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, SiO₂, 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.

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

Introduction

Silicon, the second most common element on the earth's surface, is also present in significant amounts in the shoots of the main crops produced worldwide (Guntzer et al., 2012). It is well established that the accumulation of Si in plants as phytoliths follows the same pathways as for the majority of the nutrients: root uptake from the soil solution (Liang et al., 2015). The speciation of dissolved Si (DSi) is quite simple because there is almost exclusively only one species below pH 9: the monomeric silicic acid H_4SiO_4 . At elevated pH, H_4SiO_4 dissociates into anions to form H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{2-}$ (Philippini et al., 2006). The source of DSi is ultimately the soil-forming mineral, which can include quartz, aluminosilicates, phyllosilicates, clay minerals and amorphous silica (Cornelis et al., 2011). However, the soil-forming minerals are largely resistant to weathering (Berner and Berner, 1996). As a consequence, with increasing time, the soil becomes depleted of Si, as evidenced by the "desilication" process (Buol et al., 1989), which shows with increasing weathering intensity the formation of 2/1 clay mineral, 1/1 clay mineral and ultimately only Fe-Al oxyhydroxides (Cornelis et al., 2016). Evidence of Si leaching by weathering is also documented along soil profiles using mass balance calculations, which show increases in Si loss with soil age (White, 2005; Sommer et al., 2006). Using water analysis, various approaches had similar conclusions. A comparison of DSi concentrations of the continents showed that the highest concentration of DSi occurs in African streams (12.6 mg L^{-1} on average), where hot climatic conditions prevail (Dürr et al., 2011). Another example of Si loss during weathering is found in Hawaiian volcanic soil solutions (Derry et al., 2005), where DSi decreases when the age of the soil increases. The content of minerals favorable for weathering for a given soil is therefore a stronger constraint for explaining the accumulation of Si in plants (Henriet et al., 2008).

Despite the abundant literature showing that Si is beneficial for crops (Liang et al., 2015), the bioavailability of Si remains a challenging topic (Haynes, 2014). To quantify the plant-available Si (PAS), various empirical indicators have been proposed (Nayar et al., 1977; Barbosa-Filho et al., 2001; Korndorfer et al., 2001; Narayanaswamy and Prakash, 2010; Yanai et al., 2016; Crusciol et al., 2017). These indicators are based on the use of chemical extractants of DSi from soils that give good correlations with plant Si content or yield. PAS indicators such as H_2O , CaCl_2 , acetic acid and acetate may also be useful to identify the soil depleted of PAS and eventually to justify the application of Si fertilizers (Berthelsen et al., 1999). However, the

use of these PAS indicators is still poorly evaluated because of the lack of studies documenting the Si pools that are controlling them. Indeed, the correlation between PAS indicators and soil acidity, as measured by pH, has been reported in the literature as an indicator of intensity of weathering: lower pH may be associated with low PAS in highly leached soils (Review in Haynes, 2014 and Liang et al. 2015). For instance, Miles et al. (2014) showed that pH and CaCl₂-extractable Si (Si_{CC}) are correlated in the range of pH 3.3 to pH 7 in the South African sugarcane fields. According to the authors, such a correlation is attributable to a change in mineralogy from a less weatherable pool of Si minerals at low pH to a more weatherable pool of Si minerals at higher pH, following the conclusion of Henriët et al. (2008). However, in Henriët et al. (2008), the pH range does not differ between desilicated soils and less weathered soils. In addition, Miles et al. (2014) did not document the mineral content/Si status of their studied soils, so other hypotheses are possible to explain the correlation between pH and PAS indicators. One hypothesis is that PAS is controlled by adsorbed Si. Indeed, it is well documented that Si adsorption increases with pH in a similar range as in the previously mentioned study by Miles et al. (2014), specifically if Al and Fe oxides are present (Beckwith and Reeve 1963; Kingston et al., 1972, Philippini et al., 2006; Hiemstra et al., 2007). Another hypothesis is that PAS may be controlled by the soil phytolith pool. Phytoliths are residues of Si accumulated in plants during litter decomposition and are composed of amorphous silica particles, which are considered to be among the most soluble pools of Si in soils (Frayssé et al., 2009). Because plant productivity is generally lower at low pH due to poor nutrient content and aluminum toxicity (Zheng, 2010), it is possible that a correlation between pH and PAS could be due to the phytolith content. To decipher the factors that control the PAS and to document whether pH can be used as a proxy for PAS, our approach here was to combine agronomical, physical, mineralogical and chemical properties of cultivated soils that exhibit a large pH gradient. Accordingly, we conducted a study in different rice ecosystems corresponding to acidic, slightly acidic, neutral and alkaline soils with distinct climates in the Karnataka State of South India.

Materials and Methods

The State of Karnataka forms the west central part of Peninsular India. It occupies an area of 1,91,792 km² and is divided into 4 physiographic regions: 1. the Northern Karnataka Plateau at 300-600 masl, on the Deccan Traps; 2. the Central Karnataka Plateau at 450-700 masl; 3. the Southern Karnataka Plateau at 600-900 masl, bordered by the Western Ghats in the west and south; and 4. the Karnataka Coastal Region between the Western Ghats in the East and the

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

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

Approximately 12 – 15 subsamples of 200-300 g were collected from each sampling location using a screw auger and mixed thoroughly to obtain a representative sample. Each representative soil sample was placed in a separate plastic zip-lock cover bag to avoid contamination of the samples. Soil samples were shade dried, powdered and sieved through a 2 mm mesh sieve and stored in plastic container bottles for further use. The samples were analyzed for particle size distribution (pipette method), pH (soil-water suspension of 1/2.5), electrical conductivity (E.C., soil-water suspension of 1/2.5), and cation exchange capacity (CEC, for pH<8.2: distillation method, Page et al., 1982; pH>8.2: flame photometry, Jackson, 1973). The choice of the PAS indicators was based on a critical evaluation of the literature (Sauer et al. 2006; Narayanaswamy and Prakash, 2010; Georgiadis et al., 2013; Haynes, 2014; Miles et al. 2014). We analyzed the Si extracted by 0.01M CaCl₂ (Si_{CC}, Haysom and Chapman, 1975) for the determination of the pool of readily soluble Si and the Si extracted by 0.5 M acetate-acetic acid (Si_{AA}, Korndorfer et al., 2001) for the pool of adsorbed Si. These two PAS

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

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

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

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

Results

Characterization of the 200 samples

The measurements of the 200 samples are detailed in Supplementary Material. The texture of the soils varied from sandy loam to clay. pH, EC, Si_{CC} , Si_{AA} , and CEC ranged from 4.9 to 9.5, 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} , respectively. The proportions of acidic ($\text{pH} < 6.5$), neutral ($\text{pH} 6.5-7.5$) and alkaline ($\text{pH} > 7.5$) soils were 40, 14 and 46%, respectively. Overall, the Si_{CC} values were lower than the Si_{AA} values (Student's t test < 0.05). PCA of the data (Table 1) showed that PAS indicators and pH were positively correlated. Si_{AA} was also positively correlated with EC, CEC, and the silt fraction and negatively correlated with the sand fraction. A closer analysis of the relation between pH and PAS indicators (Fig. 2) showed that the correlation identified in the PCA may not be a simple linear regression. Indeed, models such as polynomial regressions presented a better fit than a linear regression and showed that the PAS indicators may decrease (for Si_{AA}) or remain stable (for Si_{CC}) where $\text{pH} > 7.5$. 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 with best fits using power regression models. ANOVA of the soil categories showed that the ultisol and alfisol samples had both the lowest pH while the vertisol samples have the highest CEC values (Table 2). Ultisol and alfisol present the lowest PAS indicators but they are not significantly different from all soils for SiCC (except Aridisol) and from all soils for SiAA (except Entisol and Vertisol). Plotting the data into the Karnataka map showed a general trend of lower pH and PAS indicators towards the west coast, which is represented by the hilly and coastal zones (Fig. 3).

Mineralogy and geochemistry of the 40 samples

Quartz, feldspars, amphibole, goethite, gibbsite, Ti oxides and phyllosilicates were the main minerals identified in most of the samples (Table 3). Gibbsite was more frequent in the coastal zone. Calcite has been detected in 4 samples (number 2, 54, 97 and 157). The clay minerals identified included smectite, chlorite, vermiculite, illite, kaolinite, and various interlayers of illite-smectite and chlorite-vermiculite. Smectite has not been identified in the hilly and coastal zones, where kaolinite seemed to be the dominant clay. The chemistry was dominated by SiO₂ (55-88 %), Al₂O₃ (5-18 %), Fe₂O₃ (2-16 %), CaO (0.1-9 %), K₂O (0.1-4.5 %). PCA analysis (Fig. 4a) showed that both PAS indicators were significantly positively correlated with Al₂O₃. However, Si_{AA} was also significantly positively correlated with pH, Fe₂O₃, MgO, MnO and negatively correlated with SiO₂, Hf and Zr. Using our 40 subsamples, the correlation between Si_{CC} and pH became non significant (R= 0.3, figure 4a). However if we select only the samples where pH is < 7.5, we obtained a significant correlation (R= 0.4, n = 24, P= 0.05), as shown in figure 2. Projections of the two most predominant variables (F1 and F2) in the principal component space (Fig. 4b) showed that both PAS indicators are grouped at a pole constituted by pH, Al₂O₃, Fe₂O₃, MgO, TiO₂, MnO, P₂O₅ and CaO to the left and are opposed to a group constituted by SiO₂, K₂O, Na₂O Zr and Hf to the right. Organic carbon was only positively correlated with P₂O₅.

Discussion

PAS indicators and the soil weathering state

The range of Si_{CC} falls in the same range as in previous studies, particularly for acidic rice field soils in Karnataka State (Narayanaswamy and Prakash, 2009) and for sugarcane fields in

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

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

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

PAS controlled by dissolution

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

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

PAS controlled by desorption

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

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

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

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

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

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

Application in Si fertilization

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

Conclusion

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

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Figure 1. Location of the 200 studied samples in the (a) rainfall map and (b) Agroclimatic Zones (ACZ) of the Karnataka State (Karnataka State Remote Sensing Applications Center, used by permission); the white circles are the 40 subsamples out of 200 used for chemical and mineralogical studies.

Figure 2. Correlations between pH and plant available silicon (PAS) indicators (Si_{AA} and Si_{CC}) for the 200 studied samples.

Figure 3. Variation of PAS indicators a) Si_{AA} in $mg\ kg^{-1}$, b) Si_{CC} in $mg\ kg^{-1}$ and c) pH, categorized as low, medium and high in the studied area.

Figure 4. PCA of a subsample of 40 soils showing the correlation between pH, PAS indicators (Si_{AA} in $mg\ kg^{-1}$ and Si_{CC} in $mg\ kg^{-1}$) and chemical elements (in w.t.% except Hf and Zr in $mg\ kg^{-1}$): a) correlation matrix (Pearson (n); values in bold are different from 0 with a significance level $\alpha=0.05$); b) projection of the variables in factor 1 and 2.

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Table 1. Correlation matrix using PCA (Pearson (n); values in bold are different from 0 with a significance level $\alpha = 0.05$) for pH, PAS indicators (Si_{AA} in $mg\ kg^{-1}$ and Si_{CC} in $mg\ kg^{-1}$) and other parameters (E.C. : electric conductivity in dSm^{-1} ; CEC in $cmol\ (p+)\ kg^{-1}$; sand, silt and clay fractions in w.t. %) for the 200 studied samples.

Table 2 Anova using Fischer (LSD)'s test showing the variability between soil categories for the following parameters: a) pH, b) CEC in $cmol\ (p+)\ kg^{-1}$ and the PAS indicators c) Si_{CC} in $mg\ kg^{-1}$ and d) Si_{AA} in $mg\ kg^{-1}$; number of samples for each soil category is: alfisol = 106, vertisol = 41, inceptisol = 23, aridisol = 14, ultisol = 9 and entisol = 5; different letters indicate that the means are statistically different at the $P\leq 0.05$ level.

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