Research review on extracting methods of silicon from soil

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Abstract
The importance of silicon (Si) in soil nutrition is currently being recognized by its beneficial effects on many crops. Therefore it is important to determine the soil Si status and to examine different extractants for testing plant-available silicon. There is a variety of methodologies used in the soil science laboratory to extract different forms of Si from heterogeneous soil. However, the comparison of extraction methodologies is scarce and keeping it in view here methodologies are reviewed to extract different forms of Si from soils to develop recommendations for soil application of silicate materials further knowledge of the soil Si status and its availability in the amendment is essential.

Keywords: Silicon, chemical analysis, extraction methods, soil tests

Introduction
Silicon (Si) is the second most abundant element in the earth’s crust making up 27.6 atomic percent of its mineral content (Jackson, 1948) and in combination with oxygen, it forms the framework of soil. The mineral soil material develops from rocks and sediments and is mainly composed of primary crystalline silicates such as quartz feldspars mica and secondary silicates especially clay minerals. Moreover, mineral soil contains Si of biogenic origin (Jones, 1969) and pedogenic amorphous Si (Drees et al. 1989). The Si compounds in the soils are classified into soil solution as adsorbed Si forms (Monosilicic and polysilicon acids) amorphous forms (phytoliths and silica nodules) poorly crystalline microcrystalline forms (allopheine immogolite and secondary quartz) and crystalline forms (primary silicates: quartz feldspars & secondary silicates: clay minerals) (Daniela et al. 2006).

While Si compounds such as quartz crystalline silicate minerals silicate clays and amorphous silica compounds dominate the solid phase of soils whereas the soluble forms in the soil solution consist of mono-silicic acid and polysilicic acids and complexes with organic and inorganic compounds. The total Si content of the soil has little relationship with the concentration of soluble Si in soils which is an important component for plant growth. Various methods for extracting Si forms in the soils have been reported in the earlier reports and those were developed for different purposes some were intended to extract plant-available Si (Imaizumi and Yoshida, 1958) and Haysom and Chapman, 1975 others were developed for pedogenic studies in order to assess the formation of different Si fractions during soil development (Hashimoto and Jackson 1960; Biermans and Baert, 1977; Arnseth and Turner, 1988). However, there is a large variety of different methodologies used in the soil science laboratories and there has been no systematic survey of the methodologies available. This review is intended to summarize and compare previously published extraction techniques used to determine different forms of Si in soils.

Methods for extracting plant-available silicon
The addition of Si in various forms to crops shown many beneficial effects (Datnoff et al. 2001) on crop growth and yield. This has not only shown for high demand Si crops such as sugarcane and rice but also for tomato cucumber and strawberry (Korndorfer and Lepsch, 2001). Si has been reported to benefit a number of ways (Shivay and Kumar, 2009) like the stimulation of photosynthesis improvement of leaf erectness decreased susceptibility to pests and disease damage and alleviation of water and various mineral stresses (Ma et al. 2001). There is several procedures are available to determine plant-available Si and most of the methodologies are based on anion replacement with adsorbed Si.
Table (1) illustrates the diversity of some of the methods that have been used worldwide to determine the amount of Si available for plant growth and those methodologies have been applied to soil samples to extract the water-soluble Si to identify the crop Si requirement. The quantity of Si varies depending on the extracting solution used to solubilize the soil Si and the most successful extractants are acid solutions rather than neutral and other factors such as soil to solution ratio temperature and pH of the extractant solution also important.

### Table 1: Different methodologies used to determine soluble and extractable soil Si

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Extracting agent</th>
<th>Soil : Solution Ratio</th>
<th>Critical level</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O</td>
<td>Pre-wet air-dry soil at a matric suction of 0.1 bar</td>
<td>-</td>
<td>Gilman and Bell, 1978</td>
</tr>
<tr>
<td>2</td>
<td>H₂O</td>
<td>saturated paste</td>
<td>2 mg kg⁻¹</td>
<td>Fox and Silva, 1978</td>
</tr>
<tr>
<td>3</td>
<td>H₂O</td>
<td>1 g : 1 ml</td>
<td>&lt; 0.9 mg kg⁻¹ (deficient)</td>
<td>Clements et al. 1967</td>
</tr>
<tr>
<td>4</td>
<td>H₂O</td>
<td>10 g : 100 ml</td>
<td>&lt; 2.0 mg kg⁻¹ (marginal)</td>
<td>Fox et al. 1967 [15]</td>
</tr>
<tr>
<td>5</td>
<td>H₂O</td>
<td>10 g : 60 ml</td>
<td>&gt; 8 mg kg⁻¹ (high)</td>
<td>Takahashi and Nonka, 1986</td>
</tr>
<tr>
<td>6</td>
<td>H₂O</td>
<td>1 g : 4 ml</td>
<td>-</td>
<td>Sumida et al. 1998</td>
</tr>
<tr>
<td>7</td>
<td>Phosphate Acetate (pH 3.5)</td>
<td>10 g : 100 ml</td>
<td>&lt; 50 mg kg⁻¹ (deficient)</td>
<td>Fox et al. 1967 [15]</td>
</tr>
<tr>
<td>8</td>
<td>0.04 M Sodium Phosphate buffer (pH 6.2)</td>
<td>1 g : 10 ml</td>
<td>50 – 150 mg kg⁻¹ (marginal)</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Modified Truog (0.01 M H₂SO₄ containing 3 gms (NH₄)₂SO₄/liter)</td>
<td>1 g : 100 ml</td>
<td>&lt; 40 mg kg⁻¹ (deficient)</td>
<td>Fox et al. 1967 [15]</td>
</tr>
<tr>
<td>10</td>
<td>0.5 M NH₄OAc (pH 4.5 – 4.8)</td>
<td>5 g : 100 ml</td>
<td>&lt; 20 mg kg⁻¹ (deficient)</td>
<td>Wong You Cheong and Halaris, 1970 [37] &amp; Ayres, 1996</td>
</tr>
<tr>
<td>11</td>
<td>0.5 M NH₄OAc (pH 4.5 – 4.8)</td>
<td>2.5 g : 50 ml</td>
<td>-</td>
<td>Bishop, 1967</td>
</tr>
<tr>
<td>12</td>
<td>Acetate buffer (pH 4.0)</td>
<td>10 g : 100 ml</td>
<td>&lt; 20 mg kg⁻¹ (deficient to marginal)</td>
<td>Imaizumi and Yoshidai, 1958</td>
</tr>
<tr>
<td>13</td>
<td>0.01 M CaCl₂</td>
<td>1 g : 10 ml</td>
<td>-</td>
<td>Haysom and Chapman, 1975 [17]</td>
</tr>
<tr>
<td>14</td>
<td>0.01 M CaCl₂</td>
<td>1 g : 25 ml</td>
<td>&lt; 100 mg kg⁻¹ (deficient to marginal)</td>
<td>Wickramasinghe, 1994</td>
</tr>
<tr>
<td>15</td>
<td>0.005 M H₂SO₄</td>
<td>1 g : 200 ml</td>
<td>&lt; 15 mg kg⁻¹ (deficient)</td>
<td>SNP, 1991 and Kornor, 2001</td>
</tr>
<tr>
<td>16</td>
<td>0.5 M Acetic acid</td>
<td>1 g : 10 ml</td>
<td>-</td>
<td>Acquaye and Tinsley, 1964 [19, 23, 36]</td>
</tr>
<tr>
<td>17</td>
<td>0.1 M Citric acid</td>
<td>1 g : 50 ml</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**H₂O and CaCl₂ extraction method**

Schachtschabel and Heinemann (1967) [14] developed a procedure to determine water-soluble Si in loess soils of Western Germany to determine which soil properties influence the content of water-soluble Si in soils. The amount of Si in the extract increased by 10-20 % without the addition of NaN₃ and dissolve Fe, Al and Mn oxides so that the Si bound in these oxides is released. Further, they refrained from continuous shaking because McKeague and Cline (1963b) found that shaking causes an increase in Si extracted due to abrasion.

Fox et al. (1967) [15] and Khalid et al. (1978) [22] shook a 1:10 soil-water suspension for 4 hours to determine water-soluble Si in soils developed from basic volcanic rocks on Hawaii. The objective of their investigation was to study the response of sugarcane to calcium silicate slag fertilization and the fate of applied Si during 5 years of cropping. Nonaka and Takahashi (1990) [30] also used water to extract Si from soils in order to estimate the need for Si fertilization and they incubated soils at 40 °C for 1 week to obtain equilibration between soil and solution but it causes a negative impact on soil extraction.

Although water extracts have often been used to estimate readily soluble Si and it’s not a suitable method due to the low ionic strength of the solution will cause dispersion. Most of the soluble Si below pH 8 is uncharged the acid and changes in ionic strength should not significantly alter the extractable levels in the soil. In this respect, Elgawahry and Lindsay (1972) recommend the use of 0.02 M CaCl₂ as the reactive media to equalize ionic strengths and facilitate ready flocculation of colloidal Si and corresponds more closely to the levels of Si(OH)₄ expected from solubility predictions (Lindsay 1979) [25].

However, the weakest extractant after water is CaCl₂ which only extracts the easily soluble Si fraction (Berthelsen et al. 2001) [5]. Haysom and Chapman (1975) [17] compared 0.01 M CaCl₂ 0.5 M ammonium acetate and 0.005 M sulfuric acid for their ability to extract plant-available Si from soils and found that Si extracted by CaCl₂ showed the highest correlation to sugarcane yield (r = 0.82).

**Acetate and Acetic acid extraction method**

Acetic acid (CH₂COOH) and some acetates (particularly CH₃COO-NH₄⁺ CH₂COO-Na⁺) are used to remove soluble Si and some of the exchangeable Si from soils. Imaizumi and Yoshida (1958) [19], Ayres (1966) [3] and Wong You Cheong and Halais (1970) [37] used buffered acetate solutions to extract plant-available Si from soils. Fox et al. (1967) [15] used a buffered ammonium acetate solution containing 500 ppm P as Ca(H₂PO₄)₂. Snyder (2001) [36] reported an acetate acid extraction as a standard method to analyze plant-available Si in soils for rice-growing areas. Nonaka and Takahashi (1990)
found that the acetate extraction was too strong for soils previously fertilized with calcium silicates because it dissolved some nonavailable Si from the fertilizer.

**Phosphate-Acetic acid and Phosphate buffer extraction method**

The phosphate anion has been used to extract adsorbed Si from soils to assess plant-available Si. Khalid et al. (1978) \[23\] applied a water extract and a buffered extraction solution of phosphate and acetic acid to determine plant-available Si in volcanic soils. They used Si extracted by water as ‘intensity factor’ and that extracted by the phosphate buffer as ‘capacity factor’. Another phosphate extraction method introduced by Snyder (2001) \[30\] and found in contrast to the acetate buffer extraction which did not overestimate the available Si in previously fertilized soils with silicates. Because the phosphate does not dissolve residual calcium silicate fertilizer but displaces adsorbed silicic acid.

**Citric and citrate acid extraction method**

Acquaye and Tinsley (1965) \[1\] used citric acid and Sauer and Burghardt (2000) \[31\] worked with citrate to estimate the amount of adsorbed Si in soils. The extraction procedure of Sauer and Burghardt (2000) \[33\] was based on the experiments reported by Beckwith and Reeve (1964) \[4\]. Beckwith and Reeve (1963) shook soil with solutions containing up to 135 ppm of mono silicic acid for 144 hours and they found a significant decrease of dissolved silicic acid within the first 24 hours and concluded that soils have a great ability to adsorb mono silicic acid. In subsequent experiments, Beckwith and Reeve (1964) \[4\] studied the release of adsorbed silicic acid from soils and they found that the release of Si was minimal between pH 7 to 9 and soil shaking was sufficient to reach adsorption equilibrium. The authors proposed that the citrate ions occupy the sorption positions and form complexes with metal ions which otherwise could adsorb silicic acid with 0.1 and 1 M citrate solution. Breuer (1994) \[7\] used an extraction solution consisting of 40 ml of 0.3 M Na\(_2\)C\(_5\)H\(_7\)O\(_4\) and 10 ml of 1 M NaHCO\(_3\) and extracted 5 min at 80 °C and found a close correlation (r = 0.81) between Si measured in this extract and Si contents in the dithionite extract (Mehra and Jackson 1960) \[28\] which is commonly used in soil science laboratories to dissolve pedogenic sesquioxides. It consists of the Na\(_2\)C\(_5\)H\(_7\)O\(_4\)/NaHCO\(_3\) extraction as described above and subsequent addition of Na\(_2\)S\(_2\)O\(_4\) to reduce the Fe and Al and thus dissolve the oxides. From this result, a close correlation noticed between Na\(_2\)C\(_5\)H\(_7\)O\(_4\)/NaHCO\(_3\) extractants and revealed that the Si adsorbed from sesquioxide surfaces while the dithionite extraction completely dissolved the sesquioxides thereby releasing Si bound inside them.

**Sulfuric acid and sulfurous acid extraction method**

Fox et al. (1967) \[15\] compared several methods among them sulfuric and sulfurous acids have been used to extract the plant-available Si fraction and extracted significantly more Si than water. Hurney (1973) \[18\] carried out calcium silicate fertilization studies on sugarcane in Australia used a diluted sulfuric acid method to extract plant-available Si from the soil and compared with water extraction methods and found the same results.

**Studies comparing different methods to extract plant-available Si from soils**

Fox et al. (1967) \[15\] compared the capability of several anions to extract plant-available Si from an Oxisol of Hawaii. They found an increasing extraction capacity in the following order and it clearly shows that different extractants dissolve the plant-available Si but do not extract exactly the same Si fraction from the soil solution.

\[
\begin{align*}
\text{H}_2\text{O} & < \text{CaCl}_2 \quad \text{CaONO}_3\text{P}_2 \quad \text{CaO}\text{OAcP}_2 \quad \text{MgSO}_4 \\
& < \text{CaOH}_3\text{PO}_4\text{P}_2 \quad << \text{HOAc}
\end{align*}
\]

Korndorfer et al. (1999) \[24\] evaluated four extractants for plant-available Si in fertilization experiments with upland rice. They used four typical soil types of Minas Gerais Brazil and five levels of Wollastonite Si for each soil. Coefficients of determination between Si extracted from the soils and Si contents of the plants were \(r^2 = 0.84\) for water \(r^2 = 0.70\) for CaCl\(_2\), \(r^2 = 0.88\) for acetic acid and \(r^2 = 0.69\) for acetic acid/acetic buffer.

Berthelsen et al. (2001) \[8\] compared six Si extraction methods viz. CaCl\(_2\)-extraction of Haysom and Chapman (1975) \[17\] acetate procedure of Wong You Cheong and Halais (1970) \[37\] acetic acid method of Snyder (2001) \[36\] phosphate/extration acid of Fox et al. (1967) \[15\] citric acid procedure of Acquaye and Tinsley (1965) \[1\] and sulfuric acid method of Hurney (1973) \[18\]. They observed that ammonium acetate acetic acid and phosphate/acetic extracted 1 1.5 and 3 times more Si from soils than CaCl\(_2\) extraction. Diluted sulfuric acid and citric acid dissolved 12 and 16 times more Si than CaCl\(_2\) extraction. They suggested that CaCl\(_2\) extracts the easily soluble Si and the acetate acetic acid and phosphate acetate dissolve some of the exchangeable Si while citric acid and sulfuric acid extract specifically adsorbed Si. Since the two later extractants are very acidic (pH 2) and the method of Hurney (1973) \[18\] consists of 16 hours continuous shaking it must be assumed that silicates especially clay minerals are influenced both chemically and mechanically so that the amounts of plant-available Si are overestimated by these methods.

Rodrigues et al. (2003) \[32\] compared three Si extraction procedures the acetic acid method used by Snyder (2001) \[36\] the acetate/acetic acid procedure of Imaizumi and Yoshida (1958) \[19\] and the CaCl\(_2\) extraction reported by Haysom and Chapman (1975) \[17\] and found a decreasing extraction capacity in the order as acetate/acetic acid>acetic acid>CaCl\(_2\). A coefficient of determination of \(r = 0.33\) was found for the relation between Si measured in acetate/acetic acid and CaCl\(_2\) suggesting that the fractions extracted are overlapping but not identical. This finding supports the hypothesis that CaCl\(_2\) extracts only the easily soluble Si while acetate/acetic acid extracts some of the adsorbed silicon. Si dissolved by acetic acid showed a strong relation to Si extracted by acetate/acetic acid \(r^2 = 0.59\) and also to Si extracted by CaCl\(_2\) \(r^2 = 0.53\) suggesting that the extraction mechanism of acetic acid is between those of the two other extractants.

Narayanaswamy and Prakash (2009) \[29\] extract the available Si by various methods for Indian soils and they found a order of available Si as 0.005 M sulfuric acid (H\(_2\)SO\(_4\)) > 0.1 M citric acid > N sodium acetate (NaOAc) 2 > N NaOAc 1 > 0.5 M acetic acid 3 > 0.5 M acetic acid 2 > 0.5 M acetic acid 1 > 0.01 M calcium chloride (CaCl\(_2\)) > 0.5 M ammonium acetate (NH\(_4\)OAc) > distilled water 4 > distilled water 1. This variation may be attributed to the dissolution of soluble exchangeable and specifically adsorbed Si. The dissolution of some unavailable forms of Si presents in the soils because the nature of the extractant used soil to solution ratio pH of the extractant and shaking period. They also noticed a greater extraction potential of Si from soils with acetic acid H\(_2\)SO\(_4\).
and calcium dihydrogen phosphates than with water and CaCl₂ whereas dilute sulfuric acid and citric acid dissolved 12 and 16 times more Si than CaCl₂ and distilled water. Finally, the authors suggested that CaCl₂ and distilled water extracted more easily soluble Si while sodium acetate acetic acid and phosphate buffer dissolved some exchangeable Si also while citric acid and sulphuric acid extracted specifically adsorbed Si. In general, the lower pH of the extractant has a higher Si extraction power from the soil. Hence citric acid and H₂SO₄ extracted higher available Si in all the soils compared to other extractants.

Conclusion
The extraction methods in soil sciences can be subdivided according to the different purposes and they have been developed for agronomic purposes to evaluate the Si supplying power in soils to detect the need for Si fertilization. All extraction methods were intended to extract the complete amount of plant-available Si which gave good correlations with yields. The complete extraction of the water-soluble Si fraction is time-consuming by taking three weeks at room temperature (Schachtschabel and Heinemann, 1967) [34] or 1 week at 40 °C (Nonaka 1988 [31] and Takahashi, 1990 [10]). Another weak extractant that extracts only readily available Si is CaCl₂ and it has a very high correlation between CaCl₂-extractable Si and sugar cane yields (Haysom and Chapman, 1975) [17]. Numerous techniques have been applied to extract soluble and some exchangeable Si from soils using different anions to desorb the exchangeable part of the Si. In general, it can be stated that citric acid acetic acid phosphate and sulfate methods extract more Si than acetate nitrate CaCl₂ and water (Fox et al. 1967 [15]; Korndorfer et al. 1999 [24]; Berthelsen et al. 2001 [5]). Therefore extraction solutions containing sulfuric acid sulfuric acid sulfate citric acid and citrate have been interpreted to extract various amounts of the specifically adsorbed Si fraction. Fox et al. (1967) [15] found in two soils on alluvialuvial soils and three soils on basalt the following order of extraction capacities in the order of water-acetic acid-sulfurous acid sulfate-phosphate. In contrast in three of four soils on volcanic ash sulfuric acid/sulfate extracted more Si than phosphate. Another soil studied by Fox et al. (1967) [15] on Hawaii released more Si during acetic acid extraction. Berthelsen et al. (2001) [5] obtained a different order of extraction capacities as: water = acetate < acetic acid < phosphate/acetate < sulfuric acid < citric acid. It can be concluded that the efficiency of the extractants is significantly influenced by the extraction conditions (pH extraction duration etc.) and the composition of the soils used (especially with regard to primary silicates clay minerals and amorphous components).

Another important point is that more care has to be taken concerning pH and mechanical shaking during all types of extractions (water-soluble adsorbed amorphous Si). Several methods operate at extremely low pH and some procedures include several hours of continuous mechanical shaking so that it must be assumed that Si may also be released from silicates due to strong acidic conditions and abrasion. The pH during extraction of soluble and exchangeable Si should be adjusted to pH 4.5-4.8 as proposed by Ayres (1966) [31]; Fox et al. (1967) [15] and Wong You Cheong and Halais (1970) [37] to avoid clay mineral destruction. Shaking should be kept to the minimum necessary to allow equilibration between solid and solution within a reasonable time span as by regular short-time shaking to resuspend the samples at defined time intervals during the extraction or by continuous very slow shaking. Moreover using extraction techniques for different Si phases in the soil it is important to be aware of the statement of Follert et al. (1965) [14] who interpreted soil clay as a continuum from completely disordered to well-crystallized material. Although today the knowledge about poorly crystalline clay minerals such as allophanes and imogolite has significantly improved the core of that message is still relevant which means that the definitions of boundaries between crystalline poorly ordered and amorphous phases are partly arbitrary. Studies have shown that the active Si derived from plants (phytoliths) are ubiquitous and an important component of soils (Derry et al. 2005 and Farmer et al. 2005) [10, 13].

This review has summarized and compared a large variety of different methodologies used in the soil science for extracting different forms of Si from soils in order to advance the current understanding of the chemistry of Si to investigate the importance of active Si pools in the soil solution. Therefore future research is required to gain information about the different Si pools in soils from other aspects with distinct properties in terms of pedogenesis with small-scale variabilities. As the estimation of the plant-available Si pool is becoming increasingly important for the development of enhanced cropping systems for renewable resources to test the efficiency of different extracting solutions.

References