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Effect of silicon on reduction the availability of toxic elements in the soil: a brief review

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Abstract. Soil pollution is a major environmental problem and also makes food production impossible, since 95% of food produced worldwide originates in the soil. There are numerous practices that when improperly made can cause soil contamination, in agriculture the inadequate use of fertilizers and agrochemicals can cause soil contamination by toxic elements. Silicon is already present in the soil in a natural way, but in recent years research is being developed using silicon-based residues to increase plants resistance to pests and diseases, such as soil corrective and for increased productivity, the results are satisfactory. Many published studies show the benefits of silicon in reducing plants stress, but there is still little information about silicon as a remediator of toxic elements in the soil, so the objective of this work was to search for already published works on this theme. Studies were found using different silicon sources and the application occurred in soils contaminated mainly with Zn, Cd, Cu and Pb.

Keywords: Silicate, heavy metals, remediation.

Contextualization and Analysis

Soil contamination by toxic elements is a worldwide problem, and it can occur in a natural way, through the weathering of minerals or anthropicly form, through the inappropriate use of agrochemicals, fertilizers or the improper disposal of industrial waste. Toxic elements are all metals in the periodic table that can cause damage to living beings, which have high toxicological potential and the ability to bioaccumulate in nature, these elements are also called "heavy metals" (RIBEIRO, 2013).

Soils have the retention capacity of toxic elements, but when the retention limit is reached, these elements can be absorbed by plants or leached for water courses and can contaminate all living beings (SOUZA, 2012).

The soil performs numerous functions, one of which is the support of plants and nutrient supply, directly or indirectly, more than 95% of the world's food production originates in the soil (FAO, 2018). And soil contamination by toxic elements makes food production impossible, since it reduces production and depending on the concentration accumulated in

food causes damage to the health of living beings. Therefore, several researchers around the world have been looking for alternatives for soil decontamination.

Silicon is present naturally in the soil, but with the action of weathering, this silicon is leached, moreover, silicon is not always in its available form in the soil solution.

Several authors have carried out studies showing the benefits of silicon in reducing plant stress (MA et al., 2001; TAMAI & MA, 2003; MA & YAMAJI, 2006; CHANDLER-EZELL et al., 2006; LIU et al. 2015). But there are still not many studies verifying the effect of silicon in reducing the availability of toxic elements in the soil. Therefore, the objective of this work was to analyze the potential of silicon as a reducer of the availability of toxic elements in the soil, through studies already published.

Toxic elements

In general, it is considered metal every element that presents strong bonds between its atoms and still has physical characteristics such as

being able to conduct electricity, being malleable, flexible, and having brightness (BACCAN, 2004; CASTRO, 2006). Still Bacchan (2004), says that the characteristic of metal can vary according to temperature.

When the metal has high toxicological potential and still great pollution power in the environment is used the term toxic elements or "heavy metals". According to Malavolta (1994) the expression "heavy metal" can be used when the elements have a density greater than 5 g/cm³ or have an atomic number greater than 20.

A more recent classification was presented by Duffus (2002), who in his work reported that all elements with a specific mass between 3.5 and 7.0 g.cm³, atomic mass and high atomic number can be considered a toxic element.

The main properties of these elements classified as toxic elements are their high bioaccumulation and reactivity capacity (RIBEIRO, 2013). Contrary to what is thought not all of these elements cause risk to living organisms, some such as Cu, Mn, Mo, V, Sr and Zn play important roles in living organisms. This is because living organisms have the ability to metabolize small concentrations of toxic elements (RIBEIRO, 2013).

Other toxic elements such as Cd, Pb and Hg have no function in living organisms and their accumulation can cause serious risks mainly in mammals. These elements are most often released into the environment through industrial waste, and are absorbed by plants and animals resulting in poisoning along the food chain (PEREIRA; EBECKEN, 2009; RIBEIRO, 2013).

Toxic elements in the soil

The soil has the ability to retain toxic elements, however, there is a retention limit that, when exceeded, allows interaction with living organisms, and can still be leached causing contamination of the groundwater (SOUZA, 2012).

The origin of these toxic elements in the soil was divided by Allooway (1995) into lithogenic and anthropogenic elements, that is, they can originate from rock residues and by the action of weathering or human action through the inappropriate use of agrochemicals, fertilizers and improper disposal of industrial waste, respectively.

Considering that the soil can retain small concentrations of toxic elements, conama resolution 420/2009 established a maximum permitted concentration limit of toxic elements in soils, which were divided into agricultural, industrial and urban areas (CONAMA, 2009).

In the state of São Paulo, the São Paulo State Sanitation Company (CETESB) also established a permitted limit for toxic elements in the soil (CETESB, 2005). And these reference values vary in other countries, there is still no consensus of the permitted concentration, some countries allow higher levels and others lower, the values of heavy metals in Brazilian

soils, are usually within the ranges of European and American soils (TSUTIYA, 1999).

In the soil these elements can occur in the ionic or complex form in the soil solution and several factors influence the availability of toxic elements in the soil, one of these factors is the type of soil. Soils with higher clay contents tend to accumulate higher amounts, this is because clay minerals have negative sites that allow adsorption of toxic elements by electrostatic forces (SOUZA, 2012).

In addition to the type, other soil properties may influence the adsorption of toxic elements (McBRIDE, 1989) being the main:

a) Hydrogenic Potential (pH)

In drained soils the pH directly affects the availability of toxic elements. The increase in pH reduces the availability of these elements in the soil solution and also reduces cation exchange (SANTOS, 2005). This effect is linked to the formation of precipitates in the form of carbonates, phosphates, sulfate and hydroxides (ARAÚJO et al., 2002).

b) Cation-exchange capability (CEC)

This property occurring in the soil can reduce or increase the availability of toxic elements in the soil. According to some authors, the increase in CEC increases the adsorption of these elements, since with the elevation of CEC there is greater formation of negative pH-dependent loads (CROOKE, 1981; POMBO et al. 1989).

c) Organic matter (O.M)

Soil organic matter is composed of humic acids and fulvic acids and these acids have the ability to form organic complexes with toxic elements. (SANTOS, 2005). When complexes are information with humic acids, there is a reduction in the availability of these elements in the soil solution. When the formation of complexes is formed by fulvic acids, the reverse occurs, that is, there is a greater availability of these elements in the solution (STEVERSON; ANDAKANI, 1972), this is because there is a lower adsorption and consequently there is an increase in its mobility (COSTA; COSTA, 2015).

d) Content of iron oxides and hydroxides and manganese

Iron and manganese oxides and hydroxides play an important role in the retention of toxic elements and in their immobilization (FERNÁNDEZ, 2017). Toxic elements linked to iron and manganese oxides and hydroxides are bioavailable in areas where soil is subject to reducing conditions (FERNÁNDEZ, 2017).

Silicon in soil

Silicon is the second element present in greater quantity in the earth's crust, behind only oxygen. It constitutes clay minerals, participating in the process of soil formation (MENEGALE et al., 2015). However, this element is lost in the soil according to the degree of weathering suffered by

him, Brazilian soils have a high degree of weathering, due to this presenting 4% to 40% silicon in its composition (Ma et al., 2001).

Silicon Oxide (SiO_2) is classified as the primary mineral and forms the basis of the structure of most existing clay minerals, however this mineral is almost always found in the form of quartz, opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and in forms that are not available to the plant, because most soils of tropical regions are already in a high degree of weathering (BARBOSA FILHO et al., 2001).

In soil solution silicon is mostly present in a non-dissociated way as silicic acid (H_4SiO_4), and can be rapidly absorbed by plants (CATEN, 2013). There are several sources of silicic acid present in the soil solution, and can become available in soil solution through the decomposition of plant materials, dissociation of polymetric silicon acid, release of silicon (Si) of hydroxides and iron oxides (Fe) and aluminum (Al), irrigation water, dilution of crystalline or non-crystalline minerals or the addition of silicate fertilizers (FERREIRA, 2008).

The pH dependent on sesquioxidas reactions directly affects the availability of silicon in the soil solution, the solubility of this element occurs in the pH ranges from 4 to 9 (FERREIRA, 2008, CATEN, 2013). Another factor that can reduce the availability of silicon (Si) is soil compaction, this is because in compacted soils there is an increase in the level of polysilicic acids, which consequently decreases the silicon content available to the plant (H_4SiO_4) (MATYCHENKOV et al., 1995; MARONDI, 2011).

In soil solution, the behavior of silicon (Si) is like that of a weak acid (CATEN, 2013), and its concentration is 0.1 to 0.6 mmol. L^{-1} (EPSTEIN; BLOOM, 2006). However, continuous crops reduce the availability of this element in the soil (KORNDÖRFER and DATNOFF, 1995) leading to the need for application of silicate fertilizers to complement the availability of silicon plants.

Silicon and toxic elements

Studies in hydroponic system were conducted with high doses of some elements classified as toxic elements and stress reduction was verified in plants when silicon was added to the solution.

Song et al. (2011) conducted an experiment in a hydroponic system with two rice cultivars submitted to different levels of zinc with or without silicon and concluded that the reduction of zinc toxicity by silicon occurs by antioxidant transport and reaction.

Khaliqa et al. (2016) conducted a cotton experiment in a hydroponic system with two nickel concentrations (50 and 100 μM) without the presence and with 1 mM of silicon and observed that in the plants that were added silicon there was a reduction in the adverse effects caused by nickel.

Shi et al. (2018) also conducted a hydroponic system assay with wheat crop evaluating silicon as a mitigating factor of cadmium effects and observed that silicon can reduce cadmium toxicity in wheat

seedlings and also allow the plant to increase its antioxidant capacity and reduce cadmium absorption. Freitas et al. (2017) conducted an experiment in solution to verify the effect of silicon in the reduction of aluminum toxicity in upland rice plants and observed that silicon reduced the effect of aluminum toxicity in rice, it was also noticed an increase in the growth of rice plants even in the presence of aluminum and the authors came to the conclusion that silicon behaves like a toxicity attenuator in high ground rice plants, under experiment conditions.

These studies show that silicon attenuates the effect caused by toxic elements in plants, however, they are all performed in hydroponic system. Soil is a heterogeneous system, that is, it is constantly changing, the effect of silicon on the attenuation of toxic elements can be influenced, for example, by the material of origin of the soil, as well as by the biological fraction.

Silicon in the reduction of toxic elements in the soil

Paim et al. (2003) evaluated the effect of phosphorus-associated silicon on soil reduction and these authors observed that there was a reduction in the availability of toxic elements, specified in Cd and Zn contents, however the levels of these elements were still above what was allowed.

Two experiments were carried out in pot by Liang, Wong and Wei (2005) to evaluate the effect of silicon (Si) on soil contaminated by cadmium (Cd), both experiments received doses of 20 and 40 mg kg^{-1} which differed was the concentration of silicon applied, the first received 400 mg kg^{-1} and the second 50 mg kg^{-1} in the form of sodium metasilicate. These authors noticed with this experiment that there was a reduction in cadmium concentration in the soil solution when the dose of 400 mg kg^{-1} was used regardless of the level of cadmium contamination.

When the second experiment was evaluated using the lower silicon concentration (50 mg kg^{-1}) there was no difference when compared with the treatment that did not receive silicon application. The same occurred when cadmium solubility was evaluated in water. It was concluded by the authors that silicon can reduce the availability of cadmium in the soil and this reduction may be linked to increased pH (LIANG; Wong, I.A. WEI, 2005).

An experiment was conducted in an environment controlled by Treder and Cieslinski (2005), two soil types (sandy and clayey) were used and these were contaminated with increasing doses of cadmium (Cd), silicon was applied in the form of potassium silicate and these authors did not evaluate cadmium reduction in soil, but lower cadmium absorption was observed by strawberry plants that were grown in sandy soil with silicon application, which shows noticeably that there was a reduction in cadmium availability in the soil, when compared with the treatment that there was no silicon application.

Accioly et al. (2009) conducted an experiment with the objective of verifying the reduction of toxic elements with the use of calcium

silicate, the soil presented three levels of contamination (moderate, intermediate and severe), a reduction in available zinc levels was observed regardless of the level of contamination, there was a linear reduction of zinc transfer to the roots as silicon doses increased. These authors also observed a difference in pH after calcium silicate application and the reduction of cadmium transfer from soil to roots was not significant.

Faria (2010) in a field experiment, installed on a red soil Latosol evaluated two sources of silicon based on MgO and CaO in increasing doses in the mitigation of toxic elements in the soil and no significant difference was observed in the reduction of these elements or in the other soil attributes.

Gu et al. (2011) conducted two experiments, the first in a greenhouse and second in the field, with soil already contaminated with cadmium, zinc, lead and copper. In the greenhouse experiment, two concentrations of steel abrasions (steel foundry residue) and two concentrations of fly ash (residue of mineral coal combustion) were used as a silicon source, respectively 20 and 40 g kg⁻¹ and 3 and 6 g kg⁻¹, of the dry weight of the soil and concluded that both by-products reduced the availability of zinc, copper, cadmium and lead.

In the field experiment, fly ash and steel abrasion were used at concentrations 20 and 3 g kg⁻¹, respectively, and the same effect of the vessel experiment was also observed. The authors concluded that both sources of silicon used have the potential to attenuate the availability of these heavy metals in the soil and this effect may be related to the silicon potential of forming complexes with these elements, which consequently makes them less soluble in soil solution (GU et al. 2011).

Rizwan et al. (2012) evaluated the effect of amorphous silicon on the reduction of heavy metals of a sandy soil, the experiment was conducted in a greenhouse, three different doses equivalent to 1, 10 and 15 t ha⁻¹ with and without plants of *Triticum turgidum* L. cv were applied. Claudio W. and noticed that there was a reduction in cadmium availability with and without the plant when applied 10 t ha⁻¹ of amorphous silicon.

Other authors also verified in potrice cultivation, silicon in the alivium of various toxic elements and concluded that there was no reduction in the total content of cadmium, copper and zinc in the soil, but there was a difference in chemical states when applied silicon, which consequently reduced the availability of these elements, these authors reported that this effect of reduced availability occurred because there were changes in soil pH (NING et al., 2016).

Zama et al. (2018) conducted an experiment in a controlled environment, with the objective of the effect of conventional and modified charcoal with silicon on the mitigation of soil contaminated with arsenic, doses at 1 and 5% were applied. These authors noticed that up to ten days of incubation there was an increase in arsenic concentration in all

treatments and after ten days there was a reduction when silicon-modified charcoal was used.

Huang et al. (2018) conducted a research with the objective of verifying the reduction of toxic elements in rice crop at different levels of development and noticed a reverse effect, there was an increase in the availability of Cd in the soil, however, there was a reduction in the amount absorbed by the plants, possibly a change in the shape of the Cd in the soil, being in a form not available for the plant.

Rehman et al. (2019) evaluated the split application of silicon in the form of potassium silicate in cadmium mitigation in soil and rice plants, the bilotment was based on the stages of plant development (transplantation, pertrethyent, beginning of panicle formation and after complete panicle formation) and they observed that there was a greater reduction in cadmium availability in the soil when silica was applied in transplantation, byedonting and beginning of panicle formation.

Mu et al. (2019) evaluated the effect of a silicon-based residue associated with biochar on the reduction of toxic elements in soil and accumulation in grass and they observed that silicon-based residue with or without the association of biochar contributed to the immobilization of Cd and Pb in the soil and commented that this effect may be related to the effect of the pH increase.

It was compared by Zhao et al. (2020) the influence of silicon in reducing cadmium availability in two soil types (acid and alkaline), silicon was applied in increasing doses in the form of sodium silicate and it was observed that cadmium availability was reduced in treatments that received silicon, regardless of soil type. The authors also commented that there was no reduction in the total cadmium content in the solution and one of the factors that may have reduced availability was the formation of water-soluble complexes (ZHAO et al., 2020).

Final considerations

Soil contamination by toxic elements is a global environmental problem and the application of silicon to reduce the availability of these elements in the soil can be an alternative for the management of these soils. The research already published shows positive results and indicates that silicon has the potential to reduce the availability of toxic elements such as zinc, copper, arsenic cadmium and lead.

It has not yet been possible to reach a conclusion of what causes this effect of reduction in the availability of toxic elements, some studies show that the total content of the toxic element is not reduced, what occurs is a change in its state, which consequently contributes to a lower solubility in the soil solution.

The explanation for the change of state may be related to the increase in pH or the formation of complexes with silicon ions. Further studies need to be carried out to investigate whether silicon can be used as a remediator of soils contaminated by toxic elements, since there are still few studies and most of

them have been conducted in a greenhouse and with short duration. It is necessary to investigate the use in the mitigation of other toxic elements and perform long-term field experiments to verify if this effect of reduction of availability is long-lasting and also verify the ideal amount to achieve this effect, besides it is necessary to evaluate whether over time becomes a problem.

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