and contains high amounts of Si, the refining process of this mineral is labor-intensive and expensive, which limits its mass production as a fertilizer (Park, 2001; Maxim et al., 2008). Using this process, high application rates alone can make this Si fertilizer extremely expensive on top of its transportation cost to the field and machinery costs for application. In the United States, the expenses allotted to transportation and machinery may be affordable because of relatively good infrastructure and crop subsidies, but these expenses could be more problematic elsewhere in the world, particularly in developing countries. Nowadays, byproducts of industrial procedures such as the smelting of wollastonite, Fe, and Mg ore, and electric production of P are commonly used as Si fertilizers (Elawad and Green, 1976; Snyder et al., 1986). These are relatively inexpensive sources of Si for crop production. Compared with wollastonite, silicate slags contain smaller fractions of easily soluble Si, but they have added benefits such as liming agents, typically with similar Ca carbonate equivalent and as sources of some plant-essential nutrients (Heckman et al., 2003; Gascho, 2001; White et al., 2014). In addition, some slags, unlike wollastonite, can provide a balanced supply of Ca and Mg.

The amount of plant-available Si and composition of silicate slags differ because of differences in speeds of cooling and granular size of the material (Takahashi, 1981; Datnoff et al., 1992; Datnoff et al., 2001). While silicate slags are more economical to use as Si fertilizer versus wollastonite as Si fertilizer, producers should not overlook the amount of plant-available Si present in the silicate slag. Several methods for quantifying plant-available Si from industrial byproducts have been tested and thus far identified that the Na_2CO_3 + NH_4NO_3 extraction methods have been identified as suitable for solid Si sources, whereas the HCl + HF digestion was suitable for liquid sources (Buck et al., 2011). Recently, the 5-day Na_2CO_3-NH_4NO_3 soluble Si extraction method was developed for solid fertilizer products (Sebastian, 2012; Sebastian et al., 2013). Total Si and soluble Si of some industrial byproduct sources are reported in Table 5. Included in the list are organic sources: biochar, rice hull ash, and livestock manure composts. Straw from wheat and other small grain crops contains high amounts of Si; wheat straw Si concentrations range from 1.5 to 12 g kg^{-1} (Heckman, 2012). In addition to this, fresh rice straw can be a potential source of Si. The potential of fresh straw as source of Si is encouraging based on recent findings by Marxen et al. (2016), indicating that this plant material contains large amount of highly soluble phytoliths. This in turn can replenish the amount of plant-available Si taken up by plant from the soil solution.

TABLE 5. Total and Soluble Si Content of Different Sources of Silicon Fertilizer

Source	Silicon Content		Chemical Composition	References
	Total Si, g kg^{-1}	Soluble Si*, g kg^{-1}		
Wollastonite	242	36	Calcium silicate	Sebastian et al., 2013
	242	65	Calcium silicate	Haynes et al., 2013
$MgSiO_3$ (talc)	285	1.0	Magnesium silicate	Sebastian et al., 2013
Silica gel	467	58	Not known	Sebastian et al., 2013
Silica blend (monocal or with $FeSO_4$, NH_4NO_3, KCl)	121	18	Calcium silicate (mainly)	Sebastian et al., 2013
$CaSiO_3/MgSiO_3$ blend	120	22	Calcium/magnesium silicate	Sebastian et al., 2013
Liquid/solution				
K_2SiO_3 liquid	97	76	Potassium silicate	Sebastian et al., 2013
$NaSiO_3$ liquid	56	—	Sodium silicate	Abed-Ashtiani et al., 2012
Silicic acid	360	64	—	Sebastian et al., 2013
Industrial by-product				
Iron/steel slag	54	4.6	Calcium silicate	Haynes et al., 2013
Electric furnace slag	211	148‡	Calcium/magnesium silicate	Gascho and Korndorfer, 1998
	203	5.0		Sebastian et al., 2013
Blast furnace slag	173	17	Calcium/magnesium silicate	Haynes et al., 2013
Processing mud	68	0.4	—	Haynes et al., 2013
Fly ash	291	0.3	—	Haynes et al., 2013
	230	0.1		Raghupathy, 1993
Plant/organic material				
Miscanthus biochar	383	—	Silica	Houben et al., 2014
Rice hull fresh	70–92	—	Silica	Sun and Gong, 2001
Rice hull ash	>280	—	Silica	Kalapathy et al., 2002
Cattle manure compost	95	—	—	Kobayashi et al., 2008
Swine manure compost	34	—	—	Kobayashi et al., 2008
Poultry manure compost	17	—	—	Kobayashi et al., 2008

‡2% Citric acid procedure.

*Five-day Na_2CO_3-NH_4NO_3 soluble Si extraction method.

Adapted from Tubana and Heckman (2015). Adaptations are themselves works protected by copyright. So in order to publish this adaptation, authorization must be obtained both from the owner of the copyright in the original work and from the owner of copyright in the translation or adaptation.

The use of Si-containing solution applied as foliar spray has an advantage in terms of ease of application at manageable rates and not altering soil pH brought about by high application rates of solid Si sources with high liming potential (Tubana et al., 2012; Haynes et al., 2013). While there is a growing interest on the use of foliar Si solution, limited studies have been conducted in the United States (Kamenidou, 2002; Kamenidou et al., 2009; Lemes et al., 2011; Tubana et al., 2013; Agosthinho et al., 2014). In addition, even if there was a positive plant response to foliar Si, the foliar absorption of Si remains questionable because no transport mechanisms have been found to occur in this plant organ to date (Rodrigues et al., 2015).

Analytical methods are available to determine soluble Si analysis for liquid and solid Si fertilizers; however, soil is a dynamic entity, which unfortunately is understudied in Si research. Tubana et al. (2014) reported that the amount, time, and duration of release of plant-available Si from added silicate slag (12% Si) determined by the 0.5 M acetic acid extraction procedure were influenced by clay and organic matter content of the soil. They used soils from Indiana, Louisiana, Michigan, Mississippi, and Ohio that varied in soil pH (5.0–7.4), organic matter content (0.3%–5.0%), and texture (fine sandy loam to silty clay), with initial plant-available Si ranging from 22 to 165 mg kg^{-1}. Increases in plant-available Si were seen 30 days after application across all soil types. However, different trends were observed following this release of plant-available Si: (*a*) a drastic decline throughout the 120-day period was observed for soils containing high sand and clay fractions, presumably due to leaching and adsorption, respectively; and (*b*) continuously increased up to 90 days after application then declined for silt loam–textured soil containing moderate amounts of organic matter. Across all soils 120 days after application, the level of plant-available Si was found to remain substantially higher than the control (no Si added). A laboratory incubation study was conducted by Babu et al. (2014) to evaluate the release pattern of H_4SiO_4 from wollastonite and Ca silicate slag (12% Si) applied to soils of Louisiana varying in clay content and chemical properties. They concluded that the amount of H_4SiO_4 measured in solution (0.1 M NaCl) was influenced by the adsorption capacity of soils, which was highly determined by soil pH, organic matter, and clay content.

Synthesis

The establishment of Si fertilization as an agronomic practice in crop production is perceived to be pursued only in regions where there is lack of sufficient supply of plant-available Si. Perhaps the oldest reason justifying fertilization in agricultural lands was a compelling circumstance related to sugarcane production in

the geologically old soils of Hawaii and the organic and sandy soils of the south Florida EAA. The overwhelming published literature about the beneficial contributions of Si fertilization to crop productivity in production areas where disease and insect pressure is high and abiotic stresses are present has prompted research on Si to proliferate in the United States in the 1990s (Datnoff et al., 2001).

The principal crops in US agriculture collectively can take up 9.55 million tons Si in shoots annually (Table 2) or remove as much as 11.1 million tons from the soils planted to these crops (Table 3). The estimated amount of Si taken up in a given area by each crop showed that removal rates of Si from the soil can be substantial and even higher than primary essential nutrients (e.g., P, K) especially for rice (329 kg Si ha^{-1}), sugarcane (160 kg Si ha^{-1}), and wheat (108 kg Si ha^{-1}). These crops are classified as high–Si-accumulating plants. From the limited information collected in this review, it appears that the estimated shoot Si uptake is significantly much higher (1,408 kg ha^{-1}) than the rest of the crops in the list, even though this crop is a dicotyledon, which are considered to be low–Si-accumulating plants. The shoot Si used in the computation was based on the research of Draycott (2006), indicating that sugar beet top dry matter can contain as much as 115 g Si kg^{-1}. Nevertheless, the estimated amount of Si removed annually by these crops is generally substantial and faster than in natural ecosystems. Based on the total cropland area in the United States (USDA-NASS, 2007) and the average plant Si (Bazilevich, 1993), the total amount of Si removed annually is approximately 21.1 million tons. This is about 10% of the world annual Si removal rate by crops of 210 to 224 million tons reported earlier (Bazilevich, 1993; Reimers, 1990; Savant et al., 1997a). The amount of plant-available Si in solution is characterized as low, ranging from 0.1 to 1.6 kg Si ha^{-1} in the upper 20-cm soil layer; this is either due to the desilication (leaching) process common in highly weathered soils (Oxisols, Ultisols) or simply due to the fact that the solubility of most Si-bearing minerals in soils is low. The replenishment of plant-available Si in soil solution is critical and may be characterized as slow based on soil Si dissolution kinetics and Si release from organic sources, including crop residues and burned rice husk. The latter, however, was reported to have long-term positive effects. Faimon (1998) studied the kinetics of release of Si from feldspar, grandiorite, and amphibolite, revealing solutions can attain supersaturation with respect to Si; consequently, this may lead to Si flowing out from the solution forming secondary minerals or their amorphous equivalent. This process essentially reduces the amount of plant-available Si.

Silicon chemical dynamics in soils have been understudied until recently. The research thus far reveals that the chemical dynamics between Si and many soil components influence the amount of plant-available Si released to soil solution. This could challenge the assumption that based on the amount of 2:1 layered silicate clay minerals that most soils in the United States are capable of supplying high concentrations of plant-available Si to crops. A recent study showed a significant increase in grain yield of rice even when grown on a soil rich in 2:1 layered silicate clays with high initial levels of 0.5 M acetic acid–extractable Si at 160 μg g^{-1} (Tubana et al., 2014). Babu et al. (2014) pointed out that the release of H_4SiO_4 to soil solution is critical to the amount of soil solution plant-available Si and is influenced by different processes (e.g., desorption, polymerization) and soil properties other than pH. This explained the unexpected response to Si of rice grown on soil despite high initial Si level and clay content. In this context, the need for Si fertilization not only may be justified by having low plant-available Si, but also could be based on the soil's ability to replenish the Si removed by plants from the soil solution, especially for soils under continuous, intensive farming systems. Clearly, a soil's clay content, pH, organic matter content, and Al and Fe oxide content are essential factors to consider when making a recommendation for a Si fertilizer.

The success of US agriculture as an industry has been attributed to modernization and adoption of intensive crop farming approaches that have enabled the country to become a net exporter of food (USDA-ERS, 2013). This trend is likely to continue, and so will the removal of Si from US cropland soils. Climate change is foreseen to bring more challenges and limitations to crop production in the forms of higher disease pressure, drought, waterlogged conditions, and salt stress. In addition, continuous cropping is always accompanied by removal of basic cations and fertilization, which in turn will eventually lead to soil acidification, making liming programs indispensable in crop production to secure maximum yield. For all these reasons, Si fertilization using low-cost industrial byproduct sources with high liming potential may become an agronomic practice in many crop production systems in the United States, especially for the purpose of alleviating biotic and abiotic stresses that may limit yields as well as for correcting soil pH.

ACKNOWLEDGMENT

Published with the approval of the Director of the Louisiana Agricultural Experiment Station as publication 2016-306-27516.

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