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

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Abstract

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

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

Results. PCA of the 200 samples showed that PAS indicators and pH were positively correlated. Si_{AA} was also positively correlated with electric conductivity (EC), CEC, and the silt fraction and negatively correlated with the sand fraction. A separation of the data arbitrarily made at pH 7.5 showed that below 7.5, the correlation between PAS indicators and pH was better than considering the whole 200 samples. The distribution of Si_{AA} with pH matched the curve of adsorbed Si given in the literature. Soils characterized by low pH and high contents of sand, SiO_2 , Zr and Hf, showed a higher degree of weathering. They were preferentially located along the coast, where the rainfall is the most abundant. The depletion of PAS indicators was also in good agreement with the predominance of kaolinite instead of smectite, which characterizes a higher degree of desilication.

Conclusion. We demonstrated that the correlation between pH and PAS indicators is explained by natural Si depletion (weathering intensity) and the effect of Si adsorption. We suggest that at pH values up to 7.5, pH can be used as a proxy for PAS in similar types of pedo-climatic 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 H_4SiO_4 . At elevated pH, H_4SiO_4 dissociates into
49 anions to form H_3SiO_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 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 H_2O , 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 CaCl₂-extractable Si (Si_{CC}) 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 km² 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 CaCl₂ (Si_{CC}, 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_{AA}, 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, Si_{CC} , Si_{AA} , and CEC ranged from 4.9 to 9.5,
165 0.02 to 1.07 dSm^{-1} , 1.4-82.9 $mg\ kg^{-1}$, 6.7 to 370.2 $mg\ kg^{-1}$ and 9.2 to 115.2 $cmol\ (p+)\ kg^{-1}$,
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 Si_{CC} values were lower than the Si_{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. Si_{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 Si_{AA})
174 or remain stable (for Si_{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_{CC} (except Aridisol)
180 and from all soils for Si_{AA} (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 SiO₂
192 (55-88 %), Al₂O₃ (5-18 %), Fe₂O₃ (2-16 %), CaO (0.1-9 %), K₂O (0.1-4.5 %). PCA analysis
193 (Fig. 4a) showed that both PAS indicators were significantly positively correlated with Al₂O₃.
194 However, Si_{AA} was also significantly positively correlated with pH, Fe₂O₃, MgO, MnO and
195 negatively correlated with SiO₂, Hf and Zr. Using our 40 subsamples, the correlation between
196 Si_{CC} 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, Al₂O₃, Fe₂O₃, MgO, TiO₂, MnO, P₂O₅ and CaO to the left and are opposed to a group
201 constituted by SiO₂, K₂O, Na₂O Zr and Hf to the right. Organic carbon was only positively
202 correlated with P₂O₅.

203

204 **Discussion**

205

206 PAS indicators and the soil weathering state

207

208 The range of Si_{CC} 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_{AA} (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_{CC} and Si_{AA} 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 Al₂O₃, Fe₂O₃, 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:



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 CaCl₂ 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⁻¹, 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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501 Table 1. Correlation matrix using PCA (Pearson (n); values in bold are different from 0 with a
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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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