

Physico-Chemical Variability of Acid Sulfate Soils at Different Locations along the Kelantan Plains, Peninsular Malaysia

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ABSTRACT

Mineralogy and physico-chemical properties of pyritic soils from three sites along the coastal plains of Kelantan, Peninsular Malaysia were studied. The aim of the study was to identify the variability and principal components of soil properties in this area. Soil sampling was conducted at three sites, stretching from North (Bachok) to south (Pasir Puteh) of the plains. Soil samples were taken from different depths at each site based on the presence of pyritic evidence. Soil physico-chemical properties were determined using standard laboratory methods while X-ray diffraction and SEM-EDX were carried out to determine the shape and stages of pyrite disintegration. Soils with sulfidic materials were found to be sporadically distributed throughout the plains, exhibiting different properties and distribution with depth. The soils with a sulfidic materials layer close to the soil surface had pH values below 3.5. Based on principal component analysis (PCA), the variables of all sites could be classified into three components, namely, soil pH, soil nutrients and organic matter content, which accounted for 83% of the site variability. The different dominant controlling factors in soil variables among the studied sites suggest that acid sulfate soils occurring in the area may have embraced many distinctive features even if they occur close to each other. This is a result of the multiple complex reactions after the sea level rose 3-5 m above the present level many thousands of years ago. Generally, the productivity of the soils in the area is low due to the occurrence of excessive acidity and the presence of toxic amounts of Al in the soils.

Keyword: Acid sulfate soils, principal component analysis, pyrite, acidity, soil productivity.

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INTRODUCTION

In most years, part of the Kelantan Plains (Figure 1) in the east coast state of Peninsular Malaysia is submerged during the monsoon season of November to January. To reduce the effects of flooding in this area, the government of Malaysia established the Kemasin-Semerak Integrated Agricultural Development Project (IADP) in 1984. The land in the flood-affected area was drained and irrigation canals were constructed; this was to make way for agriculture, especially for rice cultivation.

The land along the coastal plains in Kelantan was inundated by seawater some time during the Holocene (Enio *et al.* 2011). It was reported that the sea level in these areas was 3-5 m above the present (Tjia *et al.* 1977; Pons *et al.* 1982) about 6,000 years BP (Haile 1970). The occurrence of sandy beach ridges along the coastal plains in Peninsular Malaysia (Roslan *et al.* 2010) and the presence of notch-like features above the mean high water tide on cliffs at Langkawi Islands, Malaysia (Hodgkin 1970), have been used as evidence for the sea level rise during the Holocene. It was during this period of sea level rise that pyrite (FeS₂) was mineralised in the alluvial sediments of the Kelantan Plains (Enio *et al.* 2011). It was, therefore, assumed that the shoreline was a few km away from the present. As the sea prograded, a series of sandy ridges was formed (Roslan *et al.* 2010) and peaty materials accumulated on the top of the pyrite-bearing sediments, forming the present peat soils in the plains.

Some years after development, the paddy fields in the area were mostly degraded due to the occurrence of extreme acidity resulting from the oxidation of pyrite present in the soils (Shazana *et al.* 2013). Oxidation of pyrite had resulted in the formation of jarosite [KFe₃(SO₄)₂(OH)₆], appearing as yellowish mottles in the soil profile (Shamshudin and Auxtero 1991; Shamshuddin *et al.* 1995; Shamshuddin *et al.* 2004a). This pyrite was formed when the area was inundated with seawater during the Holocene (Roslan *et al.* 2010). The paddy fields are on acid sulfate soils that are not only low in pH (< 3.5), but also contain toxic amounts of Al and/or Fe (Shamshuddin 2006). Acid sulfate soils are chemically degraded and therefore unfit for agricultural production unless they are properly alleviated with appropriate amendments.

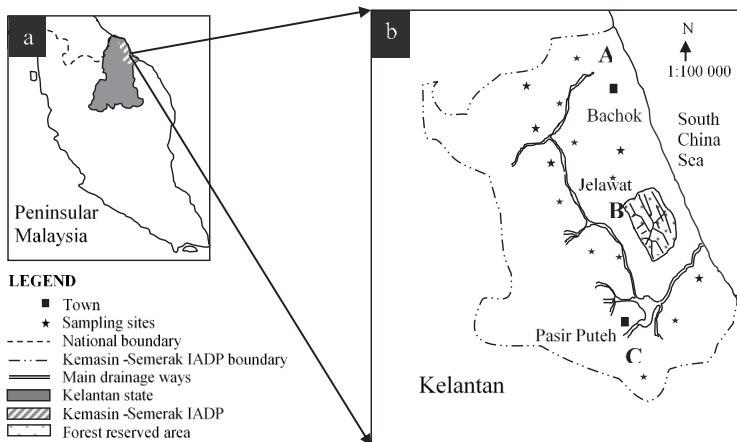


Figure 1. (a) Kelantan Plains and (b) Kemasin-Semerak IADP

MATERIALS AND METHODS

Study Area

The area investigated is situated within the Kemasin-Semerak Integrated Agricultural Development Project (IADP), Kelantan, Malaysia (Figure 1b). The total area of this development project is about 200 ha. There are three sites with pyritic soil layer denoted as A (Bachok), B (Jelawat) and C (Tok Bali, Pasir Puteh). These three sites were chosen based on evidence of the presence of pyrite after a series of preliminary samplings conducted to decide the sites for this study. Kemasin-Semerak IADP stretches from Bachok, the northern part of the Kelantan Plains to Pasir Puteh at the south. Most of the area has been drained since 1984 for agricultural development but then an area in the middle of the IADP was left undisturbed for future development; this area (denoted as site B), situated in Jelawat-Rusa Irrigation Scheme, is occupied by acid sulfate soils overlain by peaty materials. This area is now covered by local plant species called gelam (*Melulueca leucadendron*) and nipah palm (*Nipa frutescens*). These plant species are known to survive well even under very acidic conditions. Meanwhile site A (Bachok), which has sandy topsoils, is under grass. At site C (Tok Bali), pyrite presence on the surface was easiest to identify during the preliminary surveys.

Field Observations and Soil Sampling

Generally, pyrite was found to occur at varying depths (close to the surface, below 2 m or in between the two). Additionally, the soils with pyrite at the study sites showed different degrees of association with peaty materials (organic matter). During preliminary sampling, the soil profiles were dug and were described at each site. At several locations in Jelawat-Rusa Irrigation Scheme and Bachok, the soil samples were taken only up to 75cm depths due to a high water table. Based on the presence of pyritic or jarosite under the soil profile, three sites were

specially marked for detailed study and designated as A, B and C, based on the depth of the pyritic layer (Figure 1b).

After finalising these sites and the spots for sampling, an auger was used to take the soil samples from each soil horizon. The samples were then placed and sealed in plastic bags before transferring to the laboratory. The time for this process did not exceed 24 h to make sure minimal oxidation occurred in the sample. Upon reaching the laboratory, these soil samples were quickly dried using the vacuum freeze dryer as a measure to avoid oxidation of pyrite. After freeze-drying, the samples were then crushed and sieved to mesh size.

Laboratory Analyses

The pH of the soil was determined in water (1:2.5), while electrical conductivity (EC) was determined using saturated paste. Cation exchange capacity (CEC) was determined using 1 M NH_4OAc buffered at pH 7 (Soil Survey Laboratory Staff 1992). The basic cations (Ca, Mg, K and Na) present in the NH_4OAc extract were measured by atomic absorption spectrophotometer (AAS). Exchangeable Al was extracted by 1 M KCl (1:5) and the Al in the extract was determined by AAS. Total carbon (TC) was analysed by the dry combustion method using CNS analyser. Total N was determined by the Kjeldahl method (Bremner and Mulvaney 1982) and available P was determined by the method of Bray and Kurtz (1945). Soil texture was analysed by sedimentation (Soil Survey Laboratory Staff 1992) and the clay fraction was used for mineralogical analysis. The clay was treated with Mg, Mg-glycol, K and K-heated at 550°C. The minerals in the clay fraction were identified by XRD analysis using Philips PW3440/60 X'Pert Pro. The samples containing sulfidic materials were studied under scanning electron microscope (SEM).

Statistical Analyses

All statistical analyses were performed using the Microsoft XLStat 2003. Arithmetic mean values and statistically significant differences between all study sites were determined by analysis of variance. For clarification of the study sites, principal component analyses (PCA) was performed. Correlation between soil properties was assessed using the Spearman rank correlation coefficient. All statistical considerations were based on 0.05 significant levels.

RESULTS AND DISCUSSION

Pyritisation of the Kelantan Plains

The sediments at location A were found to have a pyritic layer deep down the soil profiles. This is a plausible explanation for the pyritisation process. In the northern part of the study area (Figure 1), the areas bordering the shoreline were probably at a higher level. It was assumed that the seawater was able to seep through the porous riverine alluvial materials a few metres below the surface. Iron was present in high amounts in the sediments of the area (Table 1). We believe that

organic matter required by the microbes was also present in sufficient amounts. Under such conditions, pyrite was mineralised continuously.

At location B, swamps were formed after the sea was prograded. The water in these swamps was probably brackish due to intrusion of seawater. In this area, Gelam and nipah palms had provided sufficient organic matter for the reduction process to proceed. Pyrite was consequently mineralised in the sediments. The area was waterlogged and therefore organic matter from the plant species growing in the swamps had accumulated, forming an organic layer above the sediments. Hence, soils in these areas now contain pyrite overlain by peaty materials. The area at location C (in the southern part) was flat and located close to the

TABLE 1
Soil chemical properties

Sites/ Horizons	Depth (cm)	pH	EC (dS/m)	Al	CEC (cmol _c /kg)	Ext. Fe	Avail. P (mg/kg)	Total N	Total C	Sand (%)	Silt	Clay
SITE A												
Sulfic Endoaquept												
A	0-15	5.5	0.14	7.9	10.0	2.3	17.6	0.3	3.3	72.3	12.2	15.5
B	15-55	3.6	0.12	6.0	9.0	1.5	19.1	0.2	1.4	61.4	36.3	2.3
Bw	55-150	3.9	0.10	15.7	9.5	11.3	14.2	0.1	1.3	9.5	52.1	38.4
Cg	>150	4.2	0.08	10.2	12.4	11.9	75.1	0.2	4.2	1.0	57.4	42.1
SITE B												
Typic Sulphemists												
Oe	0-20	3.2	0.12	16.2	14.2	10.8	10.0	0.2	4.4	n.a	n.a	n.a
A	20-30	3.1	0.17	15.5	11.7	10.4	9.5	0.1	2.0	1.6	51.2	47.3
Bwg	30-45	3.1	0.16	13.8	9.3	8.1	10.1	0.8	0.9	4.9	58.7	36.4
Cg	45-60	3.3	0.18	15.2	17.6	9.1	10.3	0.4	4.6	n.a	n.a	n.a
SITE C												
Typic Sulfaquept												
Ap	0-10	4.0	0.34	8.1	20.4	10.2	14.4	0.4	9.3	3.7	20.5	75.8
Bj	10-35	3.5	0.42	6.2	14.3	10.1	14.6	0.2	5.3	4.0	21.7	74.3
Bw	35-45	3.1	0.14	15.7	20.1	10.5	17.4	0.5	13.3	0.7	25.8	73.5
Cg	45-75	2.8	0.42	32.1	10.7	10.3	17.0	0.3	15.1	n.a	n.a	n.a

present coastline, which is always flooded during the rainy season. Gelam and nipah palms were also found in this area. Seawater must have intruded this area a few thousand years ago, during which pyrite was mineralised. We detected straw-yellow jarosite (which is the product of pyrite oxidation) in the topsoil.

The area at location C (in the southern part) was flat and located close to the present coastline, which is always flooded during the rainy season. Gelam and nipah palms were also found in this area. Seawater must have intruded this area a few thousand years ago, during which pyrite was mineralised. We detected straw-yellow jarosite (which is the product of pyrite oxidation) in the topsoil.

Mineralogical Properties of Soils

The mineralogy of the clay fraction of the soils under study was determined. Based on the XRD diffractograms obtained (Figure 2), the Mg-treated sample gave XRD reflections at 9.90, 7.10, 4.98, 4.84, 3.57 and 3.33 Å, which show the presence of mica (9.90, 4.98 and 3.33 Å), kaolinite (7.10 and 3.57 Å) and gibbsite (4.84 Å). Smectite was present as shown by the Mg-saturated and glycolated samples which gave reflection at 15.60 Å. When the K-saturated sample was subjected to X-ray, a peak at about 12 Å appeared, and when this sample was heated, 14-15 Å peak did not appear on the diffractogram. This gives an indication of the absence of chlorite in the soils of the Kelantan Plains. We strongly believe that the smectite occurring in the soils came from the weathering of mica. Pyrite or jarosite was not detected because during the process of clay separation, these minerals undergo a transformation process.

The presence of pyrite in the soils was proven by scanning electron microscopy using undisturbed/unoxidised samples. SEM studies of the samples from the sulfidic layers at each study site indicated the presence of pyrite in various forms, basically as a result of oxidation (Figure 3). Some of the samples showed

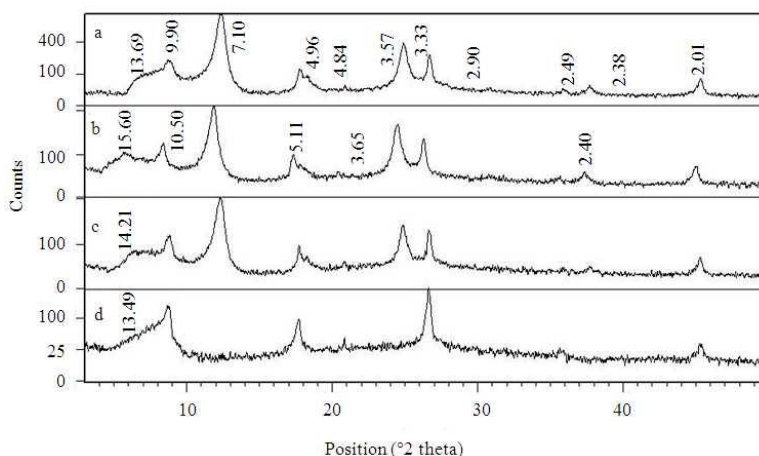


Figure 2. XRD diffractograms of the treated clay fraction of the soil: (a) Mg-sat; (b) Mg-glycolated; (c) K-saturated; (d) K-heated

pyrite undergoing oxidation while some showed its original form beginning to disintegrate. The SEM-EDX images first showed pyrite crystals in its globular form which was sampled from site A, but when the soil was slightly exposed to oxidation, the pyrite globule disintegrated and we could see the individual pyrite crystals in its cubical shape. This image of pyrite disintegration was captured from site B while in site C, we found that as the pyrite crystals underwent extensive oxidation, their cubical shape had begun to form edgeless crystals. This is consistent with the fact that this pyritic layer lies on the surface where the ploughed topsoil exposes the sulfidic materials to the atmosphere. In the soils, pyrite oxidises to form jarosite and during the process, acidity is produced and Al is released into the soil system. This ultimately affects the productivity of the soils. When jarosite is observed in a soil, soil pH is almost always sure to be low (<3.5) (Shamshuddin and Auxtero 1991; Shamshuddin *et al.* 1995; Shamshudin *et al.* 2004b).

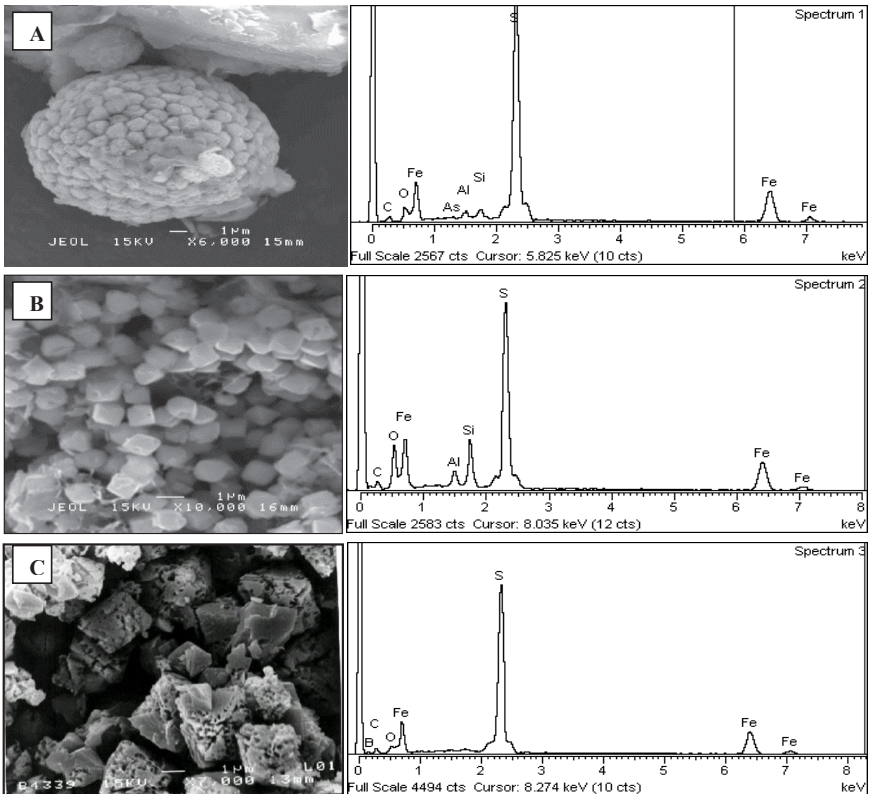


Figure 3. SEM-EDX images of pyrite crystals taken from Site A (Bachok), Site B (Jelawat-Rusa Irrigation Scheme) and Site C (Tok Bali), respectively

Physico-chemical Properties of the Soils

Detailed chemical properties of the soils were studied at selected points (Table 1) and the minerals present in the clay fraction of the soils were identified (Figure 2). At these locations, pyrite was found to occur at different depths in the soil profiles. In general, the soils were low in pH, ranging from 3.2 to 4.9; however, exchangeable Al was high (>5 cmol_c/kg). This means that acidity is high in the soils, which could affect crop growth. The CEC was low, which is a reflection of kaolinitic mineralogy.

The distribution of the sulfidic materials with depth in the soil profiles located within the Kemasin-Semerak IADP is shown in Figure 4. Some of the locations where sulfidic materials were present in the sediments are marked as bold stars in Figure 1b. The sulfidic materials were found to occur at three conspicuous depths, namely below 2 m, between 0 to 50 cm and in the topsoil. The first type was found mostly at location A (the northern part of the study area), while the second type was found at location B (the peaty area in the middle part). The third type was found at location C (the southern part of the study area) (Table 1; Figure 1b).

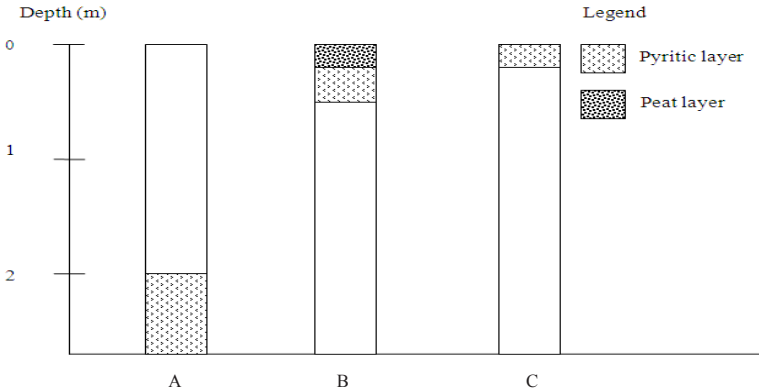


Figure 4. Occurrence of pyrite in soil at Sites A, B and C

We had problems locating the depth of the sulfidic materials in the soils of the northern part of the study area. In this area, the pyritic layer was too deep to be determined by a soil auger. However, at the time of the soil survey, the drainage canals were undergoing maintenance. This gave us the opportunity to study the sediments from the subsoil which were removed by heavy equipment. These samples were left to dry to check if they contained pyrite. It was observed that yellowish mottles appeared in the samples within days and the soil pH was found to be about 3. These yellowish mottles are actually jarosite formed from the oxidation of pyrite as observed by Shamshuddin and Auxtero (1991) and Shamshuddin *et al.* (2013). Note that the drainage canals were more than 2 m deep.

The soils in the middle part of the study area were mostly overlain by peaty materials. In this area, samples were taken based on depth using a soil auger. Within 50 cm depth, the pH of the soils was mostly below 3.5, which is consistent with the pH of Sulphemists (acid sulfate soils) as defined by soil taxonomy (Soil Survey Laboratory Staff 2010). The air-dried samples indicated the presence of yellowish jarosite, proving yet again that the soils were acid sulfate soils.

The soils in the southern part of study area were found to be mostly acidic, especially at depth, and yellowish jarosite mottles appeared within the topsoil. The soils can be classified as Sulfaquepts (Soil Survey Laboratory Staff 2010) as pyrite/jarosite occurred within the top 50 cm of the soils. The paddy fields in this area were abandoned because the soils were too acidic for crop growth. Purun (*Eleocharis dulcis*), a plant species which is Al-tolerant was found to be growing in the abandoned paddy fields.

Characterisation of Sites

Principal component analysis (PCA) was performed using the data from the three sampling sites together to determine the major principal components that are associated with soil properties. The results of the PCA for the soil variables in sites A, B and C in this study are shown in Table 2. From the results of the initial eigen values, the first three principal components were considered, which accounted for 86% of the total variance. The first principal component (PC1) accounted for 46% of the total variance, and correlated highly with soil pH, exchangeable Al, total N and total C ($r > 0.8$) (Table 3), characterising soil acidity and organic matter content for each site. PC2 accounted for 25% of the total variance with a strong correlation with the extractable Fe, Ca and Mg ($r > 0.8$), characterising the nutrient content of the soils. PC3 accounted for 12% of the total variance, and was loaded solely by the soil K ($r > 0.8$), characterising the nutrient content.

TABLE 2
Variance of soil properties explained by various components of the PCA

	PC1	PC2	PC3
Eigenvalue	5.06	2.76	1.34
Variability (%)	46.01	25.09	12.14
Cumulative %	46.01	71.10	83.24

TABLE 3
Correlation matrix of the PCA for soil chemical properties

	PC1	PC2	PC3
pH	-0.93	-0.06	-0.19
EC (dS/m)	0.93	0.14	-0.25
Exc.Al	0.92	-0.02	-0.16
Extract Fe	0.35	0.81	-0.06
P	-0.29	0.48	-0.16
CEC	0.81	-0.41	0.33
K	-0.12	-0.21	0.90
Ca	0.15	0.86	0.32
Mg	0.46	0.81	0.14
Total N	0.72	-0.37	-0.30
Total C	0.91	-0.26	0.13

The numbers in bold indicate definite assignment to respective components. Figure 5 shows the correlation circle of soil properties in all sites. From the correlation circle, we know that there is significant negative correlation between soil pH and exchangeable Al ($r=-0.85$), while total N is positively correlated with CEC ($r=0.82$). Other variables show indirect correlation (low r), but still contribute to site variability. The high amount of exchangeable Al greatly influences the low soil pH at all sites. The peat layer which is a source of high N content contributes to the CEC. Soil pH and exchangeable Al are two of the most important contributing factors for all the sites studied.

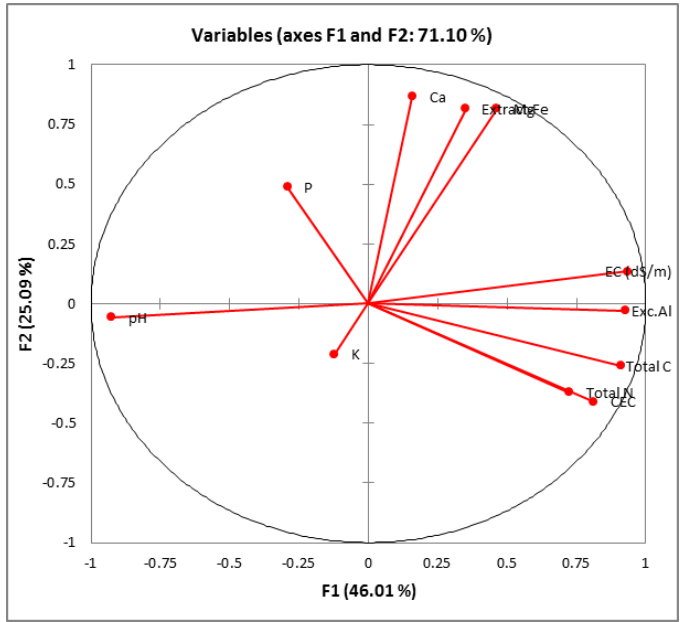


Figure 5. Correlation circle of soil chemical properties

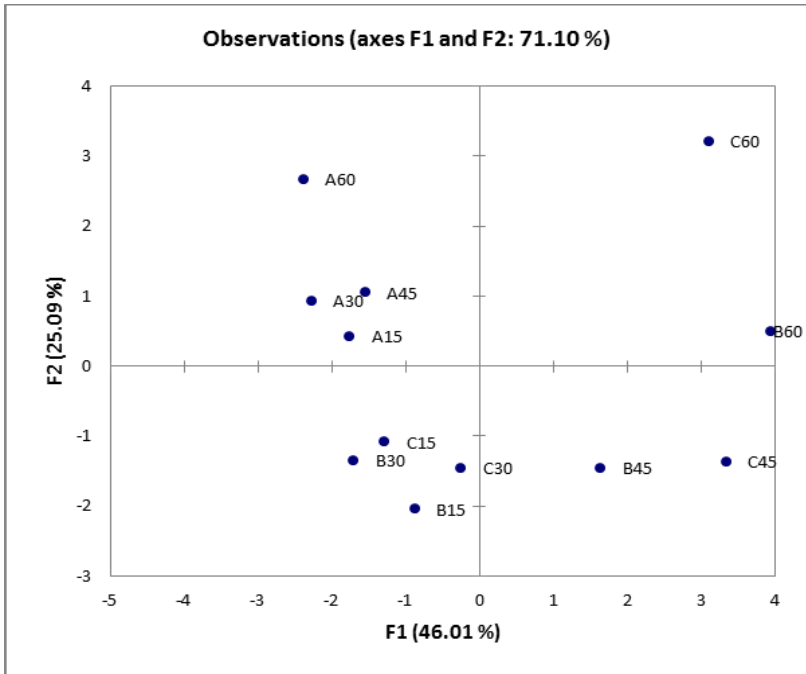


Figure 6. Dimensional map of sites A, B and C according to depth

Figure 6 shows the dimensional map of sites A, B and C according to depth. From the dimensional map, we can see that the sites are well grouped. Site A is significantly different from B and C in terms of all variables at all depth levels, while sites B and C show a similar trend and tabulation according to depth.

CONCLUSIONS

Acid sulfate soils occurring along the Kelantan Plains were uniquely formed when the sea level was higher than the present, some 6,000 BP. Pyritic sediments were found to be sporadically distributed in the plains and indicate the areas where acid sulfate soils occur. These pyrite-bearing sediments are easily distinguishable from each other based on their properties and depth. The oxidation of pyrite leads to high acidity and the presence of extremely high concentration of Al and Fe in the soils. The peaty materials in the soils contribute to the apparently high total N and C. Based on PCA, the principal components belong to soil acidity and organic matter content. The other factor is the nutrient content, contributed by Ca, Mg and K. Due to severe acidity and the presence of high Al and Fe, the productivity of the soils in the area is low. In future, studies should be conducted to ameliorate the soils in the Kelantan Plains for sustainable rice production.

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