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## pH as a proxy for estimating plant-available Si? A case study in rice fields in Karnataka (South India)

Jean-Dominique Meunier, Kollalu Sandhya, Nagabovanalli Prakash, Daniel Borschneck, Philippe Dussouillez

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2 **pH as a proxy for estimating plant-available Si? A case**  
3 **study in rice fields in Karnataka (South India)**  
4

5 **Jean-Dominique Meunier<sup>1</sup>, Kollalu Sandhya<sup>2</sup>, Nagabovanalli B. Prakash<sup>2</sup>, Daniel**  
6 **Borschneck<sup>1</sup>, Philippe Dussouillez<sup>1</sup>,**  
7

8 <sup>1</sup> Aix Marseille Univ. CNRS, IRD, INRA, Coll France, CEREGE, Aix en Provence, France

9 <sup>2</sup> University of Agricultural Sciences, Dpt of Soil Science & Agr Chemistry, GKVK, Bengaluru  
10 560065 Karnataka, India  
11

12  
13 **Abstract**

14 *Background and aims.* Although Si is recognized as a beneficial element for crops, the  
15 determination of plant-available silicon (PAS) in soils has become challenging. A correlation  
16 between pH and PAS indicators has been reported in the literature due to the higher degree of  
17 weathering of acidic soil. We tested this hypothesis in the cultivated rice fields of Karnataka  
18 State, India, which exhibit gradients of pH and climate.

19 *Method.* Two hundred surface soil samples were collected from rice fields representing nine of  
20 the ten agro-climatic zones (ACZs) defined for Karnataka. We analyzed the Si extracted by  
21 calcium chloride (Si<sub>CC</sub>) and the Si extracted by acetate-acetic acid (Si<sub>AA</sub>) as PAS indicators. The  
22 samples were analyzed for particle size distribution, pH, electrical conductivity and cation  
23 exchange capacity. Forty subsamples were selected for mineralogical and chemical analysis.

24 *Results.* PCA of the 200 samples showed that PAS indicators and pH were positively correlated.  
25 Si<sub>AA</sub> was also positively correlated with electric conductivity (EC), CEC, and the silt fraction  
26 and negatively correlated with the sand fraction. A separation of the data arbitrarily made at pH  
27 7.5 showed that below 7.5, the correlation between PAS indicators and pH was better than  
28 considering the whole 200 samples. The distribution of Si<sub>AA</sub> with pH matched the curve of  
29 adsorbed Si given in the literature. Soils characterized by low pH and high contents of sand,  
30 SiO<sub>2</sub>, Zr and Hf, showed a higher degree of weathering. They were preferentially located along  
31 the coast, where the rainfall is the most abundant. The depletion of PAS indicators was also in  
32 good agreement with the predominance of kaolinite instead of smectite, which characterizes a  
33 higher degree of desilication.

34 *Conclusion.* We demonstrated that the correlation between pH and PAS indicators is explained  
35 by natural Si depletion (weathering intensity) and the effect of Si adsorption. We suggest that  
36 at pH values up to 7.5, pH can be used as a proxy for PAS in similar types of pedo-climatic  
37 conditions.

38

39 **Keywords** Plant available silicon/ Weathering/ Adsorption/ Rice/ Karnataka State

40

## 41 **Introduction**

42

43 Silicon, the second most common element on the earth's surface, is also present in significant  
44 amounts in the shoots of the main crops produced worldwide (Guntzer et al., 2012). It is well  
45 established that the accumulation of Si in plants as phytoliths follows the same pathways as for  
46 the majority of the nutrients: root uptake from the soil solution (Liang et al., 2015). The  
47 speciation of dissolved Si (DSi) is quite simple because there is almost exclusively only one  
48 species below pH 9: the monomeric silicic acid  $\text{H}_4\text{SiO}_4$ . At elevated pH,  $\text{H}_4\text{SiO}_4$  dissociates into  
49 anions to form  $\text{H}_3\text{SiO}_4^-$  and  $\text{H}_2\text{SiO}_4^{2-}$  (Philippini et al., 2006). The source of DSi is ultimately  
50 the soil-forming mineral, which can include quartz, aluminosilicates, phyllosilicates, clay  
51 minerals and amorphous silica (Cornelis et al., 2011). However, the soil-forming minerals are  
52 largely resistant to weathering (Berner and Berner, 1996). As a consequence, with increasing  
53 time, the soil becomes depleted of Si, as evidenced by the "desilication" process (Buol et al.,  
54 1989), which shows with increasing weathering intensity the formation of 2/1 clay mineral, 1/1  
55 clay mineral and ultimately only Fe-Al oxyhydroxides (Cornelis et Delvaux, 2016). Evidence  
56 of Si leaching by weathering is also documented along soil profiles using mass balance  
57 calculations, which show increases in Si loss with soil age (White, 2005; Sommer et al., 2006).  
58 Using water analysis, various approaches had similar conclusions. A comparison of DSi  
59 concentrations of the continents showed that the highest concentration of DSi occurs in African  
60 streams ( $12.6 \text{ mg L}^{-1}$  on average), where hot climatic conditions prevail (Dürr et al., 2011).  
61 Another example of Si loss during weathering is found in Hawaiian volcanic soil solutions  
62 (Derry et al., 2005), where DSi decreases when the age of the soil increases. The content of  
63 minerals favorable for weathering for a given soil is therefore a stronger constraint for  
64 explaining the accumulation of Si in plants (Henriet et al., 2008).

65 Despite the abundant literature showing that Si is beneficial for crops (Liang et al.,  
66 2015), the bioavailability of Si remains a challenging topic (Haynes, 2014). To quantify the  
67 plant-available Si (PAS), various empirical indicators have been proposed (Nayar et al., 1977;  
68 Barbosa-Filho et al., 2001; Korndorfer et al., 2001; Narayanaswamy and Prakash, 2010; Yanai  
69 et al., 2016; Crusciol et al., 2017). These indicators are based on the use of chemical extractants  
70 of DSi from soils that give good correlations with plant Si content or yield. PAS indicators such  
71 as  $\text{H}_2\text{O}$ ,  $\text{CaCl}_2$ , acetic acid and acetate may also be useful to identify the soil depleted of PAS  
72 and eventually to justify the application of Si fertilizers (Berthelsen et al., 1999). However, the

73 use of these PAS indicators is still poorly evaluated because of the lack of studies documenting  
74 the Si pools that are controlling them. Indeed, the correlation between PAS indicators and soil  
75 acidity, as measured by pH, has been reported in the literature as an indicator of intensity of  
76 weathering: lower pH may be associated with low PAS in highly leached soils (Review in  
77 Haynes, 2014 and Liang et al. 2015). For instance, Miles et al. (2014) showed that pH and  
78 CaCl<sub>2</sub>-extractable Si (Si<sub>CC</sub>) are correlated in the range of pH 3.3 to pH 7 in the South African  
79 sugarcane fields. According to the authors, such a correlation is attributable to a change in  
80 mineralogy from a less weatherable pool of Si minerals at low pH to a more weatherable pool  
81 of Si minerals at higher pH, following the conclusion of Henriët et al. (2008). However, in  
82 Henriët et al. (2008), the pH range does not differ between desilicated soils and less weathered  
83 soils. In addition, Miles et al. (2014) did not document the mineral content/Si status of their  
84 studied soils, so other hypotheses are possible to explain the correlation between pH and PAS  
85 indicators. One hypothesis is that PAS is controlled by adsorbed Si. Indeed, it is well  
86 documented that Si adsorption increases with pH in a similar range as in the previously  
87 mentioned study by Miles et al. (2014), specifically if Al and Fe oxides are present (Beckwith  
88 and Reeve 1963; Kingston et al., 1972, Philippini et al., 2006; Hiemstra et al., 2007). Another  
89 hypothesis is that PAS may be controlled by the soil phytolith pool. Phytoliths are residues of  
90 Si accumulated in plants during litter decomposition and are composed of amorphous silica  
91 particles, which are considered to be among the most soluble pools of Si in soils (Frayssé et al.,  
92 2009). Because plant productivity is generally lower at low pH due to poor nutrient content and  
93 aluminum toxicity (Zheng, 2010), it is possible that a correlation between pH and PAS could  
94 be due to the phytolith content. To decipher the factors that control the PAS and to document  
95 whether pH can be used as a proxy for PAS, our approach here was to combine agronomical,  
96 physical, mineralogical and chemical properties of cultivated soils that exhibit a large pH  
97 gradient. Accordingly, we conducted a study in different rice ecosystems corresponding to  
98 acidic, slightly acidic, neutral and alkaline soils with distinct climates in the Karnataka State of  
99 South India.

100

## 101 **Materials and Methods**

102

103 The State of Karnataka forms the west central part of Peninsular India. It occupies an area of  
104 1,91,792 km<sup>2</sup> and is divided into 4 physiographic regions: 1. the Northern Karnataka Plateau at  
105 300-600 masl, on the Deccan Traps; 2. the Central Karnataka Plateau at 450-700 masl; 3. the  
106 Southern Karnataka Plateau at 600-900 masl, bordered by the Western Ghats in the west and  
107 south; and 4. the Karnataka Coastal Region between the Western Ghats in the East and the

108 Arabian Sea in the west. The climate varies from tropical wet along the coast to tropical wet  
109 and dry to the center and semi arid to the east. The rainfall is profoundly affected by the  
110 monsoon season between June and September and shows a gradient from 512 mm to 4700 mm  
111 westward (Fig. 1a). The rainfall has a strong influence on the soil type, with ultisols and alfisols  
112 prevailing along the coastal region, aridisols in the Central Karnataka Plateau and vertisols in  
113 the Northern Karnataka Plateau (Hajira Sajini and Shivanna, 2017). The parent rocks mainly  
114 consist of Archean gneisses, granites and charnockite rocks. Others consist of Proterozoic  
115 sedimentary formations, the Deccan basalts (to the North) and Tertiary and Quaternary  
116 sediments toward the west coast (Radhakrishnan and Vaidyanadhan, 1997).

117 Two hundred soil samples were collected from rice fields representing nine out of ten agro-  
118 climatic zones (ACZs) defined for Karnataka (Fig. 1b). ACZs serve as focal areas for  
119 conducting location-specific research (Ramachandra et al., 2004). ACZs are based on rainfall  
120 patterns, topography, soil type, climate and cropping patterns. The sampling was mainly  
121 performed after the harvest of rice crops during 2014 and 2015 using an auger sampler to a  
122 depth of 0-15 cm and by recording the coordinates (latitude and longitude) of each location.  
123 Basic location information, such as district, taluk, village and cropping system, was also  
124 recorded and is presented in Appendix 1. Due to introduction of combine harvesters, most of  
125 the farmers are incorporating rice straw to their agricultural fields (rice fields), which otherwise  
126 would serve mainly as fodder to cattle. However, rice husk is being used for different purpose,  
127 which ranges from serving as fuel source in rice mills, hotels etc., to packing material and also  
128 as bedding material in poultry industries.

129         Approximately 12 – 15 subsamples of 200-300 g were collected from each sampling  
130 location using a screw auger and mixed thoroughly to obtain a representative sample. Each  
131 representative soil sample was placed in a separate plastic zip-lock cover bag to avoid  
132 contamination of the samples. Soil samples were shade dried, powdered and sieved through a 2  
133 mm mesh sieve and stored in plastic container bottles for further use. The samples were  
134 analyzed for particle size distribution (pipette method), pH (soil-water suspension of 1/2.5),  
135 electrical conductivity (E.C., soil-water suspension of 1/2.5), and cation exchange capacity  
136 (CEC, for pH<8.2: distillation method, Page et al., 1982; pH>8.2: flame photometry, Jackson,  
137 1973). The choice of the PAS indicators was based on a critical evaluation of the literature  
138 (Sauer et al. 2006; Narayanaswamy and Prakash, 2010; Georgiadis et al., 2013; Haynes, 2014;  
139 Miles et al. 2014). We analyzed the Si extracted by 0.01M CaCl<sub>2</sub> (Si<sub>CC</sub>, Haysom and Chapman,  
140 1975) for the determination of the pool of readily soluble Si and the Si extracted by 0.5 M  
141 acetate-acetic acid (Si<sub>AA</sub>, Korndorfer et al., 2001) for the pool of adsorbed Si. These two PAS

142 indicators were strongly correlated with Si uptake and yields in rice grown on acidic soils  
143 originated from Coastal and Hilly zones (Narayanaswamy and Prakash, 2010). We used  
144 Quantum GIS (QGIS) 2.14 to map the studied parameters in Karnataka State.

145 Out of 200 samples, 40 representative samples with varied pH (acidic, neutral and alkaline) and  
146 silicon content were selected for chemical and mineralogical studies. The mineralogical  
147 composition was measured on bulk samples finely ground using a PANanalytical X'Pert Pro  
148 (Cobalt anti-cathode,  $\lambda = 1.79 \text{ \AA}$ ) X-ray diffractometer running at 40 kV and 40 mA.

149 The clay composition was determined on oriented plates after destruction of organic matter  
150 (using hydrogen peroxide) and carbonate (using hydrochloric acid) and extraction of the clays  
151 by Stokes' law. Organic carbon (O.C.) was measured using the chromic acid titration method.  
152 Major elements were measured by fusion/XRF, and trace elements were measured by four  
153 acid/ICP-MS at ALS Minerals, Seville, Spain ([http://www.alsglobal.com/Our-](http://www.alsglobal.com/Our-Services/Minerals)  
154 [Services/Minerals](http://www.alsglobal.com/Our-Services/Minerals)). We chose to analyze Zr and Hf because they have refractory properties that  
155 can be used to trace the intensity of weathering (Kurtz et al., 2000; Braun et al., 2005).

156 PCA, ANOVA, Student's t test and regressions were calculated using Excel (Microsoft)  
157 and Xlstat (Addinsoft).

158

## 159 **Results**

160

### 161 Characterization of the 200 samples

162

163 The measurements of the 200 samples are detailed in Supplementary Material. The texture of  
164 the soils varied from sandy loam to clay. pH, EC,  $\text{Si}_{\text{CC}}$ ,  $\text{Si}_{\text{AA}}$ , and CEC ranged from 4.9 to 9.5,  
165 0.02 to 1.07  $\text{dSm}^{-1}$ , 1.4-82.9  $\text{mg kg}^{-1}$ , 6.7 to 370.2  $\text{mg kg}^{-1}$  and 9.2 to 115.2  $\text{cmol (p+) kg}^{-1}$ ,  
166 respectively. The proportions of acidic (pH < 6.5), neutral (pH 6.5-7.5) and alkaline (pH > 7.5)  
167 soils were 40, 14 and 46%, respectively. Overall, the  $\text{Si}_{\text{CC}}$  values were lower than the  $\text{Si}_{\text{AA}}$   
168 values (Student's t test < 0.05). PCA of the data (Table 1) showed that PAS indicators and pH  
169 were positively correlated.  $\text{Si}_{\text{AA}}$  was also positively correlated with EC, CEC, and the silt  
170 fraction and negatively correlated with the sand fraction. A closer analysis of the relation  
171 between pH and PAS indicators (Fig. 2) showed that the correlation identified in the PCA may  
172 not be a simple linear regression. Indeed, models such as polynomial regressions presented a  
173 better fit than a linear regression and showed that the PAS indicators may decrease (for  $\text{Si}_{\text{AA}}$ )  
174 or remain stable (for  $\text{Si}_{\text{CC}}$ ) where pH > 7.5. A separation of the data arbitrarily made at pH 7.5  
175 showed that below 7.5, the correlation between PAS indicators and pH was better than

176 considering the whole 200 samples with best fits using power regression models. ANOVA of  
177 the soil categories showed that the ultisol and alfisol samples had both the lowest pH while the  
178 vertisol samples have the highest CEC values (Table 2). Ultisol and alfisol present the lowest  
179 PAS indicators but they are not significantly different from all soils for Si<sub>CC</sub> (except Aridisol)  
180 and from all soils for Si<sub>AA</sub> (except Entisol and Vertisol) Plotting the data into the Karnataka  
181 map showed a general trend of lower pH and PAS indicators towards the west coast, which is  
182 represented by the hilly and coastal zones (Fig. 3).

183

184 Mineralogy and geochemistry of the 40 samples

185

186 Quartz, feldspars, amphibole, goethite, gibbsite, Ti oxides and phyllosilicates were the main  
187 minerals identified in most of the samples (Table 3). Gibbsite was more frequent in the coastal  
188 zone. Calcite has been detected in 4 samples (number 2, 54, 97 and 157). The clay minerals  
189 identified included smectite, chlorite, vermiculite, illite, kaolinite, and various interlayers of  
190 illite-smectite and chlorite-vermiculite. Smectite has not been identified in the hilly and coastal  
191 zones, where kaolinite seemed to be the dominant clay. The chemistry was dominated by SiO<sub>2</sub>  
192 (55-88 %), Al<sub>2</sub>O<sub>3</sub> (5-18 %), Fe<sub>2</sub>O<sub>3</sub> (2-16 %), CaO (0.1-9 %), K<sub>2</sub>O (0.1-4.5 %). PCA analysis  
193 (Fig. 4a) showed that both PAS indicators were significantly positively correlated with Al<sub>2</sub>O<sub>3</sub>.  
194 However, Si<sub>AA</sub> was also significantly positively correlated with pH, Fe<sub>2</sub>O<sub>3</sub>, MgO, MnO and  
195 negatively correlated with SiO<sub>2</sub>, Hf and Zr. Using our 40 subsamples, the correlation between  
196 Si<sub>CC</sub> and pH became non significant (R= 0.3, figure 4a). However if we select only the samples  
197 where pH is < 7.5, we obtained a significant correlation (R= 0.4, n = 24, P= 0.05), as shown in  
198 figure 2. Projections of the two most predominant variables (F1 and F2) in the principal  
199 component space (Fig. 4b) showed that both PAS indicators are grouped at a pole constituted  
200 by pH, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, MnO, P<sub>2</sub>O<sub>5</sub> and CaO to the left and are opposed to a group  
201 constituted by SiO<sub>2</sub>, K<sub>2</sub>O, Na<sub>2</sub>O Zr and Hf to the right. Organic carbon was only positively  
202 correlated with P<sub>2</sub>O<sub>5</sub>.

203

## 204 Discussion

205

206 PAS indicators and the soil weathering state

207

208 The range of Si<sub>CC</sub> falls in the same range as in previous studies, particularly for acidic rice field  
209 soils in Karnataka State (Narayanaswamy and Prakash, 2009) and for sugarcane fields in

210 Maharashtra state, India (Phonde et al., 2014). The range of  $Si_{AA}$  is in good agreement with the  
211 results of Naryanaswamy and Prakash (2009) but falls in the lower range of the sugarcane fields  
212 published by Phonde et al. (2014). The  $Si_{AA}$  values are slightly more elevated than the  $Si_{CC}$   
213 values, as previously shown in the literature (Narayanaswamy and Prakash 2009; Hohn et al.,  
214 2008), confirming that the two chosen PAS indicators do not cover the same Si pools in soils.  
215 The positive correlation between  $Si_{AA}$  and  $Si_{CC}$  is also in good agreement with previous studies  
216 (de Lima-Rodriguez et al., 2003), showing that the pools extracted by the two PAS indicators  
217 are not independent and that the fraction of Si extracted by calcium chloride is also included in  
218 the fraction of Si extracted by acetic acid.

219 By combining physical (grain size), chemical and mineralogical data, our results show  
220 that soils that are low in PAS indicators are those characterized by low pH and by higher  
221 contents of sand (Table 1),  $SiO_2$ , Zr and Hf (Fig. 4), all parameters that may indicate a higher  
222 degree of weathering. Higher content of sand and  $SiO_2$  is interpreted as the quartz contribution  
223 in acidic weathered soils. Acidic weathered soils are preferentially located along the coast,  
224 where the rainfall is the highest (Fig. 1a). The depletion of PAS indicators is also in good  
225 agreement with the predominance of kaolinite instead of smectite, which characterizes a higher  
226 degree of desilication (Cornelis and Delvaux, 2016).

227 Accordingly, our results demonstrate that higher weathering and desilication lead to the  
228 depletion of PAS indicators, as previously suggested by some authors (Winslow et al., 1997;  
229 Bethelsen et al., 1999; Miles et al., 2014; Tavakoli et al., 2011). CEC was not significantly  
230 lower in the ultisols and alfisols, contrary to what is shown elsewhere, where low pH means  
231 low soil exchangeable bases (Maire et al., 2015). Such a discrepancy may be due to a flaw in  
232 soil categorization or may result from perturbation due to agricultural practice (addition of N,  
233 P, K fertilization, for instance). The level of Si extracted by either calcium chloride or acetic  
234 acid depends on the complex interaction of molecules at the mineral-water interface and may  
235 be controlled by dissolution (Dove, 2006) and/or by desorption (Hiemstra et al., 2007).

236

237 PAS controlled by dissolution

238

239 The good correlation between pH and PAS indicators up to pH 7.5 is in good agreement with  
240 the results of Miles et al. (2014) from sugarcane fields in South Africa. Miles et al. (2014)  
241 attributed this correlation to a change of minerals controlling the solubility of Si when pH  
242 increases: kaolinite at the lowest pH and more soluble aluminosilicate minerals such as feldspar  
243 or smectite at higher pH. Such a hypothesis is supported by our XRD data because kaolinite

244 seems to be the major clay minerals in the Coastal Zone; however, those soils are not totally  
245 depleted of feldspar, and amphibolite and other clay minerals are present. Accordingly, soils  
246 located in most weathered zones from Karnataka are not totally depleted of weatherable Si  
247 minerals (aluminosilicates) that can be potential sources of dissolved Si (DSi). Because those  
248 highly weathered soils are also enriched in quartz, it is likely that the low PAS may be  
249 attributable to the low proportion of weatherable minerals. In addition, if PAS indicators mimic  
250 the amount of dissolved Si from the soil mineral, values may not necessarily increase with pH  
251 because the dissolution rates of aluminosilicate minerals follow a V-shaped pattern with a  
252 minimum at pH values of approximately 7-8 (Frayssé et al., 2009), contradicting our data, which  
253 show a linear increase or a bell curve, specifically for Si<sub>AA</sub> (Fig. 2). The pH increase with PAS  
254 indicators may otherwise be explained by the kinetics of silica mineral dissolution. Indeed, rates  
255 of quartz and phytolith dissolution are known to increase regularly from pH 4 to pH 9 (Frayssé  
256 et al., 2009; Dove, 2006). Here, an increase in PAS indicators is observed up to pH values of  
257 approximately 7, as it should be observed if silica particles (quartz and phytoliths) are  
258 controlling PAS. However, dissolution of quartz is a slow process, and we can assume that the  
259 contribution of quartz to explaining the PAS indicators is limited below pH 7.5. It is well  
260 documented that soil organic carbon (OC) and phytolith content can be well correlated in natural  
261 ecosystems (Alexandre et al., 1997, 2011), but we did not analyze the phytolith composition of  
262 the soils. We found no significant correlation between OC and PAS indicators (Fig. 4). Hence,  
263 if we postulate that soil OC is a proxy for phytoliths, we can suggest that Si<sub>CC</sub> and Si<sub>AA</sub> indicators  
264 were not significantly controlled by phytolith dissolution. Based on the solubility and  
265 dissolution properties of phytoliths (Frayssé et al., 2009), it is unlikely that the protocols that  
266 we used (non alkaline solutions for 16h) would be favorable to a significant dissolution of  
267 phytoliths. Therefore, new protocols should be tested to evaluate the role of the phytolith pool  
268 as controlling PAS.

269

270 PAS controlled by desorption

271

272 Alternatively, PAS indicators are controlled by the adsorption of Si on the surfaces of  
273 soil material. Adsorption is, however, a complex mechanism (Manceau et al., 2002) that  
274 includes physisorption, chemisorption, organo-mineral complexation, and complexation to  
275 bacteria. Although the adsorption of Si on organics and bacteria in soils has not yet been  
276 demonstrated, the adsorbed Si on minerals seems to follow a double layer structure with an  
277 inner-sphere complexation (chemisorption) and an outer-sphere complexation (physisorption)

278 (Hiemstra et al., 2007). The physisorbed molecules are retained by electrostatic interactions and  
279 correspond to the exchangeable fraction also measured by the CEC. The chemisorbed fraction  
280 is linked to the surface by sharing one or several ligands (like O) of the molecule and the sorbent.  
281 To explore whether the PAS indicators are extracting Si that is adsorbed from DSi originating  
282 from the dissolution of soil particles, the correlation between PAS indicators and chemistry can  
283 be helpful. Indeed,  $Si_{AA}$  positively correlated with  $Al_2O_3$ ,  $Fe_2O_3$ ,  $MgO$  and  $MnO$ , which  
284 indicates that this extractant assesses the fraction of Si adsorbed on the surface of  
285 oxides/oxihydroxides of Fe and Al (Hiemstra et al., 2007) as well as clays (Georgadis et al.,  
286 2013; Nguyen et al., 2017) or other Mg-bearing silicate minerals such as amphibole.

287  $Si_{CC}$  is generally lower than  $Si_{AA}$  which suggests that the calcium chloride extractant  
288 gives preferential access to the physisorbed Si, while the acetic acid extractant gives access to  
289 physisorbed and chemisorbed Si. The solvent capacity of the acetic acid extractant can be  
290 explained by the following reaction:



293  
294 The release of protons gives its acidic character, which explains why the acetic acid  
295 extractant has a more powerful extracting capacity than the  $CaCl_2$  extractant. If the extractant  
296 solutions are able to dissolve the Si that is chemisorbed on the soil mineral surfaces, a positive  
297 correlation with increasing pH similar to the correlation observed in the experiment of Si  
298 adsorption as a function of pH is expected. Our data show that the correlation of pH with  $Si_{AA}$   
299 gives a much better match than the correlation with  $Si_{CC}$  (Fig. 2). Accordingly, the acetic acid  
300 procedure is a better approach than the calcium chloride procedure to estimate the Si pool that  
301 is chemically sorbed.

302 The increased adsorption of Si with pH increasing shows quite similar maximum values  
303 according to the material involved: approximately 9 for clay minerals (Nguyen et al., 2017);  
304 between 9 and 10 in an acid brown forest soil from Wales (Obihara and Russell, 1972), between  
305 9 and 10 on goethite and gibbsite (Hingston et al., 1972) and between 7 and 10 on Al and Fe  
306 sesquioxides (Beckwith and Reeve, 1963). Here, a maximum around pH 8 may be seen using  
307 our polynomial regression model for  $Si_{AA}$  data in fairly good agreement with the Si adsorption  
308 experiments (Fig. 2). Indeed, the shape of the polynomial curve found for  $Si_{AA}$  vs. pH (Fig. 2)  
309 looks very similar to the curve of the percentage of Si adsorption on goethite and siderite given  
310 by Philippini et al. (2006). Si adsorption with pH up to 9 can be explained by the interaction of  
311 Si with the surface and not to a change of Si speciation (Hiemstra et al., 2007). The interaction

312 of Si with the protonated surface implies a release of protons after adsorption. The Si at the  
313 surface forms species such as Fe oxide-monosilicate bi-dentate complexes on iron oxides  
314 (Hiemstra et al., 2007). Therefore, the lower the pH (the higher the presence of protons) is, the  
315 higher the chance to desorb Si.

316

### 317 Application in Si fertilization

318

319 The PAS indicators used in the cultivated surface soils in Karnataka are therefore controlled  
320 both by the solubility of soil silicate minerals and sorption mechanisms. Narayanaswamy and  
321 Prakash (2009) used pot experiments with south Indian soils fertilized with silicates to estimate  
322 the critical level of PAS based on the procedure of Cate and Nelson (1971). Briefly, in a plot of  
323 a laboratory test (here PAS indicators in abscissa) vs yield (ordinate), critical level is the vertical  
324 line that divide the population into 2 categories (high probability of response and low  
325 probability of response). Below the critical level, Si is considered deficient and will probably  
326 limit crop yield. Narayanaswamy and Prakash (2009) also found that the critical levels using  
327  $Si_{AA}$  and  $Si_{CC}$  were 54 and 43 mg kg<sup>-1</sup>, respectively. Applying those critical levels to our data  
328 shows that approximately 88 and 38 percent of the total soil samples were categorized as  
329 depleted of PAS as extracted by calcium chloride and acetic acid, respectively. A closer look at  
330 the coastal and hilly zones, where alfisols are dominant, shows that nearly 90 and 82 percent of  
331 the soils are depleted of PAS as extracted by calcium chloride and acetic acid, respectively. To  
332 improve Si uptake and yield in acidic soils, several modalities of fertilization may be  
333 recommended: liming, which may lead to enhanced PAS by increasing pH; Si fertilization; or  
334 both modalities. Because PAS indicators increase with pH, liming of highly acidic soils may be  
335 enough to enhance the delivery of Si in the soil solutions, assuming that PAS is controlled by  
336 adsorption/desorption processes. However, our data show that extremely acidic soils are also  
337 those that are the most enriched in quartz and kaolinite, which are the least favorable Si source  
338 for DSi. Hence, the addition of lime alone will not be favorable for increasing PAS, contrary to  
339 what may be concluded from the graphs in Fig. 2 alone if the mineralogical composition is not  
340 given. Another practical application of this study is that a simple measure of pH can be used as  
341 a proxy for PAS using the equations presented in Fig. 2, for pH values up to 7.5.

342

### 343 Conclusion

344

345 Our results show that soils that are low in PAS indicators are the acidic soils that are common  
346 along the coastal zone, where rainfall is the highest. The acidic soils are characterized by higher  
347 contents of quartz, Zr and Hf, all parameters indicating a higher degree of weathering. The  
348 depletion of PAS indicators is also in good agreement with the predominance of kaolinite, which  
349 characterizes a higher degree of desilication. The positive correlation of pH with PAS indicators  
350 is also compatible with the adsorption of Si, which depends ultimately on the amount of Si  
351 source available in the soil. We suggest that pH measurements may be useful as a proxy for  
352 PAS.

353

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357

358

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484 permission); the white circles are the 40 subsamples out of 200 used for chemical and  
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486

487 Figure 2. Correlations between pH and plant available silicon (PAS) indicators ( $Si_{AA}$  and  $Si_{CC}$ )  
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501 Table 1. Correlation matrix using PCA (Pearson (n); values in bold are different from 0 with a  
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505

506 Table 2 Anova using Fischer (LSD)'s test showing the variability between soil categories for  
507 the following parameters: a) pH, b) CEC in  $cmol\ (p+)\ kg^{-1}$  and the PAS indicators c)  $Si_{CC}$  in  
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509 vertisol = 41, inceptisol = 23, aridisol = 14, ultisol = 9 and entisol = 5; different letters indicate  
510 that the means are statistically different at the  $P\leq 0.05$  level.

511

512 Table 3. Mineralogical (XRD) and chemical composition of the 40 selected soils from the 7  
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