

METHODS FOR SILICON ANALYSIS IN SOIL, PLANT AND FERTILIZERS

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Abstract

To develop recommendations for field applications of silicate materials, knowledge of the soil Si status and the availability of Si in the amendment are essential. To determine a crops response to application of Si requires calibration of soil Si status and plant uptake. While a method for determining plant Si levels using the auto-clave induced digestion procedure (Elliott and Snyder, 1991) is well established, the challenge for routine testing of soils and amendment materials is the development of simple, dependable and robust methods that correlate well with changes in soil Si status and corresponding plant tissue levels.

The total Si content of soils can have little relationship to the concentration of soluble Si in soils, which is the component important for plant growth. The concentration of soluble Si is dynamic, and although leaching of Si from the soil and plant uptake are important processes determining Si concentrations, the equilibrium concentration is largely controlled by adsorption/desorption reactions. A number of chemical extraction procedures have been developed to determine the 'plant available' soil Si status, and a range of these are compared when used on different soil types. However, a complication occurs when Si is added to soil, as it reacts rapidly with amorphous surfaces, and amount and rate of Si adsorption is dependant on the sesquioxide content of the soil, soil pH, and the presence of other anions. Although many soil tests are effective in predicting 'sub-optimality', there may be a need to refine soil-testing techniques that enables an assessment of 'responsiveness' to silicate additions. These soil reactions also influence the solubility of, and hence availability of Si in various amendments, causing poor correlation with laboratory chemical extraction procedures for determining available Si in a material and plant uptake once that material is added to the soil. Various methods to determine the potential for a material to supply 'plant available' Si are compared.

Index terms: Chemical analysis, silicon, soil, plant, amendment

Total silicon content of soils, plants and fertilizers

Silicon (Si) is abundant in nature, and as such, the total silicon content of soils, plants and materials suitable for use as soil amendments for agricultural purposes, can be high.

In soil, Si exists in a wide variety of forms and stabilities. It is estimated to represent about 28 percent of the earth's crust, and as aluminosilicates and quartz can be as much as 75 - 95 percent of the inorganic fraction of soil (Jackson *et al.*, 1948). Silica (SiO_2) can occur in different crystalline forms, of which quartz is the most common, or as amorphous Si-containing substances. Also present in soils are amorphous forms of Si, including allophane, a non-crystalline Si-containing colloidal mineral substance, and the hydrated forms of silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), commonly known as phytoliths, resulting from plant decomposition. Phytoliths can be relatively stable and usually concentrate in the surface horizon of soils. Amounts of opal phytoliths commonly range from <1 to 30 g/kg on a total soil basis (McKeague and Cline, 1963a).

Silicon represents a major mineral constituent of plants, and is present in plants in concentrations similar to that of the other macronutrients. At 0.1 percent, Si is equivalent to the levels of macronutrients, Ca, Mg, P and S; while the upper levels of 10 percent exceed the concentrations of the mineral nutrients like K and N (Epstein, 1994 and 1999). However, the Si content of different plants, and of various plant parts, is extremely variable. Different plant species differ in both their concentrations of Si, and their accumulation of Si from the soil solution. Jones and Handreck (1967) divided plants into three major groups according to the SiO_2 percent of the leaf tissue on a dry weight basis. "Wetland" grasses (e.g. paddy-grown rice) have the highest levels at 5 - 15%; "dryland" grasses having intermediate levels of 1 - 3%; and the dicotyledons generally having the lowest levels of less than 1%.

There are many types of silicated materials suitable for use as soil amendments/fertilizers, however, their effectiveness is more dependent on their reactivity rather than total Si content. An excellent review of sources suitable for agriculture is provided by Gascho (2001). As mentioned plant material can have high concentrations of Si, and crop residues (e.g. rice hulls and sugar mill wastes) are commonly used, although high rates are usually necessary. There are a few naturally occurring mineral materials, such as wollastonite (CaSiO_3), olivine (MgSiO_3) and diatomaceous earth, which can have total silicon contents of approximately 55%, 30% and >70% SiO_2 respectively, but often availability limits their potential use. By far the most common forms of silicated materials used as soil amendments are various industrial by-products, for example, calcium silicate slag, a by-product from the production of elemental phosphorus.

The total Si content of soils, plants and fertilizers can be easily determined using X-ray fluorescence spectroscopy (XRF). This is a non-destructive analysis requiring the preparation of dry-powder pellets made from finely ground material. There are a range of other techniques used for total Si analysis, generally requiring pre-solubilization of the Si using various digestion methods. Snyder (2001) has provided a comprehensive review of the various gravimetric, digestion and non-destructive methods that can be used, so more detail will not be provided here, except to make mention of the ease of using the autoclave-digestion procedure for determining plant Si content (Elliott and Snyder, 1991). This procedure produces consistently reliable results,

and the only special equipment required is an autoclave and spectrophotometer. This allows the analysis of large sample batches to be carried out using the equipment available in most standard laboratories.

Measurement of plant available silicon in soils

While Si compounds such as quartz, various crystalline silicate minerals, silicate clays and amorphous silica compounds dominate the solid phase of all soils, the soluble forms in the soil solution consist of monosilicic acid ($\text{Si}(\text{OH})_4$) and polysilicic acids, and complexes with organic and inorganic compounds. The total Si content of soils can have little relationship to the concentration of soluble Si in soils, which is the component important for plant growth. The concentration of soluble Si in soils is dynamic. Monosilicic acid will remain in solution in the monomeric state in neutral and weakly acid solutions. However, rapid polymerization occurs at high solution concentrations, with increasing soil pH and in the presence of oxides and hydroxides of aluminium and iron.

Table 1 illustrates the diversity of some of the methods that have been used world wide to determine the amount of Si available for plant growth. The quantity of Si varies depending on the extracting solution used to solubilize the soil Si. In general, the most successful extractants are acid rather than neutral solutions, and dissolution is further increased by chelating agents (due to decreased Si sorption resulting from the lower concentration of Al and Fe in solution). Other factors such as the method of equilibration, soil:solution ratio, temperature, and pH of extractant solution are also important. Once in solution, $\text{Si}(\text{OH})_4$ can be measured by the silicomolybdate blue colour method (Iler, 1979).

Although water extracts have often been used to estimate readily soluble Si this is generally not a suitable method since the low ionic strength of the solution will cause dispersion (Lindsay, 1979). As most of the soluble Si below pH 8 is uncharged monosilicic acid, changes in ionic strength should not significantly alter extractable levels in most soils. In this respect, Elgawhary and Lindsay (1972) recommend the use of 0.02 M CaCl_2 as the reactive media to equalize ionic strengths and facilitate ready flocculation of colloidal Si. Soils extracted with dilute CaCl_2 measure Si in the soil solution, and corresponds more closely to the levels of $\text{Si}(\text{OH})_4$ expected from solubility predictions (Lindsay, 1979).

A study comparing a number of extractant methods over a wide range of soil types from north Queensland in Australia resulted in Si values, which although differing by scales of magnitude, still demonstrated a general relationship between each other (Berthelsen, 2000). This relationship between extractants was supported by the relativity between the 'critical levels' established for the different extractants despite the fact that they were established in independent studies. The different extractants tended to target Si held within different components of the soil matrix, as the Si solubilized was related to other soil properties specific to the soil type. Dilute salt solutions (e.g. 0.01M CaCl_2) provided a measure of the readily available Si present in the soil solution, while results obtained using NH_4OAc and acetic acid indicated that the Si solubilized was likely to be the more simple polymers affected by changes in pH, CEC and the ratio of soluble Si:Al in the soil solution. However, clay content and relationships between extractable Si and Fe and Al were more prominent factors in Si extracted by phosphate acetate, citric acid and 0.005M H_2SO_4 ,

Table 1. Methods used to determine soluble and extractable soil Si

Extractant	Soil : Solution Ratio (or recommended weights and volumes)	Method	Suggested critical level	Reference
H ₂ O	pre-wet air-dry soil at a matric suction of 0.1 bar	incubate at 25°C for 1 day and centrifuge at 900g (RCF) for 1 hr.		Gillman and Bell, 1978; Menzies and Bell, 1988
H ₂ O	saturated paste		2 mg/kg	Fox and Silva, 1978
H ₂ O	1 g : 1 mL	allow to stand 2 weeks with repeated shaking, filter and centrifuge		Clements <i>et al.</i> , 1967
H ₂ O	10 g : 100 mls	continuous shaking for 4 hrs. and centrifuge at 24,000g (RCF)	< 0.9 mg/kg (deficient) < 2.0 mg/kg (marginal) 8.0 mg/kg	Fox <i>et al.</i> , 1967; Elawad <i>et al.</i> , 1982
H ₂ O	10 g : 60 mls	'incubation method' - shake, degass, seal bottle, incubate at 40°C for 1 week without shaking.		Takahashi and Nonaka, 1986
H ₂ O	1:4	'supernatant method' - shake, degass, fill to replace all air space, seal bottle, incubate at 30°C for 4 weeks		Sumida <i>et al.</i> , 1998
Phosphate acetate (pH 3.5) [500ppm P as Ca(H ₂ PO ₄) ₂ and 0.1 M (H ₄ NH ₄)OAc]	10 g : 100 mls	continuous shaking for 4 hrs. and centrifuge	< 50 mg/kg (deficient) 50-150 mg/kg (marginal - adequate)	Fox <i>et al.</i> , 1967
0.04 M sodium phosphate buffer (pH 6.2)	1 g : 10 mls	continuous shaking for 24 hrs at 40°C		Kato and Sumida, 2000
Modified Truog - [0.01 M H ₂ SO ₄ containing 3 gms (NH ₄) ₂ SO ₄ /liter]	1 g : 100 mls	continuous shaking for 30 minutes	< 40 mg/kg (deficient) 40-100 mg/kg (marginal - adequate)	Fox <i>et al.</i> , 1967
0.5 M NH ₄ OAc (pH 4.5-4.8)	5 gms : 100 mls	continuous shaking for 1 hr.	< 20 mg/kg (deficient) 20-40 mg/kg (marginal - adequate) < 50 mg/kg (deficient)	Fox <i>et al.</i> , 1967 Wong You Cheong and Halais, 1970; Ayres, 1966
0.5 M NH ₄ OAc (pH 4.5-4.8)	2.5 gms : 50 mls	2.5 gm soil leached with 10 * 5 ml aliquots of extractant		Bishop, 1967
acetate buffer, pH 4.0	10 g : 100 mls	intermittant shaking over 5 hours at 40°C		Imaizumi and Yoshidai, 1958
0.01 M CaCl ₂	1:10	continuous shaking for 16 hrs and centrifuged	< 20 mg/kg (deficient - marginal)	Haysom and Chapman, 1975
0.01 M CaCl ₂	1:25	shake for 7 days, with a few drops of chloroform on a recipicol shaker at 250 C		Wickramasinghe, 1994
0.005 M H ₂ SO ₄	1 : 200	continuous shaking for 16 hrs and centrifuged	< 100 mg/kg (deficient-marginal)	Hurney, 1973
0.5 M Acetic acid	1:10	1 hr shake, rest 15 minutes, decant and filter, rest 12 hrs before analysis	< 15 mg/kg (deficient)	Snyder, 1991; Korndorfer, G. (per. comm.)
0.1 M Citric acid	1:50	2 hr shake, rest O/N, 1 hr shake, centrifuge		Acquaye and Tinsley, 1964

suggesting that the Si solubilized was more strongly sorbed onto the Al and hydroxides, and possibly to some extent, also some of the crystalline and noncrystalline soil minerals.

Work done in different cropping systems demonstrate that many of the extractants listed in Table 1 can correlate well with plant uptake and may provide excellent crop response curves, allowing an estimation of the required soil Si concentration necessary to achieve maximum crop growth under various rates of Si fertilization, (Korndorfer *et al.*, 2001; Ma and Takahashi, 2002; Kingston *et al.*, this conference). However, as reported by Ma and Takahashi (2002), after a long history of silicate slag additions, extractants such as the acetate buffer method can over-estimate the plant-available Si. Many silicate fertilizers have inherently low solubility, and stronger extractants may dissolve non-available Si from the silicate amendment previously added to the soil (Savant *et al.*, 1997).

This highlights the problem of choosing a soil extractant that will best predict sub-optimality. A study carried out in north Queensland, Australia (Berthelsen *et al.*, 2003), illustrated the challenge of choosing the appropriate extractant. Soil and plant 'top visible dewlap' (TVD) samples were collected from approximately 200 sites, representing all the major soil types from all the sugarcane growing areas of north Queensland, Australia. Plant available soil Si was determined following extraction with 0.01M CaCl_2 , and also a stronger extractant, 0.005M H_2SO_4 . Determination of Si in the TVD leaf samples used the "Auto-clave digestion" procedure described by Elliott and Snyder (1991). It was notable that plant Si levels were significantly related to readily soluble soil Si levels (0.01M CaCl_2) but showed no relationship to soil levels obtained using the stronger acid extractant (0.005M H_2SO_4). The variability observed between all the soils sampled in this survey suggested that interpreting soil Si status using strong extractants should be done with caution, particularly on soils with poor drainage or high Si sorption ability and high organic matter content. Similar observations have been reported by Fox *et al.* (1967) and Medina-Gonzales *et al.* (1988), who observed highly significant relationships between plant Si and water extractable Si, but not with any other soil extractant.

The 'capacity' of the soil to supply Si to the soil solution depends on solid phases that are less soluble than amorphous Si but are more soluble than quartz (Elgawhary and Lindsay, 1972). If the concentration of soluble Si in the soil solution is controlled by the most soluble silicate mineral, regardless of the amount present in the soil (Herbillon *et al.*, 1977), then factors controlling solubility become important in ensuring that adequate amounts are available for plant growth. Important factors include soil mineralogy (including the Si:sesquioxide ratio), soil pH, organic carbon content, clay content, concentration and solubility of plant phytoliths in the silt fraction and soluble Al. Many of these factors are inherent soil characteristics, but can be greatly affected by the cultural practices involved with crop production. Therefore, to adequately predict a response to silicate additions, knowledge of past fertilizer history is important. Previous fertilizer history with silicate fertilizers should be taken into account, as discussed by Ma and Takahashi (2002). In addition, the history of other agronomic practices such as liming should be considered. The increase in soil pH following liming promotes polymerization of Si and the formation of alumino-silicate compounds, which can have a marked influence on the solubility and availability of Si. In this respect, the stronger extractant again may overestimate the Si available for plant growth, by dissolving these compounds of lower solubility.

Plant available soil Si levels need to be considered from three aspects: 'intensity' (concentration of Si in the soil solution available for immediate plant use); 'capacity' (the reserve supply of Si present as solid phases in the soil); and 'buffer capacity' the factors that affect the sorption/desorption reaction in the soil (ability of the solid phase to replenish the soil solution following depletion through leaching or plant use). The difference in Si obtained using different extractants has led many researchers to suggest using two methods of extraction. The first in water or a dilute salt solution to provide a solution concentration near equilibrium with the soil system (an 'intensity' factor), and the second, using a stronger extractant such as phosphate acetate, citric acid and 0.005M H₂SO₄, to provide an index of the adsorbed soil Si (a 'capacity' factor) (Khalid *et al.*, 1978; Berthelsen *et al.*, 2003).

It is also generally agreed that most of the rapidly soluble Si is derived from sorption sites and not from any specific compound of Si (McKeague and Cline, 1963a, 1963b, 1963c; Beckwith and Reeve, 1964; Jones and Handreck, 1967). Therefore the importance of the role of Al and Fe compounds in the dissolution kinetics of soil Si has led many to propose that concurrent examination of the Si:Fe and Si:Al ratios should be considered in conjunction with extractable Si levels. Acquaye and Tinsley (1964) recommended the use of citrate solutions and citric acid for the simultaneous extraction of Si, Al and Fe, and Beckwith and Reeve (1963) suggested that the determination of Si and Al following extraction with 0.005M H₂SO₄ was effective in differentiating soils with respect to supplying Si providing an assessment of both 'intensity' and 'capacity' factors of the 'reactive' Si status. The differing ability to adsorb added Si can also be determined using an Index of Silica Reactivity (ISR), which may prove to be a useful research tool in understanding and developing application rates of silicate amendments (Gallez *et al.*, 1977). An Index of Silica Saturation (ISS), which takes into account both the solubility and the sorption characteristics of the soil with respect to Si, can be calculated using the ISR %, and the concentration of readily available soil Si as determined following extraction with 0.01M CaCl₂ (Herbillon *et al.*, 1977). Sumida (1991) reported that a method measuring the simultaneous dissolution and adsorption of Si of various soils with different histories of fertilizer management provided better correlation with Si content of rice straw than other standard methods, and was a valuable method for diagnosing the Si supply capacity of paddy soils.

It is possible that no single measure is adequate to determine plant available Si. However, if a single measure is required, extraction with a dilute salt such as 0.01M CaCl₂ may be preferable. As 'intensity' and 'quantity' are linked, it is unlikely that readily available Si will be high unless there is sufficient 'capacity'. As 0.01M CaCl₂ extractable Si represents the Si available in the soil solution, it also reflects the net effects of the sorption/desorption reactions that control solubility, thus giving a true measure of current availability. To assist in developing recommendations for the amelioration of sub-optimal levels of plant available soil Si, useful additional information could include, the 'capacity' of the soil Si reserves and the sesquioxide content and a measure of the buffer capacity of the soil to sorb Si (as determined by the 'index of silica reactivity' and the 'index of silica saturation').

However, it is clear a number of extractants can be successfully used to estimate soil Si. The choice of extractant will often be based on its ease of adoption for a particular laboratory and its suitability for specific soil characteristics, which will in turn be reflected in its ability to correlate with plant uptake of Si. In this respect, it must be remembered that plant levels vary with variety, plant part, age, ratoon age (as with sugarcane), so consistency in plant sampling is critical. It is

also very important that when trial work is reported, that the extractant methodology used to obtain the results (including information regarding suggested 'critical levels') is provided to allow comparisons.

Measurement of plant available silicon in fertilizers

Unfortunately selecting a suitable silicate materials and assessing its efficacy is difficult. While a number of chemical extractant methods have been used to estimate both total and soluble Si in silicate materials, often the results obtained do not correlate well with plant uptake of Si, once the material is applied to the soil. In addition to the effect on particle size on solubility, other chemical characteristics of the material such as pH, molar ratio of CaO:SiO₂ have been shown to influence Si availability (Ma and Takahashi, 2002). Once a product is added to the soil, soil chemical reactions, for example, the increase in soil pH due to the dissolution of Ca and Mg from the material can further influence the solubility and hence availability of Si (Ma and Takahashi, 2002). Consequently, it is possible that there is not a universal extractant that is suitable for determining available Si that will cover all types of materials, and for all soils and soil conditions (Gascho, 2001).

However there is a need for a rapid laboratory test to provide an initial assessment of different silicate sources. This would be useful to screen materials, allowing further glasshouse and field testing to concentrate on materials with the most potential. A number of different chemical extractants for estimating available Si in silicate materials have been used to varying success. Extraction with 0.5M NH₄OAc or 0.5M HCl are two of the earliest methods recorded, and at various stages were standard methods in Japan. However, these, plus many other acidic extractants commonly used, including citric acid and acetic acid have lost favour as they have generally shown poor correlation with crop uptake of Si. Simple water extractions of calcium silicate slags have also been used, however, as it was found that dissolution of the calcium silicate resulted in increases in pH and Ca in solution, both of which repressed further dissolution of the product, this method was modified to include a weakly acidic cation exchange resin in the water to both moderate pH and adsorb Ca (Kato and Owa, 1997). Based on the dissolution principles of Kato and Owa (1997), Snyder (2001) developed a 'column' technique which maintains neutral solution pH, low Ca concentration near the Si source and low dissolved Si concentration to minimize polymerization. More recently, Pereira *et al.* (2003) proposed an extraction method that they stated would quantify the Si potentially available to plants by using an alkaline extractor (using different extraction ratios and extraction/resting times) of Na₂CO₃ + NH₄NO₃.

Berthelsen *et al.* (2003) compared the effectiveness of a number of chemical extraction methods described in the literature on a diverse selection of silicated materials (including calcium silicate slag, cement, wollastonite, olivine, diatomaceous earth, flyash and filtercake scrubber waste). These same materials were then compared through indirect chemical extraction after soil incubation, and then an assessment of plant Si uptake and changes in soil Si status was undertaken following glasshouse pot studies. This series of experiments indicated that the extraction method developed by Kato and Owa (1997), using the addition of a weakly acidic cation exchange resin in the H⁺ form (Amberlite IRC-50) to the extraction medium, provided the best indicator of plant-available Si, which correlated well with both the indirect chemical extraction results and also soil and plant Si and yield when the materials were used in the

glasshouse pot studies. These results are supported by recent work by Pereira *et al.* (2003) who compared a similar range of extraction methods and tested them against 12 different sources of Si material and also found a high correlation with Si content and Si uptake in rice using this 'resin' method.

As various forms of calcium silicate materials are the most widely used Si fertilizer, most proposed methods are based on estimating available Si from this source. Other silicate materials may possibly behave quite differently. Whatever method is used, it is important to keep a wide product to solution ratio, to keep the concentration of monosilicic acid low and prevent polymerization from occurring. In addition, as generally Si availability increases with decreasing particle size, it is important to define and standardize particle size when attempting to determine their reactivity and Si availability.

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