



What effect does liming have on silicon availability in agricultural soils?

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ABSTRACT

Controversy surrounds the effects of pH on Si availability in agricultural soils with some workers reporting a negative and others a positive relationship. The factors contributing to this contradiction are examined and discussed. Because soil development typically involves both desilication and decreasing pH, when a group of soils from a region with different ages and weathering rates are compared, there is typically a positive relationship between pH and Si extractability. Raising pH by liming can effect Si availability through a number of mechanisms including weathering. Over the normal range of liming (i.e. pH 4.5 to 6.5) increased pH decreases the solubility of crystalline and amorphous aluminosilicates but above about pH 7 their solubility increases. Specific adsorption of monomeric monosilicic acid (the major form found in soil solution) is at a maximum between pH 9 and 10 (pK₁ for silicic acid is 9.8). Thus, increasing pH increases the proportion of Si adsorbed and decreases that present in soil solution leading to a negative relationship between pH and soil solution Si. With time, polymerization of monomeric Si can occur at the surface of metal oxide surfaces and this may hinder desorption reactions. Nonetheless, Si is generally highly mobile in soils and easily leached so that in the longer term, it is conceivable that increased adsorption may be a retention mechanism which effectively increases Si availability. Soils contain a biogenic pool of amorphous silica (mainly of plant phytolith origin) and its solubility has been shown to increase greatly with increasing pH from 2 up to pH 12. Thus, liming would increase Si availability in the short-term by increasing dissolution of biogenic Si but in the longer term it would tend to decrease Si availability through diminution of the biogenic pool of Si. The most common Si fertilizers are slag materials which are both sources of Si and liming materials. Thus when soils with different histories of slag application are compared, there is often a positive relationship between pH and Si extractability. The relationship between pH and Si solubility/availability can therefore be positive or negative depending on the situation and which pool(s) of potentially available Si (lithogenic/pedogenic, biogenic, adsorbed or residual fertilizer Si) is the most important source of soluble and available Si.

1. Introduction

Although silicon is considered as a beneficial rather than an essential plant nutrient (Epstein, 2001) it is increasingly being applied to agroecosystems. Indeed, increased yields in response to Si fertilizer applications have frequently been recorded in rice and sugarcane as well as a range of other crops (e.g. wheat, barley, maize, sorghum, soybean and peanut) (Savant et al., 1997, 1999; Guntzer et al., 2012a; Liang et al., 2015). For that reason, Si fertilizers are routinely applied to rice in South East Asia, the Indian subcontinent, northern, central and southern America (Savant et al., 1997; Liang et al., 2015; Tubana et al., 2016) and sugarcane in Australia, South Africa, northern and southern America (Savant et al., 1999, Kingston, 2008; Liang et al., 2015). Yield increases occur because elevated intercellular Si concentrations accelerate/intensify basal defence responses to a range of abiotic (salinity drought, heavy metals) and biotic (insect pests and plant pathogens)

stresses resulting in increases in plant resistance/tolerance to such stresses (Haynes, 2017a).

Despite the increasing importance of soil applications of Si in agriculture, the relative importance of various soil factors in influencing Si availability is not well understood (Haynes, 2014). Indeed, most soil fertility text books mention Si in passing but do not cover the topic of its availability and crop use. One contentious issue is the influence of pH (i.e. liming) on Si availability. Some workers have recorded a negative relationship between soil pH and Si extractability/availability (Beckwith and Reeve, 1963; McKeague and Cline 1963a; Haynes et al., 2013; Berthelsen et al., 2003) but others have noted a marked positive relationship (de Camargo et al., 2007; Miles et al., 2014; Phonde et al., 2014; Szulc et al., 2015; Ning et al., 2016). Thus, while some reviews have concluded that Si availability decreases with increasing pH (Savant et al., 1999; Haynes, 2014; Tubana and Heckman, 2015), others have concluded the opposite (Korndörfer et al., 2005; Liang et al.,

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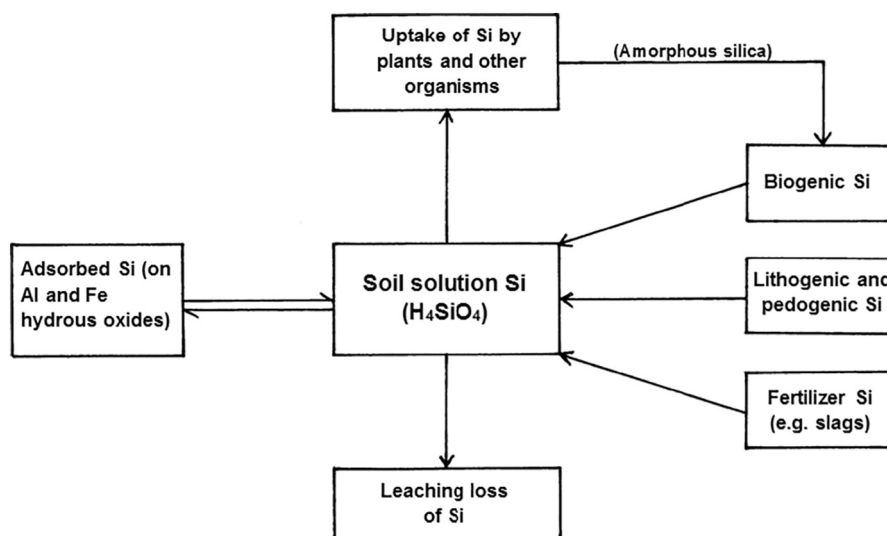


Fig. 1. A schematic diagram of the relationship between soil solution Si and the other main pools of Si in soils.

2015). The effects of pH are of great significance since soil acidification is a natural process hastened in agricultural soils by factors such as acid rainfall and use of ammonium fertilizers while liming to raise soil pH is a common agricultural practice. Sustainable management of native and fertilizer Si requires an understanding of how common soil management practices (e.g. liming) influences its availability. The purpose of this brief review is, therefore, to discuss the major factors involved in the effects that pH has on Si availability and then present a schematic model of how soil pH and liming can influence Si availability in soils.

2. Si availability in soils

A summary of the major factors influencing Si availability in soils is shown in Fig. 1. Silicon is present in soil solution mainly as silicic acid and this is the form that is taken up by plants and that is leached from soils. Concentrations of Si in soil solution are typically in the range of 0.1 to 0.6 mM (Epstein, 2001; Sommer et al., 2006). In most soil solutions monomeric monosilicic acid (H_4SiO_4) is the dominant form of Si present but in alkaline soils significant concentrations of monomeric H_3SiO_4^- may also be present (Wonisch et al., 2008). Monosilicic acid molecules can become linked together to form polymeric silicic acids but such species are generally only stable under alkaline conditions ($\text{pH} > 10.0$) and at elevated Si concentrations (Iler, 1979; Knight and Kinraide, 2001). In acid soils, monosilicic acid makes up about 90% of soil solution Si (Riise et al., 2000; Wonisch et al., 2008) with polymeric Si accounting for the remainder. The presence of Al in acid soil solutions favours polymeric Si since polymerized Si–Al clusters are precursors for formation of secondary aluminosilicates (Wonisch et al., 2008). The presence of some organic molecules in soil solution (e.g. amino acids, amines and peptides) can also favour Si polymerization (Tadashi et al., 1998; Coradin and Livage, 2001).

The solubility of primary (lithogenic) and secondary (pedogenic) minerals present in the soil is often the most important factor controlling Si concentrations in soil solution (Cornelis and Delvaux, 2016). In general, soil solution Si concentrations are strongly related to the stage of soil development and the content of weatherable silicate minerals with moderately weathered temperate soils maintaining very much higher solution Si concentrations than highly weathered tropical soils (Fox et al., 1967; Sommer et al., 2006).

Like other nutrient anions, silicate is specifically adsorbed to soil colloid surfaces. The major adsorption surfaces are those of Fe and Al hydrous oxides (Hingston et al., 1972; Goldberg and Glaubig, 1988). Aluminium oxides are generally more effective than those of Fe (Jones and Handreck, 1967) and, because of their larger surface area,

amorphous minerals adsorb more Si than their crystalline counterparts (Delstanche et al., 2009). The greater the adsorption of Si, the lower will be soil solution Si concentrations.

Silicon is also present in the soil in a biogenic Si pool which consists of amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) (Haynes, 2017b). This is mainly of plant origin (phytogenic Si) but also contains small amounts of silica originating from protozoa, fungi, bacteria and diatoms (Sommer et al., 2006; Ehrlich et al., 2010; Puppe et al., 2015). Plants and other organisms take up silicic acid from soil solution and this is then accumulated and precipitated as amorphous silica (Ehrlich et al., 2010). In plants, most of the absorbed Si is translocated to shoots where it is deposited as amorphous silica in cell lumen, cell walls and intracellular spaces (Sangster et al., 2001; Currie and Perry, 2007) as fibrillar, globular and sheet-like motifs (Sangster et al., 2001). Much is accumulated in the intracellular layer under the cuticle as sheet-like solid particles known as phytoliths. This phytogenic amorphous silica is returned to the soil when plant litter enters the soil system (Currie and Perry, 2007).

The most commonly used Si fertilizers are by-products of the iron and steel industries and include blast furnace slag, steel slag, converter slag, ferromanganous slag and silica fume (Gascho, 2001; Pereira and Cabral, 2005; Kingston, 2008). Silicate slag is also produced during phosphorus production in an electric arc furnace (Liang et al., 2015). The major components of these materials are calcium and/or magnesium silicates and they dissolve to release silicic acid.

Below, and availability of Si is discussed, as a function of pH and liming, in relation to the major sources of soil solution Si, as shown in Fig. 1 (namely lithogenic/pedogenic Si, adsorbed Si, biogenic Si, and residual fertilizer Si).

3. Parent material and weathering

3.1. General

When primary silicate minerals are weathered during pedogenesis, basic cations, Al, Fe and Si (as silicic acid) are released into soil solution and soil pH progressively declines. Part of the Si released is leached (thus lowering the total Si content of the soil) and the remainder reacts with the released Al, Fe, and Mg to form secondary clay minerals. Intense weathering results in breakdown of secondary silicate minerals and the mineralogy becomes dominated by Al and Fe oxides. Weathering is most pronounced in humid tropical climates (under high rainfall and high temperatures) and, in comparison with most temperate soils, highly weathered acid Ultisols and Oxisols developed under

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