

# Forms of Silicon in Rice Soils of Kerala, India

## ABSTRACT

**Aim:** The plant-available silicon (PAS) content is highly influenced by different forms/fractions of silicon (Si) in which it exists in the soil. The solubility of these forms varies and affects the Si concentration in soil solution. Quantification of Si pools in soils is needed for a better understanding of biogeochemical processes that govern Si dynamics in soils, the magnitude of the Si release, and Si-cycling between soil and plant systems. In this context, an attempt was made to elucidate the status and distribution of Si pools in major rice-growing soils of Kerala.

**Methodology:** The soil samples were collected from five different locations representing the major rice growing tracts (*Kuttand, Kole, Pokkali*, sandy and lateritic soils) of Kerala, India. The processed soil samples were analyzed to estimate various physicochemical properties. Then, using standard procedure, different fractions of Si in these soils were estimated and their correlation with physico-chemical properties of soils were worked out.

**Results:** The forms of Si estimated in these soils were mobile Si, adsorbed Si, organic Si, amorphous Si, and residual Si. The percentage distributions of Si pools in these soils were mainly in the order; of residual Si > amorphous Si > occluded Si > organic Si > mobile Si > adsorbed Si. Mobile and adsorbed Si were the smallest fractions and amorphous Si was the largest fraction in these soils.

**Conclusion:** Mobile and occluded Si were found to be the major contributors of PAS in major rice soils of Kerala.

**Keywords:** plant available silicon, silicon fractions, rice soils, sequential extraction, silicon solubility

## 1. INTRODUCTION

Soil health management practices often place more attention on the supply of essential plant nutrients for sustainable crop production. The enhancement of crop productivity through the management of beneficial elements has also to be thoroughly understood. Being a beneficial plant nutrient, silicon (Si) plays a significant role in imparting both biotic and abiotic stress resistance and enhances productivity. Though the agricultural soils are largely composed of silicate minerals, most of the Si is held in the crystalline structure of silicate minerals and exists as  $\text{SiO}_2$ , which is unavailable for plant absorption. The amount of total Si in soils depends on parent material, soil type, pedogenic process, and landscape [1]. Despite high Si occurrence in soil, most of the Si compounds are insoluble in soil solution and it is not available for plant uptake. Hence, the majority of the soils are deficient in plant-available Si (PAS). The solubility and bioavailability of Si in soil are affected by pH, textural composition, minerals, organic matter, and oxides or hydroxides of iron and aluminium. Slow hydrolysis during chemical weathering of primary silicates (e.g., feldspar, mica, and quartz) can release monosilicic acid ( $\text{H}_4\text{SiO}_4$ ) into the soil solution, which is the only plant-available form of Si in soil solution. However, the natural release of monosilicic acid from silica is a slow process [2]. The amounts of monosilicic acid depend on parent material, soil development, adsorption effects, depth, water balance, temperature, and biochemical activity [3]. Si concentration in soil solution varies between 0.4 and 2000  $\mu\text{mol l}^{-1}$  [4].

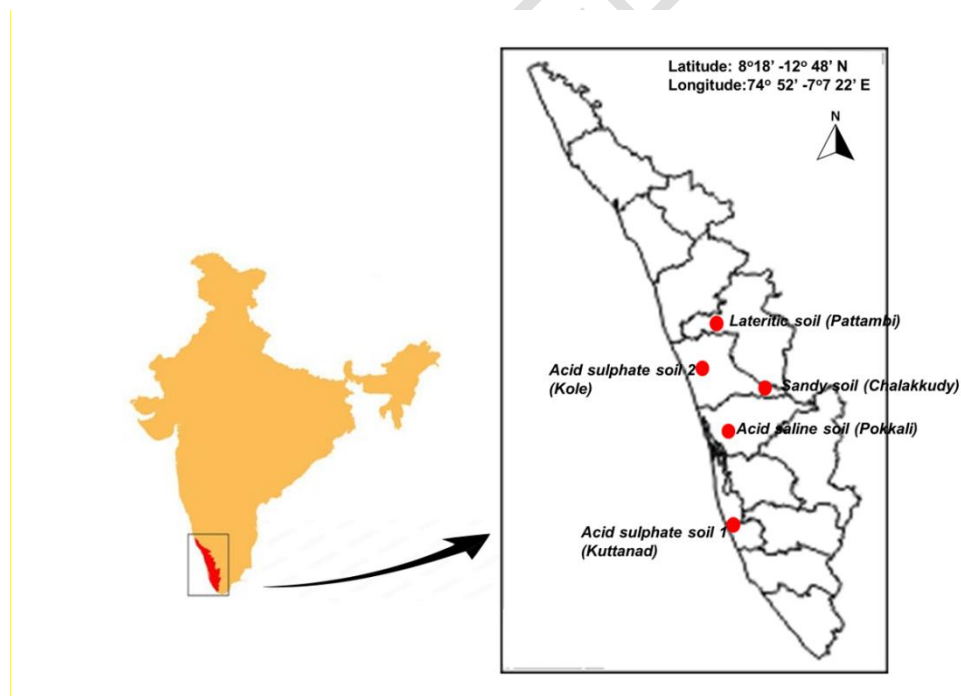
The translocation as well as immobilization of Si result in various Si pools in soils. The PAS content is significantly influenced by different forms/fractions in which it exists in the soil. The solubility of these forms varies and affects the Si concentration in soil solution. Cornellis *et al.* [5] identified the components of the readily soluble Si pool which includes dissolved Si and amorphous Si (biogenic and

pedogenic). According to Klotzbucher *et al.* [6], Si forms that contribute to the pool of readily soluble Si in soils are soluble and adsorbed Si, poorly crystalline aluminosilicates, and amorphous Si. Though the agricultural soils are largely composed of different fractions of Si, the majority of the soils are deficient in PAS. Quantification of Si pools in soils is needed for a better understanding of biogeochemical processes that govern Si dynamics in soils, the magnitude of the Si release and also Si-cycling between soil and plant systems.

In Kerala, a humid tropical climate with a high degree of weathering led to desilication, which resulted in the development of acid soils high in iron and aluminium oxides and low in available Si. Since, rice is a siliceous plant, monocropping and intensive cultivation of rice might have also resulted in the mining of available Si in rice soils of Kerala. The productivity of rice is comparatively low in the tropical soils of Kerala and Si content might be limiting to sustainable rice production. In this context, an attempt was made to elucidate the status and distribution of Si pools in major rice-growing soils of Kerala so as to evolve suitable techniques for efficient management of this beneficial nutrient with the ultimate aim of achieving better crop yield.

## 2. MATERIAL AND METHODS

The soil samples were collected from five different locations representing the major rice growing tracts *viz.* Kuttanad (Acid sulphate soil 1), Kole (Acid sulphate soil 2), Pokkali (Acid saline soil), Chalakkudy (sandy soil) and Pattambi (lateritic soils) regions of Kerala, India (Fig.1). The soil samples were air dried, processed, and sieved through 2 mm sieve. The processed soil samples were analyzed to estimate various physicochemical properties *viz.* soil reaction (pH), electrical conductivity (EC), organic carbon (OC), anion exchange capacity (AEC), cation exchange capacity (CEC), silica: sesquioxide ratio, particle size analysis and PAS using standard procedures (table.1) with three replications. These soil samples were subjected to fractionation of soil Si (Fig.2). The standard procedure developed by Georgiadis *et al.* [7] was followed for the extraction and determination of fractions of soil Si in this study. Triplicates of each soil type were used for fractionation study.



**Fig. 1 Soil sampling locations in major rice growing tracts of Kerala**

**Table 1: Analytical procedures adopted for soil analysis**

| Sl. No. | Soil parameters              | Method  |
|---------|------------------------------|---|
| 1       | pH                           | Potentiometric method using a pH meter (1:2.5 soil:water suspension) [8]  |
| 2       | EC                           | Conductivity bridge using conductivity meter (1:2.5 soil:water suspension) [8]  |
| 3       | OC                           | Chromic acid Wet digestion [9]  |
| 5       | Available Si                 | Extracted with 0.5 M acetic acid and estimated colorimetrically by ANSA using spectrophotometer [10]                                      |
| 6       | Total Si                     | Digestion with HF (48%) and estimation using ICP-OES [11]   |
| 7       | Exchangeable cations and CEC | Extracted with 0.1M BaCl <sub>2</sub> and estimation using Atomic Absorption Spectrophotometer [12]                                       |
| 8       | AEC                          | Extracted with 0.01M phosphoric acid and estimated colorimetrically by ascorbic acid blue colour method using spectrophotometer [13]      |
| 9       | Soil texture                 | International pipette method[14]  |
| 10      | Total sesquioxide            | Digested and precipitation with 8N HCl, HNO <sub>3</sub> and ammonium hydroxide. Ignition of precipitated residue in a muffle furnace[15] |

## 2.1 Sequential Extraction of Different Forms of Silicon in Soil

*Mobile silicon (Si<sub>m</sub>):* This fraction was extracted with 0.01 M CaCl<sub>2</sub> solution using a soil to solution ratio of 1:5. The samples were shaken slowly end-over-end on a horizontal shaker for 24 hours (h), only for 1 min h<sup>-1</sup> in order to accelerate the extraction but at the same time to avoid Si abrasion from mineral grains.

*Adsorbed Si (Si<sub>ad</sub>):* This fraction was obtained by extraction with 0.01 M acetic acid using a soil to solution ratio of 1:10. After the first step, the samples were rinsed with distilled water, and then 10 ml of the extractant was added and shaken for 24 h.

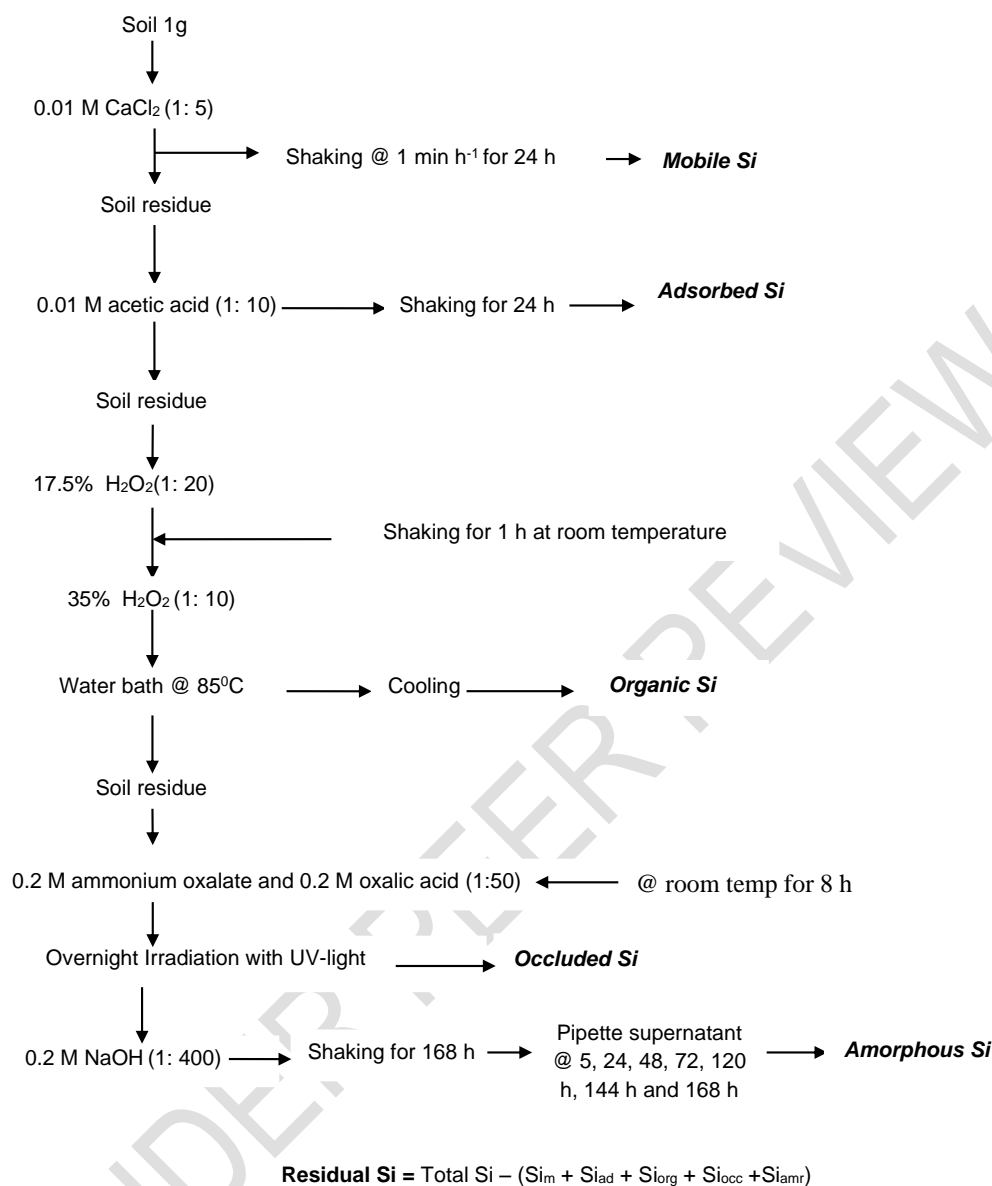
*Organic Si (Si<sub>org</sub>):* To estimate Si<sub>org</sub>, the samples were treated with 20 ml of 17.5% H<sub>2</sub>O<sub>2</sub>, manually shaken 4 – 6 times and kept at room temperature for 1 hour. Then, 10 ml of 35% H<sub>2</sub>O<sub>2</sub> was added and the samples were kept in a water bath at 85 °C, until the reaction is completed. After cooling, it was filtered.

*Occluded Si (Si<sub>occ</sub>):* This fraction was extracted with 0.2 M ammonium oxalate and 0.2 M oxalic acid under UV-light. First, the extractant was applied at daylight and room temperature for 8 h, using a soil to solution ratio of 1:50. Then, the suspensions were irradiated with UV light overnight (with a distance between the sample and the UV lamp of approx. 20 cm). During the whole time, the samples were shaken horizontally for 1 min h<sup>-1</sup>. After shaking, it was filtered.

*Amorphous Si (Si<sub>amr</sub>):* This fraction was extracted with 0.2 M NaOH solution by shaking slowly for 168 h at room temperature, using a sample to solution ratio of 1:400. 7 ml aliquots were pipetted off the supernatant solution after 5 h, 24 h, 48 h, 72 h, 120 h, 144 h and 168 h were filtered. The filtered extracts at each step were analyzed for Si.

*Residual Si (Si<sub>res</sub>):* was estimated by subtracting the sum of Si<sub>m</sub> + Si<sub>ad</sub> + Si<sub>org</sub>+Si<sub>occ</sub>+ Si<sub>ba</sub> + Si<sub>ta</sub> from total Si.

Fig. 2 Flow diagram of fractionation of Si in soil



### 3. RESULTS AND DISCUSSION

#### 3.1 Physico-chemical properties of major rice growing soils of Kerala

The data on physico-chemical properties of major rice-growing soils are presented in **Table 2**. Among different soils, *Pokkali* and *Kuttanad* soils were extremely acidic in nature. The acid release from the sulfuric horizon might be the reason for the extreme acidity of these soils. The *Pokkali* soil showed higher EC. It might be due to sea water or brackish water intrusion into *Pokkali* field. Higher organic carbon content was observed in *Kole*, *Kuttanad* and *Pokkali* soils. Continuous cultivation of high yielding rice varieties followed by incorporation of rice straw into these fields and fish/prawn cultivation would lead to the enrichment of organic matter in these soils. Sandy soils of Chalakudy recorded the lowest organic carbon. It might be due to the association of free or labile fraction of organic matter which is easily lost from light-textured sandy soils. Sandy soils with very little organic matter (OM) have a low CEC, but heavy

clay soils with high levels of OM have a much greater capacity to hold cations. The highest AEC was recorded in the sandy soils of Chalakudy and the lowest in *Kole* lands. The *Kole* and *Kuttanad* soils were clayey soils with more of 2:1 clay mineral. Soils containing montmorillonite generally exhibited low AEC. The highest silica: sesquioxide ratio was recorded in the sandy soils of Chalakudy and the lowest in *Kole* lands. This could be ascribed due to the presence of the higher amount of silicate minerals in sand fraction. The plant-available silicon ranged from 7.70 mg kg<sup>-1</sup> in sandy soils to 34.91 mg kg<sup>-1</sup> in *Kole* land soil. Despite Si being one of the most abundant elements and found in most soils in substantial quantities, the quantity of available Si was low. Clay soils with higher concentrations of phyllosilicates show higher concentrations of Si than sandy soils.

### 3.2 Forms of silicon in five major rice growing soils of Kerala

Five soil samples, representing major rice-growing regions of Kerala were subjected to fractionation of soil silicon employing the standard procedure (Figure 1). The results are presented in Table 3.

#### 3.2.1 Mobile Si

The mobile Si ranged from 2.9 to 39.0 mg kg<sup>-1</sup>. This fraction represents the immediately available Si fraction of the readily soluble Si pool. The highest value of mobile Si was recorded in *Pokkali* soils of Vyttila and the lowest value was recorded in the sandy soils of Chalakudy. The *Kole* land soils also showed a higher value for mobile Si. *Pokkali*, *Kole*, *Kuttanad*, and lateritic soils have clay content of more than 20 percent and showed higher concentration of mobile Si than sandy soil. The clay mineral surface would act as a major source of mobile Si. This could be the reason for a higher concentration of mobile Si in *Pokkali* and *Kole* land soils noticed in the present study. This is also found to be true with the findings of Georgiadis *et al.*[7] and Vandevenneet *al.*[16] who have reported a positive relationship between easily soluble Si and clay content.

#### 3.2.2 Adsorbed Si

Adsorbed Si is the main immediate insoluble source of Si in soil solution. This fraction constituted the silicic acid adsorbed by the soil minerals *viz.*, smectite, gibbsite, goethite, kaolin etc. Iron and aluminium hydroxides play a key role in the interaction between the solid and liquid Si phases in soils and Si is chemically adsorbed on the surfaces of carbonates, hydroxides, and oxides [17]. The content of adsorbed Si in major rice-growing soils of Kerala ranged from 3.3 to 27.0 mg kg<sup>-1</sup>. The highest value of adsorbed Si was recorded in *Kole* and the lowest value was recorded in the sandy soils of Chalakudy. The soils of *Kuttanad* also registered lower values of adsorbed Si. Dietzel [18] reported that adsorption of monosilicic acid takes place through a surface reaction between the monosilicic acid and the hydroxyl groups of the clay mineral surfaces. In the present investigation, the content of adsorbed Si was lower than the mobile Si, except in sandy soil. In this study, the mobile and adsorbed Si fractions represent immediately available fractions of Si in soil.

#### 3.2.3 Organic Si

The organic Si is the fraction of Si in soil that is associated with organic matter. The organic Si pool was obtained through the destruction of soil organic matter. The lowest value of organic Si (36.8 mg kg<sup>-1</sup>) was recorded in the sandy soils of Chalakudy and the highest (811.1 mg kg<sup>-1</sup>) in *Pokkali* soils of Vyttila. *Kuttanad*, *Kole* and lateritic soils recorded 420.4, 366.6 and 452.9 mg kg<sup>-1</sup> of organic Si respectively. The soils rich in clay content (> 20%) and OC content showed a higher amount of organic Si. Chalakudy soil characterized by comparatively higher sand content and low OC evidenced a lower organic Si pool. This showed clearly the involvement of clay and OC in the retention of Si in the soils.

#### 3.2.4 Occluded Si

The occluded Si was in the range of 201.7 to 1035.9 mg kg<sup>-1</sup>. The highest value of occluded Si was associated with *Kole* land soil and the lowest with sandy soil. The occlusion of dissolved Si depends upon the chemical composition of the soil solution, the mineral surface, and the nature of dissolved silica

[18]. The Si concentration in soil is controlled by the dissolution of the siliceous materials and by the sorption reactions between soluble silica and reactive soil materials, particularly the pedogenic oxides and hydroxides. Other anions and soil pH also influence the reactions [19].

### 3.2.5 Amorphous Si

The amorphous Si pool includes both minerogenic (non-biogenic silica) and biogenic silica. The minerogenic silica corresponds to non-crystalline inorganic fractions, such as opal formed at supersaturated soluble Si levels, volcanic glasses, and opal coatings on secondary minerals while biogenic silica comprises phytolith, diatoms, and sponge spicule [20]. This fraction is assumed to play a major role in Si availability and cycling since it is more soluble than crystalline minerals [21]. The amorphous Si was lowest in sandy soils ( $3902.4 \text{ mg kg}^{-1}$ ) and highest in lateritic soils of Pattambi ( $62614.0 \text{ mg kg}^{-1}$ ). *Kuttanad*, *Kole* and *Pokkali* soils recorded 32876.0, 45954.6, and 29596.0  $\text{mg kg}^{-1}$  of amorphous Si, respectively. The variation in amorphous Si content might be attributed to the texture and organic matter content of the soils. In general, clay soils with higher organic matter content recorded higher amorphous Si. The sandy soil with less organic matter content recorded lower amorphous Si content and thereby established the fact that the amorphous Si pool is well associated with the clay content of the soils.

The residual Si content ranged from 36293.0 to 172420.9  $\text{mg kg}^{-1}$ . The highest value of residual Si was observed in sandy soils and the lowest was in lateritic soils. *Kuttanad* and *Pokkali* soils also showed a very high content of residual Si among different fractions estimated.

The percentage distributions of Si pools in major rice growing soils of Kerala were mainly in the order of residual Si > amorphous Si > occluded Si > organic Si > mobile Si > adsorbed Si. Mobile and adsorbed Si were the smallest fractions and amorphous Si was the largest fraction in these soils. Within the labile Si fractions, the largest fraction was amorphous Si.

### 3.3 Soil Si pools in relation to soil properties

The correlation coefficients for different fractions of Si with physico-chemical properties of soil are presented in Table 4. Mobile Si had a significant positive correlation with silt (0.700\*\*), EC (0.560\*), OC (0.907\*\*) and CEC (0.960\*\*). Sand (-0.633\*), pH (-0.645\*\*), AEC (-0.746\*\*) and  $\text{SiO}_2/\text{R}_2\text{O}_3$  (-0.787\*\*) had a significant negative correlation with mobile Si in soil. The significant positive correlation of organic carbon with mobile Si revealed that a major proportion of mobile Si was present in the organic layer and topsoil [7]. This is confirmed by the findings of Morsy [22] and Zhang [23]. McKeague and Cline [17] reported that the amount of mobile silicon decreased with increasing pH. The percentage distribution of mobile Si was very low in all soils (0.002 to 0.036 percent). Danilova *et al.* [24] also reported that the amount of mobile Si was very small in the soil of SW Germany. Cornelis *et al* [5] reported that  $\text{CaCl}_2$ -extractable Si content represents a very small amount of the Si pool in forest soils of France. Regression analysis (Table 7) indicated that zinc is the single most important factor in predicting mobile Si status, explaining 92.2 percent variability.

The adsorbed Si had a significant positive correlation only with clay (0.554\*) content of soils, but had a significant negative correlation with EC (-0.207), AEC (-0.835\*\*), and  $\text{SiO}_2/\text{R}_2\text{O}_3$  (-0.823\*\*). The PAS had significant positive correlation with adsorbed Si. The significant negative correlation of adsorbed Si with AEC and positive correlation with clay content of soil obtained in the present study is in agreement with the findings of Georgiadis *et al.* [7]. A stepwise regression analysis (Table 7) indicated that manganese was the single most important factor in predicting adsorbed Si status explaining 82.5 percent variability.

**Table 2.** Physico-chemical properties of major rice growing soils of Kerala

| Soil type       | pH  | EC<br>d Sm <sup>-1</sup> | OC<br>% | AEC<br>cmol(-) kg <sup>-1</sup> | CEC<br>cmol(+) kg <sup>-1</sup> | SiO <sub>2</sub> /<br>R <sub>2</sub> O <sub>3</sub> | Sand  | Silt<br>% | Clay  | Textural class  |
|-----------------|-----|--------------------------|---------|---------------------------------|---------------------------------|---|-------|-----------|-------|-----------------|
| <i>Kuttanad</i> | 4.4 | 0.18                     | 2.70    | 3.49                            | 8.60                            | 12.00   | 21.55 | 33.53     | 44.93 | Clay            |
| <i>Kole</i>     | 4.7 | 0.18                     | 3.60    | 2.21                            | 9.64                            | 1.81  | 29.73 | 24.30     | 45.98 | Clay            |
| <i>Pokkali</i>  | 3.4 | 1.68                     | 3.30    | 3.70                            | 12.84                           | 3.54  | 48.53 | 30.45     | 21.03 | Loam            |
| Sandy           | 5.1 | 0.30                     | 0.60    | 5.34                            | 3.93                            | 15.26   | 89.20 | 5.10      | 5.70  | Sand            |
| Laterite        | 5.1 | 0.05                     | 1.20    | 3.35                            | 7.14                            | 1.94  | 60.60 | 10.08     | 29.33 | Sandy clay loam |

**Table 3.** Fractions of Si in five major rice growing soils

| Soil Type       | Mobile Si           | Adsorbed<br>Si | Organic<br>Si | Occluded<br>Si | Amorphous<br>Si | Residual<br>Si | Total Si           |
|-----------------|---------------------|----------------|---------------|----------------|-----------------|----------------|--------------------|
|                 | mg kg <sup>-1</sup> |                |               |                |                 |                | g kg <sup>-1</sup> |
| <i>Kuttanad</i> | 19.6                | 5.1            | 420.4         | 474.3          | 32876.0         | 157584.6       | 191.2              |
| <i>Kole</i>     | 33.3                | 27.0           | 366.6         | 1035.9         | 45954.6         | 44345.1        | 91.8               |
| <i>Pokkali</i>  | 39.0                | 10.1           | 811.1         | 404.9          | 29596.0         | 151237.9       | 182.1              |
| Sandy           | 2.9                 | 3.3            | 36.8          | 201.7          | 3902.4          | 172420.9       | 176.6              |
| Lateritic       | 20.2                | 16.6           | 452.9         | 412.3          | 62614.0         | 36293.0        | 99.8               |

Silicon in soil organic matter (SOM) was obtained through the destruction of SOM. The lowest value of organic Si was recorded in the sandy soils of Chalakudy and the highest in *Pokkali* soils of Vyttila. The highest organic Si recorded in *Pokkali* soils explains the clear role of organic matter in the retention of Si which in turn has a positive significant correlation with CEC. *Kuttanad*, *Kole* land, and lateritic soil also recorded higher concentrations of organic Si. The percentage distribution of organic Si ranged from 0.021 to 0.454 per cent. Silt (0.669\*\*), EC (0.711\*\*), OC (0.694\*\*) and CEC (0.694\*\*) were positively correlated with organic Si, while pH (-0.742\*\*) and  $\text{SiO}_2/\text{R}_2\text{O}_3$  (-0.638\*) were negatively with this fraction of Si. The significant positive correlation of organic Si with organic carbon revealed that this fraction was associated with SOM. Significant positive correlation of CEC, exchangeable Na, K, Ca, Mg, and Al with organic Si could be due to the direct effect of soil organic matter. This could be the reason for a higher concentration of organic Si in *Pokkali*, *Kuttanad*, and *Kole* land soils. Regression analysis (Table 7) indicated that zinc was the single most important factor in predicting organic Si status explaining 84.1 percent variability.

Occluded Si is the fraction of Si that is associated with pedogenic oxides and hydroxides in soil. This fraction of Si is bound to poorly crystalline constituents (allophane and imogolite). Pedogenic oxides and hydroxides that are abundant in soils play an important role in the adsorption, occlusion, and release of silicic acid in soils. The highest value of occluded Si was found in *Kole* and the lowest in sandy soil. The presence of aluminium and iron oxides and hydroxides decreases the amount of silicon in soil solution [25]. This might be the reason for the higher concentration of occluded Si obtained in *Kole* land soil in this study. It constituted 0.11 to 1.13 percent of total Si.

The amounts of Si occluded in sesquioxide are very small in the upper horizons of all pedons and increase with depth [24]. In this study, occluded Si had a significant positive correlation with clay (0.765\*\*) and OC (0.689\*\*) and a significant negative correlation with sand (-0.669\*\*), AEC (-0.887\*\*) and  $\text{SiO}_2/\text{R}_2\text{O}_3$  (-0.581\*). The silicon adsorption was much greater than B adsorption indicating that some of the sorption sites showed anion preference [26]. Soil Si content tends to be decreased with time-lapse because of processes such as occlusion and adsorption onto aluminium and iron oxides. Also, monosilicic acid reacts with aluminium and forms slightly soluble aluminosilicates. The adsorption of dissolved silica depends on the chemical composition of the solution, the mineral surface, and also on the nature of the dissolved silica [18]. Here the available and exchangeable calcium (Ca) showed a significant positive correlation with occluded Si. Adsorption of Si was weak on gibbsite in the absence of Ca [21]. There were specific interactions of Ca, silicate, and phosphate ions with surface hydroxyls of gibbsite. Regression analysis (Table 7) indicated that manganese was the single most important factor in predicting occluded Si status explaining 91.2 percent variability.

The amorphous silicon pool includes pedogenic and biogenic silica. The deposition of diatoms, plant debris and sediments during incoming tide results in an import of amorphous Si (ASi) to tidal marshes. Especially young marshes that frequently inundate and still increase in elevation, act as a sink for ASi. Part of the ASi is dissolved again to DSi and becomes available for plants and diatoms via the soil pore water [27]. The rate at which Si is released from plant litter is independent of cellulose hydrolysis, which suggests that most of the litter-Si is contained in the phytoliths as a pure "inorganic" pool, and not complexed with organic matter [28]. The lowest amorphous Si was recorded in sandy soils and highest in lateritic soils of Pattambi. The occurrence of pedogenic iron oxides and hydroxides in lateritic soil could be the reason for the highest concentration of amorphous Si in Pattambi soil. *Kuttanad*, *Kole* and *Pokkali* soils recorded higher concentrations of amorphous Si. It might be due to litter deposition and the presence of a humus layer consisting of phytoliths in these soils capable of adsorbing Si. The amorphous Si was found to constitute 2.21 to 62.73 percent of total Si. The percentage distribution of amorphous Si was higher in *Kole* and lateritic soils. It was the second-largest fraction in soil. Si extracted by NaOH (amorphous silicon) constituted the largest fraction of extractable Si in almost all soil samples of SW Germany [24].

There was a significant positive correlation of clay (0.631\*) and a negative correlation of AEC (-0.764\*\*) and  $\text{SiO}_2/\text{R}_2\text{O}_3$  (-0.820\*\*) with amorphous Si. Sauer and Burghardt [28] reported that amorphous Si rises with increasing amounts of water-soluble Mg. Although these correlations may not necessarily indicate a causal relationship, they suggest that Mg enhances the precipitation of amorphous silica. This

relationship was to be expected, due to the decreasing solubility of amorphous silica with decreasing pH. They conclude that not only the chemical conditions but also the water dynamics play an important role in the formation and distribution of amorphous silica in a soil profile. Regression analysis (Table 7) clearly indicated the  $\text{SiO}_2:\text{R}_2\text{O}_3$  ratio was the single most important factor in predicting amorphous Si status explaining 64.8 percent variability.

The remaining unknown mineral fractions were together known as residual Si. The highest value of residual Si was observed in sandy soils and the lowest was in lateritic soils. *Kuttanad* and *Pokkali* soils also showed a very high content of residual Si. The residual Si was found to contribute the highest percentage of Si to total Si. It was highest (97.65 percent) in the sandy soils of Chalakudy and lowest (36.36 per cent) in lateritic soils of Pattambi. The residual Si had a significant positive correlation with AEC (0.708\*\*) and  $\text{SiO}_2/\text{R}_2\text{O}_3$  (0.796\*\*). The pH (-0.552\*) was negatively correlated with total Si, while AEC (0.619\*) and  $\text{SiO}_2/\text{R}_2\text{O}_3$  (0.715\*\*) showed a positive correlation. A stepwise regression analysis (Table 7) clearly indicated the  $\text{SiO}_2:\text{R}_2\text{O}_3$  ratio was the single most important factor in predicting residual Si status explaining 63.4 percent variability.

### 3.4 Relation between forms of Si and PAS in soil

The correlation between different fractions of Si and PAS are given in Table 5. The PAS had a significant positive correlation with mobile Si (0.824\*\*), adsorbed Si (0.875\*\*) and occluded Si (0.863\*\*). The residual Si (-0.592) and total Si (-0.594) had a significant negative correlation with PAS in soil. The mobile Si had a positive significant correlation with adsorbed (0.571), organic (0.856\*\*) and occluded Si (0.581). The adsorbed Si had a positive significant correlation with occluded Si (0.868) and amorphous Si (0.696\*\*) and negative correlation with residual Si (-0.887\*\*) and total Si (-0.896\*\*). The occluded Si had a significant negative correlation with residual Si (-0.631) and total Si (-0.638). The amorphous Si had a significant negative correlation with residual (-0.872\*\*) and total Si (-0.739). The residual Si had a significant positive correlation with total Si (0.975\*\*) and a significant negative correlation with adsorbed, occluded and amorphous silicon. Among the different Si fractions studied, the organic Si showed a correlation only with mobile Si (Table 7).

Path coefficient analysis of different fractions of Si indicating the direct and indirect effects on PAS in major rice-growing soils are given in Table 6. The mobile Si had high direct positive effect (0.693) on PAS. The indirect effect of adsorbed, occluded, and total Si through mobile Si was moderate and positive. The residual Si had an indirect moderate negative effect on available Si through mobile Si. The direct effect of adsorbed Si on PAS was low (0.192). The indirect effects of mobile and occluded Si through adsorbed Si on available Si were low and that of total Si through adsorbed Si was very high and positive. The occluded Si had a moderate direct effect (0.231) on PAS. The indirect effects of adsorbed, mobile, and total Si through occluded Si were low, moderate, and high respectively on available Si in soil. The residual Si had a high negative indirect effect on available Si through occluded Si. The direct effect of residual Si on available Si was very high and positive (1.305). The indirect effects of mobile, adsorbed, and occluded Si through residual Si were low and negative. The total Si had a very high negative indirect effect on PAS through residual Si. The total Si had a very high negative direct effect (-1.388) on PAS. The indirect effects of mobile, adsorbed, and occluded Si through total Si were low and negative; while residual Si had a very high positive indirect effect on PAS through total Si in soil.

**Table.4 Correlation between forms of Si and soil properties**

| Si fractions | Sand     | Silt    | Clay    | pH       | EC      | OC      | AEC      | CEC     | SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> |
|--------------|----------|---------|---------|----------|---------|---------|----------|---------|---|
| Mobile Si    | -0.633*  | 0.700** | -       | -0.645** | 0.560*  | 0.907** | -0.746** | 0.960** | -0.787**  |
| Adsorbed Si  | -        | -       | 0.554*  | -        | -       | -       | -0.835** | -       | -0.823**  |
| Organic Si   | -        | 0.669** | -       | -0.742** | 0.711** | 0.694** | -        | 0.922** | -0.638*   |
| Occluded Si  | -0.669** | -       | 0.765** | -        | -       | 0.689** | -0.887** | -       | -0.581*   |
| Amorphous Si | -        | -       | 0.631*  | -        | -       | -       | -0.764** | -       | -0.820**  |
| Residual Si  | -        | -       | -       | -        | -       | -       | 0.708**  | -       | 0.796**   |
| Total Si     | -        | -       | -       | -0.552*  | -       | -       | 0.619*   | -       | 0.715**   |

(\*\* significant at 1.00 % level, \* significant at 5.00 % level)

**Table.5 Correlation between forms of Si and Plant Available Si (PAS)**

| Si fractions | PAS     | Mobile Si | Adsorbed Si | Organic Si | Occluded Si | Amorphous Si | Residual Si | Total Si |
|--------------|---------|-----------|-------------|------------|-------------|--------------|-------------|----------|
| PAS          |         |           |             |            |             |              |             |          |
| Mobile Si    | 0.824** |           |             |            |             |              |             |          |
| Adsorbed Si  | 0.875** | 0.571*    |             |            |             |              |             |          |
| Organic Si   | -       | 0.856**   | -           |            |             |              |             |          |
| Occluded Si  | 0.863** | 0.581*    | 0.868**     | -          |             |              |             |          |
| Amorphous Si | -       | -         | 0.696**     | -          | -           |              |             |          |
| Residual Si  | -0.592* | -         | -0.887**    | -          | -0.631*     | -0.872**     |             |          |
| Total Si     | -0.594* | -         | -0.896**    | -          | -0.638*     | -0.739**     | 0.975**     |          |

PAS – plant available Si (\*\* significant at 1.00 % level, \* significant at 5.00 % level)

**Table.6 Path coefficient of different fractions of Si with PAS in soil**

| Si fractions | Mobile Si    | Adsorbed Si  | Occluded Si  | Residual Si  | Total Si      | Correlation Coefficient of Si pools with PAS |
|--------------|--------------|--------------|--------------|--------------|---------------|--|
| Mobile Si    | <b>0.693</b> | 0.110        | 0.135        | -0.429       | 0.317         | <b>0.824**</b>                               |
| Adsorbed Si  | 0.395        | <b>0.192</b> | 0.201        | -1.157       | 1.244         | <b>0.875**</b>                               |
| Occluded Si  | 0.403        | 0.167        | <b>0.231</b> | -0.823       | 0.886         | <b>0.863**</b>                               |
| Residual Si  | -0.228       | -0.170       | -0.146       | <b>1.305</b> | -1.353        | <b>-0.592*</b>                               |
| Total        | -0.158       | -0.172       | -0.148       | 1.272        | <b>-1.388</b> | <b>-0.594*</b>                               |

(Values on diagonal are direct effects and values on horizontal lines are indirect effects)

**Table.7 Regression equations of different forms of silicon with soil properties**

| Dependent variable  | Regression equations   | R <sup>2</sup> |
|---------------------|--|----------------|
| <b>Mobile Si</b>    |  |                |
| i                   | Mob-Si = -11.23 + 11.65**Zn  | 0.922          |
| ii                  | Mob-Si = -25.48 + 7.785**Zn + 64.109** Ex. K   | 0.989          |
| <b>Adsorbed Si</b>  |  |                |
| i                   | Ad-Si = 6.819 + 0.225**Mn  | 0.825          |
| ii                  | Ad-Si = 13.153 + 0.162**Mn – 0.693**SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub>  | 0.973          |
| iii                 | Ad-Si = 19.513 + 0.180**Mn – 0.854**SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> – 0.016**N                               | 0.994          |
| <b>Organic Si</b>   |  |                |
| i                   | Org-Si = -228.256 + 219.864**Zn  | 0.841          |
| ii                  | Org-Si = -130.396 + 349.428**Zn – 1.385**N   | 0.920          |
| iii                 | Org-Si = -205.512 + 575.443**Zn -2.776**N -223.672**EC   | 0.990          |
| <b>Occluded Si</b>  |  |                |
| i                   | Occl-Si = 314.587 + 7.660**Mn  | 0.912          |
| ii                  | Occl-Si = 518.245 + 6.584**Mn – 3.545**Sand  | 0.990          |
| <b>Amorphous Si</b> |  |                |
| i                   | Am-Si = 54525.912 – 2834.211**SiO <sub>2</sub> :R <sub>2</sub> O <sub>3</sub>  | 0.648          |
| ii                  | Am-Si = 37873.301 – 2329.994**SiO <sub>2</sub> :R <sub>2</sub> O <sub>3</sub> + 448.395** Clay                               | 0.735          |
| iii                 | Am-Si = -175959.78 – 6738.5**SiO <sub>2</sub> :R <sub>2</sub> O <sub>3</sub> + 2656.6** Clay + 49551.96**AEC                 | 0.917          |
| iv                  | Am-Si = -127596.17 – 7482.6**SiO <sub>2</sub> :R <sub>2</sub> O <sub>3</sub> + 3475.9** Clay + 45905.6**AEC –16360.9**Ex. Ca | 0.990          |
| <b>Residual Si</b>  |  |                |
| i                   | Res-Si = 54593.39 + 8382.37** SiO <sub>2</sub> :R <sub>2</sub> O <sub>3</sub>  | 0.634          |

This study provides information on varying degree of Si fractions present in major rice growing soils of Kerala and their interrelationship with various physico-chemical properties. The percentage distributions of the different fractions of Si these soils were in the order; residual Si > amorphous Si > occluded Si > organic Si > mobile Si > adsorbed Si in *Kuttanad, Pokkali*, and sandy soils, whereas it was in the order amorphous Si > residual Si > occluded Si > organic Si > mobile Si > adsorbed Si in *Kole* land soil and amorphous Si > residual Si > organic Si > occluded Si > mobile Si > adsorbed Si in lateritic soil. Mobile and adsorbed Si were the smallest and immediately available fractions and amorphous Si was the largest fraction of Si in all these soils. The results indicated that Si is more soluble in *Kole* land soil.

#### 4. CONCLUSION

The fractionation study deciphered the information on different pools of Si in major rice-growing soils of Kerala and their relative contribution to PAS. The lowest Si amounts were found in the mobile and adsorbed Si fractions. Mobile and occluded Si were found to be the major contributors of PAS in these soils. Hence, not only PAS, but other forms of Si also play an important role in the dissolution of Si into soil solution and thus, its uptake by rice plants. There is a need for further investigation on different forms of Si in different terrestrial ecosystem with a greater number of samples.

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