PRODUCTS OF SILICON:
IT HELPS THE PLANTS TO OVERCOME THE BIOTIC AND ABIOTIC STRESS
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Silicon (Si), the second most abundant element on the earth's crust after oxygen, is beneficial to the development and growth of the plants. Silicon allows plants to overcome biotic and abiotic stress. Unfortunately, the benefits of Silicon have been ignored until the beginning of 20th century, mainly because of the lack of visible symptoms of Silicon deficiency, as well as of the toxicity of Silicon in plants. For this reason, the researchers had not carried out trials or studies on this element for years. However, in many agronomical conditions, the plants are confronting several conditions of stress, especially in the soil with low or limited availability of Silicon. Thus, first in the scientific community and later among farmers, the importance of Silicon in the development of plants has started to be recognized. Five international conferences on Silicon have already been held (USA 1999, Japan 2002, Brazil 2005, South Africa2008 and China 2011). And in this way, the use of diverse formulation started to become popular among farmers. The professor, Lawrence E. Datnoff, Department of Plant Pathological and Physiological from Louisiana State University Agriculture Center in the USA, offers his vision on the incorporation of this element in the management plan and his role to potentiate the plants to the situations of biotic and abiotic stress on this edition of *New Ag International*.

Silicon refers to the chemical element Si and is in the periodical table in column IV-A, directly below Carbon. It has an atomic number 14 and is a tetravalent metalloid. The Silica (SiO2) refers to silicon dioxide and is the major constituent of the sand. The silicates (SiO 3-2) are found in association with the following cations: Ca + 2, Na +, Mg + and K + and form the following Crystalline compounds CaSiO 3, Na2SiO 3, MgSiO 3 and K2SiO3. Silicic acid, Si (OH) 4 (Also known as monosalicic acid or orto-salicylic acid) refers to the soluble form of Si that is available to be absorbed by the roots of the plants. The silicone, R2SiO – where R is an organic group - it is used in the manufacture of plastic products and gums.

A LOT OF SOIL IN THE WORLD IS DEFICIENT IN SOLUBLE SILICON

Most soils contain large amounts of soluble Si concentrations in the range of 3.5 to 40 mg of Si L-1. The concentrations of this magnitude are common in various inorganic nutrients such as SO4, K, and Ca and also can be found in excess on phosphate concentrations in the soil solution. However, the solution of Si from minerals of the soil is slow and its adsorption by soil and intensive farming practices make available Si levels available significantly reduced to the extent that it is necessary supplemented with products based on Si to obtain the desired agricultural productions. Some soils have low available levels of Si. This type of soils are commonly very washed, leached, acidic soils with a low saturation base and containing large amounts of sesquioxides (eg. aluminum oxide, Al2O3). For this reason, highly washed soil such as Oxisols and Ultisols can have low levels of Si available for plants. And highly organic soils that have low minerals, such as Histosols, may also have low levels of Si. Moreover, some soils, mainly composed of sand Quartz, silica (example, sandy entisols) may have high levels of insoluble Si but low Si levels available for plants. Many blends of soils fall into this category as well. These soil conditions with low availability of Si are found in large agricultural areas in Africa, Asia, the Americas and even Europe.

A KEY CONSTITUENT OF THE PLANTS

All plants cultivated on soil will contain Si in their tissues, and it has been shown that 44 clades of angiosperms (Representing more than 100 orders or families) also contain Silicon in their tissues. In order to determine if plants accumulated Si, the previous studies focused on measure Si in the foliage and not in other organs of the plants. Recently, it has shown that some species of vegetables - eg. Tomato and pepper – accumulate more Si at its roots than in its shoots. The extraction of silicon from shoots varies on species and on maturity of the plant, with a range of concentration ranging from 0.1% to 10%, based on dry material. The monocotyledonous plants will tend to accumulate more Si in the tissues than those of Dicotyledonous plants. In general, the moisture pastures will have between 4.6 and 6.9%, while pastures in Dry grasslands varies between 0.5 and 1.4%. Dicotyledonous plants have overall less than 0.23%. In the low part of this range, 0.1%, this is similar to the percentages of macronutrients, such as Ca, Mg, P and S. And in the high part, 10%, concentration in the tissues exceeds that of mineral nutrients N o K. For all this, it is established that Silicon is clearly a major constituent of plants. The difference in the accumulation capacity of Si between different plants attributed mainly to the different ability of root to absorb Si. As mentioned earlier, the roots extract salicylic acid and this has identified and characterized as transporters in the roots, which played a very active role in the accumulation of Si. This work has been done in wheat, soybeans, rice, corn, squash and barley.
Once you pass the root barrier, the Si moves through the xylem by transporters and/or transpiration towards the endodermis of the root, membranes cells of the vascular bundle and the cells of the leaf in the epidermis just below the cuticle. Once it's inside a cell, natural process of polymerization occurs, the process which Si converts silicon acid in insoluble silica (SiO_2-nH_2O; also known as Silica gel or phytolytes).

VARIOUS SOURCES OF SILICON IN THE MARKET

There are a number of solid and liquid sources of Si in the market, they have been used as soil amendments or fertilizers: Diatomite, calcium silicate, sodium metasilicate, potassium silicate, magnesium silicate, ortosilicic, hydrated silicon dioxide, calcium metasilicate. In order for these materials to be useful, it must meet with a series of criteria, including a relatively high content of Si Soluble, a material condition that facilitates storage and application and that does not contain substances that contaminate the soil, such as heavy metals.

The solid sources that have been successfully used in incorporations to the soil include the wallastonite – natural silicate calcium $CaSiO_3$ - a by-product of the phosphate and Steel, thermophosphate and cement. The crop residues (example, rice husk) are also a potential source, but due to its slow solubility in the soil, it does not allow them to supplement the immediate needs of the crops. Several of these materials are applied in pre-planting in rates ranging from 300 to 800 kg of silicon element per hectare. The liquid sources include silicates of potassium or silicates of sodium and are mainly used in Hydroponic production at rates of ~ 2mM Si. Also liquid silicates are used in foliar applications, mainly to control diseases. However, for different combinations host: disease (wheat /Cucumber: powdery mildew; Soybean / rust; Rice /blown spot) plants responded better with the soil applications of Si that in foliar application. In 2007, a potassium silicate (Sil-MATRIX®, PQ Corporation) was registered by the Environmental Protection Agency (EPA) in the United States and certified by Organic Materials Review Institute (OMRI) as an organic pesticide for the preventive control of powdery mildew and of mites and aphids in crops of high value crops such as vine grape, strawberries, cranberries, among others.

ESSENTIAL ELEMENT?

In the 50s, Japan and South Korea were the first countries to recognize the importance of Si in production especially in rice. They classified this element as essential. In 2004, Brazil was the third country formally recognizing silicon. The Ministry of Agriculture of Brazil, which regulates the commercial production of fertilizers, established that Si is a beneficial micronutrient. Nowadays, if it is not yet recognized as an essential element and in many countries it is sold only as a soil amendment or soil conditioner instead of fertilizer. And this is owing to the way defining the nutrients of plants, which is based on three criteria developed by Arnon and Stout (Epstein and Bloom 20051):

1) a deficiency of the element prevents that the plant completes its cycle;
2) the deficiency is specific to the concerned element
and
(3) the deficiency directly impacts nutrition of the plant, such as constituent of an essential metabolite for the action of an enzymatic system.

Epstein and Bloom (2005) have argued that there are difficulties with this definition. Because of the first criterion, a plant may have a quite severe deficiency of an essential nutrient and in spite of this, plants can complete its cycle. For the second criterion, they consider it repetitive. Finally, for the third criterion, that the element participates directly in nutrition of the plant, does not incorporate the capacity to correct unfavorable environmental situations. In fact, in many cases of discovery of essential elements, these criteria have not been met. When it was discovered that boron was essential, no one had the Evidence that the "element involved directly in the nutrition of the plant." That's why Epstein and Bloom have proposed the following:

An element is if it meets one or two of the following criteria:

(1) the element is a part of molecule that is an intrinsic component of the structure or metabolism of a plant;
(2) the Plant which is so severely deprived of such an element exhibits abnormalities in its growth, development or reproduction, compared to non-deficitiant plants.

Because the "essentiality" of Si for diatom, Equisetum arvense has been well established but could not be categorically demonstrated to other species. Epstein and Bloom have proposed that the Si is an element "Quasi-essential."

A DOCUMENTED ROLE IN THE ABIOTIC STRESS REDUCTION
The beneficial effects, direct or indirect, of the Si have been proven on plants under abiotic stress (Table 1) in a variety of crops, especially in rice. The leaves, stems and panicle of growing rice plants in the presence of Si show a erected growth, suggesting that improves the distribution of light within the canopy. Silicon can affect positively the effect of the activity of some enzymes involved in the photosynthesis in rice and in turn reduce the senescence of the rice leaf.

Table 1. Types of Abiotic Stress that Improve with Silicon Applications

Chemical
• Helps to overcome metal toxicity (Al, Cd, As, Mn, Fe)
• Help overcome stress from salts
• Help overcome nutritional imbalances (Excess of N, deficiency of P)

Physical
• Prevents compaction
• Increases resistance to high and low temperatures

• Improves resistance to water stress
• Improve resistance to heat stress

High use of N may affect erections of the leaf and therefore decrease the maximum interception capacity of light, especially in high densities of sowing. However, the Si will impact positively on the erection of the plant, improving the photosynthetic capacity. Silicon can also help to alleviate water stress by reducing the loss of water in the leaves and decrease the perspiration. Perspiration occurs mainly through the stomas and partly through the cuticle. Because the Si is deposited under the cuticle, it can decrease perspiration of this part of the plant. In addition, plants supplemented with Si, can maintain a higher stomatal conductance, higher water content and water potential. These same reasons should explain the positive impact of this element against heat stress. Under situations of stress due to P deficiency, Si empower the availability of internal P by reducing the excessive extraction of Mn and Fe. And under high concentrations of P, silicon can reduce damage to reduce P extraction or reduce perspiration. It has also been reported that silicon protects the plant from the toxicity of metals, such as Al, Cd, Fe, Mn and Zn. For metals Al, Cd, Fe and Zn, the effects of the Si attributes to the interaction between this element and these metals in the simplasto or Apoplasto. Moreover, the reduction of toxicity of these metals is believed to occurs by complexation and /or by compartmentalization with Si in the cytoplasm and sequestration in vacuoles or cell walls. Hypotheses have been established which indicate three mechanisms to decrease Mn toxicity:

(1) Silicon reduces the extraction of Mn to potentiate the oxidative potential of Mn by the parte of rhizosphere through chemical or microbial mechanisms.
(2) increases the coupling capacity of the cell wall which generates a reduction of Mn in apoplasma and/or
(3) stimulating the antioxidative defense system against oxidative damage of cells caused by toxicity of Mn. Reduction of stress from salts generated by silicon would run through two mechanisms: (1) Silicon could generate a partial block of the transpiration bypass flow, reducing the passage of Na and (2) deposition of Si at the roots would prevent the Na is transported to the xylem. In fact, the concentration of Na in the wise of Phloem was reduced from 6.2 to 2.8 mN in tests with Si.

LEGISLATION: A SPECIAL STATUS FOR SILICON FERTILIZER

North America offers a good example of the special status of fertilizers of silicon in legislation. In 2004, efforts were made to educate the Association of American Plant Food Control Officials (AAPFCO), the organization which regulates fertilizer registration in the United States, Puerto Rico and Canada use the recommendations of AAPFCO for its own regulations of fertilizers. This body seeks to generate uniformity by consensus, considering the needs of consumers, the protection of environment and maintaining fair competition between actors of the industry. AAPFCO has a definition of plant nutrients different from the one given by Aron and Stout and also to Epstein and Bloom. They put nutrients into two categories (1) primary and (2) secondary and micronutrients, this based on the quantities of nutrients required. Primary nutrients include Nitrogen (N), the available phosphate(P_2O_5) and soluble potassium (K_2O). And they are absorbed in large quantities. Secondaries and micronutrients are needed in trace amounts and are essential for the normal development of plants and in many cases are necessary to be added to the crop. Secondary nutrients include calcium, magnesium and sulfur, while micronutrients include Boron, chlorine, cobalt, copper, iron, manganese, molybdenum, sodium and zinc. Therefore, this classification does not define a place for the Si, because this element did not fit into the classification of primary nutrient, secondary or micronutrient. Consequently, the AAPFCO's registration committee proposed a new category called "Substances or Beneficial Compounds." This new category was defined as "Any substance or compound other than primary, secondary nutrients or micronutrients which can be proved to be beneficial for one or more species of plants by scientific study, when it is applied exogenously." In spite of this, Si received only tentative approval by the AAPFCO because there was no method to differentiate content of total silicon of soluble silicon. There is need to determine and validate a method to determine the available Si for the plants in fertilizer sources. Based on previous research, it was possible to determine a method of 5 Days to determine the concentrations of Silicon in products of Solid fertilizers and was approved by AAPFCO (Sebastain et al., 20132). It has been shown that this method has a good correlation with the extraction of Si by plants and can be used now for quality control, to register suitably new products and to choose the best producer of silicon for a crop. Nowadays the fertilizers carry on the label containing beneficial substances like the Si and can be sold in United States. As an example, CrossOver ™ ($CaMgSiO_3$, HARSCO) is currently being recorded and indicates that it contains the beneficial substance Si and already sold in 33 states of the USA for use in horticultural and agricultural markets. In Europe, no work has been developed to European Union level and silicon is not included in the fertilizer legislation. However, it is registered in some national legislations (Eg in several European countries from the east). In Australia and South Africa, silicon is part of the legislation on Fertilizers.

THE ROLE OF SILICON IN FRONT OF BIOTIC STRESS: MUCH MORE THAN FUNGICIDE ACTION

Many crops supplemented with Si gain resistance against foliar diseases and soil diseases, caused by By fungi, bacteria, nematodes and viruses (Table 2).

Table 2. Pathogens that cause rust, powdery mildew, leaf spots, gills, wilting and root rot that have been reported to be suppressed with silicon. (Hongos =Fungus)

Hongos	Oomycetes
• Bipolaris	• Phytophthora
• Blumeria	• Pythium
• Collectotrichum	
• Corynespora	**Bacterias**
• Diplocarpon	• Ralstonia
• Erysiphe	• Xanthomonas
• Fusarium	
• Leptosphaeria	**Virus**
• Magnaporthe	• Tobacco Ring Spot
• Phaeosphaeria	• Tobacco Mosaic
• Phakospora	• Belladona Mottle
• Rhizoctonia	
• Septoria	**Nematodos**
• Sphaerotheca	• Meloidogyne
• Sclerotinia	
• Uncinula	

Silicon affects one series of resistance components of the plant that allow to retard incubation, reduce the expansion of lesiones, reduce size and number of lesion and the production of Conidia. For this reason, with applications of Si, the severity and progress of disease are reduced. And this can make susceptible species gain resistance by equating the species partially or completely resistant. Silicon can suppress diseases so effectively as a fungicide. As the concentration of Si (soluble and insoluble) increases in the tissues of the plant, the disease suppression increases. However, it is important to highlight that the input of Si must be continuous because, otherwise, the protector effect decreases or disappears. The disease resistance is strong when the Si is applied to the soil and absorbed by roots, as opposed to foliar applications. The foliar applications of Si does not work as well as soil applications because the transporters of Si are not expressed in the leafs. Consequently, the disease suppressing effects in the cases of foliar applications are probably due to the fact that Si deposited on the surface of the leaf has an osmotic effect or effect of pH. The underlying mechanism governs the protection to diseases by the Si is not fully understood. However, the effect of Si on the resistance of plants to diseases is considered to be due to the accumulation of Si in the tissue of the Epidermos or to the responsive expression of metabolic or pathogenic defense. The accumulated monosilicic acid is polymerized into polysilicic acid and then is transformed into amorphous silica, which forms a thick membrane of si-cellulose. In this way a double layer cuticular protects and fortifies mechanically the plants. Silicon also could form complexes with compounds on the walls of the cells of the epidermis, increasing the resistance to degradation by enzymes released by fungi and bacteria Phytopathogens. There are other investigations which point to a more Si activity in plants, suggesting that silicon could be a signal between diseases and the defensive response of plants. It has been demonstrated that Silicon after a fungal infection stimulates the Chitinase activity and Peroxides and polyphenoxidases activity rapidly. It has been shown that glycosylated phenols extracted from plants that applied Si has a powerful fungicidal activity. It has also been demonstrated that plants attacked by pathogens to which Si were added generated flavoniodes and phytoalexins momylactones, low molecular weight properties antifungal compounds. These antifungal compounds seem to play a very active role in the suppression of diseases. Moreover, it was observed that in rice leaves treated with Si increase in the generation of superoxide(O -), 15 minutes after being inoculated with Magnaporthe oryzae, the causal agent of rice blast. These studies suggest that there are mechanisms that may be involved in induced resistance by the Si to diseases. A lot of evidence suggests that the Si influences the endogenous hormonal balances of resistance of plants. Through microarrays it has been confirmed that the supplements of Si induce high levels of salicylic acid, Jasmonic acid and ethylene. Recently studies at genomic level in tomato,rice and wheat grown on supplemented soils with Si and compared with control plants (without the soil) have demonstrated expressions of a number of genes involved in mechanisms and metabolism of plant defense (Table3).

Table 3: Some Defense Genes and Stress Mediated by Silicon in Different Host-pathogen Systems.

Tomate(Tomato) *Ralstonia solanacearum*
• WRKY1 transcription factor
• Protein response to
Disease resistance
• Related to Ferritin
• Abundant protein in
Late embryogenesis
• Trehalose phosphatase
• Acetoacetyl-CoA thiolase

Trigo (Wheat)*Blumeria graminis*
• -1,3 endoglucanase
• Proteins related to pathogenesis
• Germina type proteins
• Superoxide dismutase
• Peroxidase

Arabidopsis *Erysiphe cichoracearum*
• WRKY
• Proteins related to pathogenesis
• Chitinase
• Defensina
• Germina type proteins
• Peroxidase

Arroz(Rice) *Magnaporthe oryzae*
• Protein type tolerance to salinity
• Multi-type oxidase type 1
• Ferritin 1, chloroplast precursor
• Metal-bound terpene synthetase
• Phenylalanine ammonium lyase
• Peroxidase
• Anti-fungal protein
• Precursor peroxidase 52

It has also been shown that Si provides plants with resistance against Insect borer attacks and suckers (Table 4).

Table 4. Reports of Herbivores and Others Pests that are Suppressed by Silicon

Chewing insects
• Centipedes and borers
• Grasshoppers
• Worms
• Beetles
• Lobsters

Sucking insects
• Cicadélidos
• Aphids
• White fly
• Scale

Other pests
• Leaf spiders
• Mites

These effects can be direct or indirect. The direct effects may include a reduction in growth and reproduction of the insect pest. And the indirect effects may include effects on pest mortality rate that will result in a lower penetration to the plant and also silicon can have a role in the generation of volatile of the plant that can attract enemies of the pest that attacks the plant.

A Clear mechanism of action of Si against pest attacks is the increase in the hardness of the plant tissues. Plants attacked by insects increase its release of enzymes from defense as peroxidase, polyphenoloxities and phenylalanine ammonia when they receive silicon supplements. Peroxidase participates in lignification and in the synthesis of suberin that increases the hardness of the tissues of the plant and at the same time generates quinones which have antibiotic properties. The activity of the enzyme PAL increases the production of compounds Phenolics. Clearly, many of the defense compounds produced by plants supplemented with Si, when attacked by insects, functions in a manner similar to those generated when the plant is attacked by diseases.

A GREAT POTENTIAL MARKET FOR SILICON PRODUCTS

Silicon is a vital component of Soil-plant system. And Si play very important role defending and empowering to the plant in front of situations of biotic and abiotic stress. Nevertheless, the commercial potential of the Silicon has just begun to be understood by industry, both to be used as fertilizer or as a phytosanitary. Because many soils have low levels of Si available for plants and also based on that many species of plants contain something of Si in your tissues seems prudent to consider supplementation with silicon as a simple and to help maintain and enhance the health of plants.

(Citation 1) Epstein, E. and Bloom, A.J. 2005. Mineral Nutrition of Plants: Principles and Perspectives, 2nd Edition, Sinauer Associates, Inc., Sutherland, MA, 400 pgs

(Citation 2) Sebastian, D., Rodrigues, H., Kinsey, C., Korndorfer, G., Pereira, H., Buck, G., Datnoff, L., Miranda, S., and Provance-Bowley, M. 2013. A 5-day Method for determination of soluble silicon concentrations in nonliquid fertilizer materials using a sodium carbonate-ammonium nitrate extractant folded by visible spectroscopy with heteropoly blue analysis: single-laboratory validation. J. AOAC