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Pedogenesis of Acid Sulfate Soils in the Lower Central Plain of Thailand

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ABSTRACT

Several studies of acid sulfate soils in coastal lowlands have been conducted; however, little attention has been paid to the correlation between the properties of acid sulfate soils and their associated soils. This research aims to study soil properties and their influences on acid sulfate soil development as well as the pedogenesis process of acid sulfate soils. The morphological, physical, chemical and mineralogical properties of acid sulfate soils and their associated soils in the Lower Central Plain of Thailand were determined. According to the different profile forms of all soils, the results were assigned to one of four profile types (A-D). The results reveal that pyrite was accumulated in the lower parts of soils of all profile types. Most of the soils had high organic carbon levels in their subsoil and were associated with pyrite accumulation. Alkaline ions effected acid sulfate soil development and jarosite appearance. Ca was the most important alkaline cation that reacted with acidity. Most types A, B and D profile soils had high acidity but low alkalinity. These soils developed into acid sulfate soils. Type C profile soils contained excess Ca, so they developed into non-acid sulfate soil. The strong acid conditions type A, B and D profile soils efficiently elevated kaolinite formation. In contrast, the alkaline conditions of type C profile soils elevated smectite formation. Pyrite had a strong correlation with total S and consequently, the amount of pyrite in each profile type could be estimated from the total amount S in the soils.

Key words: Acid sulfate soils, sulfidic material, acidification, neutralizing agent, lower central plain of Thailand

INTRODUCTION

Acid sulfate soil formation occurs when sulfide minerals, mostly pyrite, and/or elemental sulfur in reduced sulfidic sediments oxidize upon exposure to air through drainage or earth-moving operations. The oxidation products are jarosite and sulfuric acid. Jarosite undergoes hydrolysis in an oxidizing environment, which releases iron oxyhydrates and more sulfuric acids. This set of reactions is one of the most acid producing reactions in soils. A sulfuric horizon is indicated if acid sulfate formation gives an end product pH of 3.5 or less (Natural Resources Conservation Service, 2010). Several factors are required for sulfide mineral formation these include a source of sulfate, a source of oxidizable organic carbon, reducing/saturated conditions, sulfate reducing bacteria and

reactive iron (Rabenhorst *et al.*, 2002). The oxidation of pyrite can be initiated if potential acid sulfate soils are drained, such as for cultivation. When the water-table drops, oxygen will enter the soil system and subsequently, pyrite starts oxidizing in the following reaction: $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+$. This oxidation results in the mobilization of iron, sulfate and hydrogen (Ritsama *et al.*, 1992). The degree of soil acidity or alkalinity, expressed as soil pH, is a master variable that affects a wide range of soil properties: chemical, biological and, indirectly, physical (Brady and Weil, 2002).

The world distribution pattern of acid sulfate soil has been driven mainly by postglacial sea level change but each regional pattern is determined by its unique sedimentary and geomorphological history. Distinctive patterns occur in deltas and estuaries and in humid and seasonally dry climates (Dent and Pons, 1995). Acid sulfate soils have a high spatial variability and, particularly in their natural state, they are poorly accessible. Also, their dynamic nature frustrates proper characterization and interpretation (Andriessse, 1993). The Lower Central Plain of Thailand was selected for study due to the widespread occurrence of acid sulfate soils in various types and profile forms. Acid sulfate soil occupies approximately 8,800 km² of Thailand (Land Development Department, 2006) in which about 56% of it distributes in the Lower Central Plain (Kheoruenromn, 2007). Most of acid sulfate soil areas in the plain are used for rice (*Oryza sativa* L.) cultivation (Yampracha *et al.*, 2005). Rice production is very low because of soil acidity, lack of nitrogen and phosphorus and high in aluminum, iron and manganese toxicity (Maneewan and Sa-nguansubpayakorn, 2007).

Many researchers have studied acid sulfate soil in Thailand. In the pioneering works, the researches focused on soil morphology for mapping and classification, detailing the chemistry and mineralogy of acid sulfate soil and the geochemistry of iron and sulfur compounds, whereas, later researches focused on agricultural potential, microorganism in acid sulfate soil, improvement and management of acid sulfate soils areas for land use, such as Satawathananont *et al.* (1991), Attanandana (1993), Krairapanond *et al.* (1993), Jugsujinda *et al.* (1996), Asadi *et al.* (2002), Yampracha *et al.* (2005), Maneewan and Sa-nguansubpayakorn (2007) and Satoh *et al.* (2007). However, little attention has been paid to environments in which acid sulfate soils have developed, to the correlation between properties of acid sulfate soil and associated soils and to the distribution pattern of acid sulfate soils. Recently, Janjirawuttikul *et al.* (2010) studied the initial phase of sulfidic material sedimentation and the characteristics of acid sulfate soil in relation to the paleo environment and land evolution of the Lower Central Plain of Thailand. The developed acid sulfate soils were distributed in the deltaic plain in areas occupied by the tidal flat to the salt swamp in the middle-late Holocene. Sulfidic materials accumulated in this environment; mangrove and plant roots were the organic material sources for sulfidic formation. Non-acid sulfate soil was distributed in the tidal plain where shallow marine areas and an open bay existed in the middle-late Holocene. In contrast to young acid sulfate soil, sulfidic material was accumulated recently and the soils have continued developing in the present estuary conditions.

Montoroi (1994) studied saline acid sulfate soils in the lower Casamance of Senegal, he found that kaolinite was the dominated mineral of clay fraction. The soils contained various forms of aluminum sulfate and iron sulfate minerals. Jarosite was precipitated in the central part of the valley under favourable redox conditions. Clays and clay minerals occur under a fairly limited range of geologic conditions. The characteristics common to all clay minerals derive from their chemical composition, layered structure and size (Foley, 1999). Local chemical conditions, which dynamic mineral chemistry dictates, essentially control the formation of clays (Velde, 1995). Clay mineral assemblages have previously been described to establish their natural occurrence and

estimate their stability in nature. We can then consider the evolution of clay mineral assemblages in the framework of this simplified chemical system, which is nearly closed to chemical migration and contains no perfectly mobile components. Trace elements are closely associated with cation and anion exchange capacity. The fixation of clay minerals and the binding/complexing of soil organic matter play a crucial role in the pedogenic process (Kabata-Pendias, 2001). Properties of soils are mostly reflective of their pedogenesis, which could indicate the evolution of environments. Understanding soil properties could allow us to understand the factors that influence acid sulfate soils development in the Lower Central Plain of Thailand.

Features in the soil profile reveal the location of sulfidic material and the production of acidity in soil bodies. Janjirawuttikul *et al.* (2010) categorized soil profiles into four types, A-D, to study the paleoenvironment of acid sulfate soil formation in the Lower Central Plain of Thailand. Representative acid sulfate soil profiles were collected from the plain and categorized into four profile types. The soils in each profile type have similar profile forms, which are indicated by their order in the profiles. This result could be used to describe the distribution patterns of each profile type and the spatial differences of geomorphological conditions in the Lower Central Plain of Thailand. The variety of characteristics of profile types is a result of the formation processes and subsequent changes in environmental conditions.

This study aimed to study soil properties, the correlation between these properties and the influence of these properties on acid sulfate soil development and the pedogenesis process of acid sulfate soils. In addition, the soil profiles were classified by the aforementioned profile types, A-D. We compared the analytical characteristics; the morphological, micromorphological and physical-chemical analyses; and the mineralogical and chemical compositions of all of the profile types. In this paper, statistical analyses were carried out using the descriptive statistics in the correlation analysis. Correlation matrices were used to determine the relationships among the soil properties. The correlation between many soil properties and its extension on spatial variability (topology) has led many soil scientists to use multivariate techniques in an attempt to reduce the inherently high dimensionality of the corrected data and extract the most meaningful variables, or an adequate combination of them. The identification of a reduced set of highly informative variables offers the opportunity to uncover the sequence of pedogenetic processes and elucidate the role of the participating soil parameters (Theocharopoulos *et al.*, 1997). Soil properties of each profile type were expected to elucidate the pedogenesis process and the correlation between the soil properties were expected to reveal the factors that have influenced the development of the soil profile. This method was evaluated for describing the pedogenesis of acid sulfate soil in the plain and discussing local varieties in profile form. These results could be extrapolated to other acid sulfate soil areas.

MATERIALS AND METHODS

Study site: The Lower Central Plain, or Chao Phraya Plain, is located in the upper Gulf of Thailand at 14° 30'-15° 15'N, 100° 15'-100°30'E'. Chao Phraya Delta is the third largest delta in Southeast Asia (Tanabe *et al.*, 2003). The Lower Central Plain begins at the Chainat Province, where the Chao Phraya River flows southward through a flat and low-lying plain until it reaches the Gulf of Thailand at the Samut Prakarn Province. The Chao Phraya River and its tributaries created the broad depositional surface with its well-defined meander belts, which are about 200 km long and the widest part of the plain, along the east-west axis, is about 180 km, with a total area of approximately 36,000 km². The plain is dissected by many rivers. Major rivers include the Chao Phraya, Tha Chin, Mae Khlong and Bang Pakong, which flow across the plain and drain to the Gulf of Thailand (Sinsakul, 2000).

Landforms of the Lower Central Plain were classified by several researchers (Takaya, 1971; Somboon, 1990; Dheeradilok, 1995; Umitsu *et al.*, 2002; Tanabe *et al.*, 2003). Umitsu *et al.* (2002) classified the landform of the Lower Central Plain into four major units: the Pleistocene alluvial plain in the west, the deltaic floodplain in the northwest, the deltaic plain in the east and the tidal plain in the southern part of the plain. Previously, the most important factors shaping the Lower Central Plain and determining the deposition of sediment were marine processes, particularly waves and tides in Holocene epoch. After the Late Holocene regression, marine processes were confined to the lower most part of the plain, which bordered the sea of the upper Gulf of Thailand Sinsakul (2000). This series of events is in agreement with many studies, such as Dheeradilok and Kaewyana (1986), Somboon (1988, 1990), Sinsakul (1997), Somboon and Thiramongkol (1992), Umitsu *et al.* (2002) and Tanabe *et al.* (2003). Presently, the plain landscape has been formed by fluvial and deltaic deposition by the Chao Phraya, Mae Klong, Tha Chin and Bang Pakong rivers as well as coastal progradation deposition with sediment transported into the area first by a southerly and later a northerly-directed longshore current (Dheeradilok, 1995).

Janjirawuttikul *et al.* (2010) found that sulfidic materials in the soils of the Lower Central Plain were formed in the paleoenvironment relating to Holocene transgression and high stand. The acid sulfate soils that developed were distributed in the deltaic plain where the tidal flat to salt swamp was in the period of middle to late Holocene. Sulfidic materials accumulated in this environment of which mangrove and plant roots were the organic material source of sulfidic formation. Young acid sulfate soils have been developing in the present estuary conditions, which are appropriate environments for the accumulation of sulfidic materials.

Land Development Department (2006) reported that acid sulfate soil occupies approximately 8,800 km² of Thailand. It has been observed over large areas in the Lower Central Plain which is about 8,000 km² in the Lower Central Plain (Van Breemen, 1976). General information of soil in the Lower Central Plain is explained by Vijarnsorn and Panichapong (1977). They indicate that most soils in the Lower Central Plain are low development and fine-grain in texture. They have a fluctuating level of ground water, resulting in a matrix of gray or neutral color accompanied with mottles. The degree of the alteration of primary minerals varies from place to place. The pedogenic alteration of some soils may be slight to very strong. Although the processes of reduction and segregation of the iron are intense, some soils in the flood plain may have relatively large amounts of organic matter at considerable depth.

Soil sampling: A field investigation was conducted during 2006 and 2007. Fifteen soil profiles, L1-L15, were collected in the Lower Central Plain of Thailand (Fig. 1). The soil profile description of morphology, including field pH and sampling, were studied based on standard soil survey method (Soil Survey Staff, 2006). Undisturbed soil samples were collected to Kubiena boxes. Disturbed soil samples were carefully collected from soil genetic horizons and packed in thick plastic bags with a less air. All of them were cooled in boxes and carried to laboratories.

Analytical methods: Undisturbed soils were oven-dried at 60°C for more than two weeks until they were dry. Then, they were impregnated with polyester resin solution. After the samples with solution hardened, they were sectioned, fixed on a slide and polished according to the Stoop method. Next, we analyzed the micro morphology of the samples with a microscope by following methods of Bullock *et al.* (1985) and Brewer (1964). This method entails the study of accumulated characteristics of pyrite and jarosite in the soils as well as their micromorphological transformations.

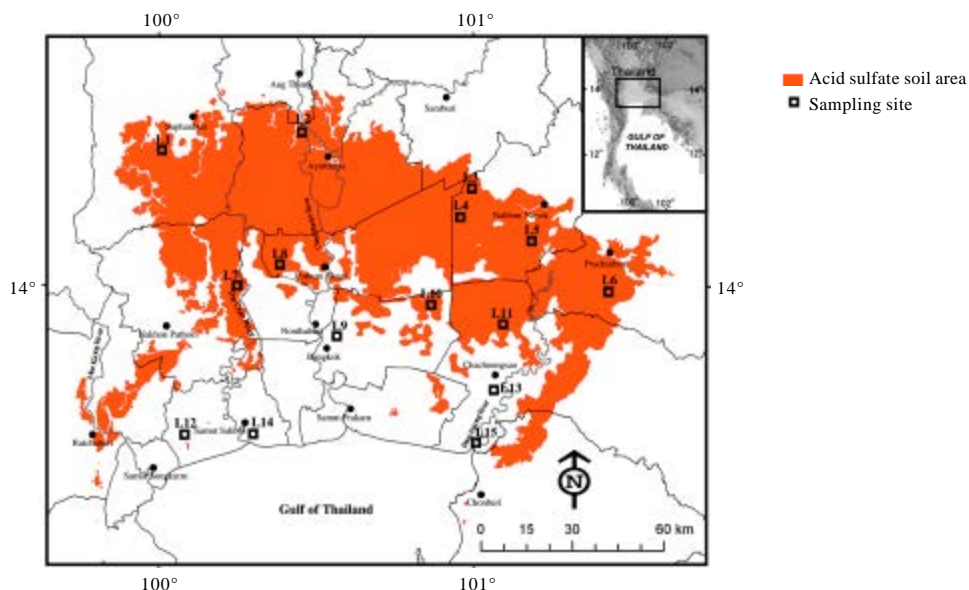


Fig. 1: The sampling sites and distribution of acid sulfate soils in Thailand (A) and in the Lower Central Plain (B) (modified after the Land Development Department (2006)) and sampling sites

The disturbed soils were divided into two subsamples. The first subsample were air-dried for 8 weeks and crushed to pass through a 2 mm sieve. The particle size distribution was determined with the pipette method (Kilmer and Alexander, 1949; Day, 1965). The soil pH was measured with a standard pH meter in water and 1 N KCl (soil:solution suspensions at a ratio of 1:1) (National Soil Survey Center, 1996). Exchangeable acidity (EA) was determined by barium chloride-triethanolamine extraction at pH 8.2 (Peech, 1965). The amount of organic carbon was determined by the Walkley and Black wet oxidation procedure (Nelson and Sommers, 1996). The amount of extractable sodium, calcium, potassium and magnesium were determined by leaching them from soil with NH_4OAc at pH 7.0 and measuring the element concentrations by atomic spectrometry (AAS) (Thomas, 1987). The Cation Exchange Capacity (CEC) was determined by saturating the soil with 1 N NH_4OAc at pH 7.0 (Chapman, 1965). The base saturation percentage for cations displaced by NH_4OAc at pH 7.0 is equal to the sum of the bases extracted by NH_4OAc saturation divided by the CEC determined by NH_4OAc and multiplied by 100 (National Soil Survey Center, 1996).

Crystalline minerals in clay and silt fractions, including crystalline jarosite, were identified by X-ray diffraction (XRD). The clay fractions ($<2 \mu\text{m}$) were examined as oriented clay by saturating with Mg and K, solvating with glycerol and heating at 550°C for 2 h (Brown and Brindley, 1980). Mineral compositions were determined for all horizons with X-ray diffraction (XRD) analysis using Philips PW-3020 ($\text{CoK}\alpha$, 25 kV, 17 mA). The clay fraction was scanned respectively from 4 to 45 degree 2θ with a step size of 0.02 degree and a scan speed of 1.2 degree per minute. The relative proportions of various minerals were calculated by comparing the XRD peak intensity with the intensity for standard minerals (Whittig and Allardice, 1986; Brown and Brindley, 1980). Random powder XRD pattern of silt fractions ($2\text{--}50 \mu\text{m}$) were scanned from 5 to 70 degree 2θ using a scan

speed of 0.02 degree per minute and identified types of minerals by comparison to analyses of certified reference materials (Brown and Brindley, 1980). Semi-quantitative determination of the amount of minerals in the fraction was performed by measuring relative peak height and peak area (Jackson, 1964).

The second subsamples were baked at 105°C for 48 h and then the samples were ground and their chemical composition was examined for the presence of Al, Si, Fe, Ti, Na, Ca, Mg, K, S, Mn, P, Cu Zn and Cl by X-ray fluorescence spectrometry (XRF) of pressed powder pellets (Norrish and Hutton, 1969). Pyrite concentration was also measured by XRF according to method developed by Osborne (1985). The fine fractions were added to 5 N HCl 100 mL and then heated in boiling water for 30 min with shaking every 10 min. After filtering passed filter-paper, the samples were washed with 150 mL 2 N HCl and 100 mL of distilled water and baked at 105°C. We measured the weight of the dried samples and the filter-paper and then crushed the samples with a Spectromill grinder before pressing the sample with 10 ton/inch² of force to pellet. The residual S concentrations of the samples were determined concentration by XRF and calculated the values to be pyrite by:

$$\text{Pyrite (\%)} = \frac{\text{Residual S} - \text{Loss on ignition}}{140} \times 1.8709$$

This study concentrates on the characteristics and properties of acid sulfate and non-acid sulfate soil. Therefore, identification of the soil by emphasis on kinds of acid sulfate soil is effective. The definitions of the terminology and concepts of acid sulfate soil used in this paper are the same used by Pons (1973), Fanning (2002) and the Soil Survey Staff (2006). The distinct acid sulfate soils were characterized as potential acid sulfate soil, active acid sulfate soil, post-active acid sulfate soil and transitional soil. All soil profiles were identified as kinds of acid sulfate soil by Janjirawuttikul *et al.* (2010). Characteristics of the soil profiles are shown in Fig. 2, they can be grouped into four types of profile forms: type A, type B, type C and type D profiles. These profiles are defined as the following:

The type A soil profile has post-active acid sulfate soil in it. The pH values are low and show small differences between field pH and air-dried pH and contain jarosite mottles. Profiles L1-L6 compose the type A profile.

The type B soil profile has deep potential acid sulfate soil or transitional soil in it. The pH values of transitional soil and potential acid sulfate soil are high in field conditions but dramatically drop to very low values after air drying. It occurs at a depth of 100 cm or more. Profile L7-L11 compose the type B profile.

The type C soil profile has only non-acid sulfate soil in it. The pH values are high both in the field and air-dried conditions. Profile L12 and L13 compose the type C profile.

The type D soil profile has shallow potential acid sulfate soil or transitional soil in it. The pH values of transitional soil and potential acid sulfate soil are high in field conditions but dramatically drop to very low values after air drying. It occurs before a depth of 100 cm. Profile L14 and L15 compose the type D profile.

Statistical analyses: A correlation analysis was applied to the whole data set. In the correlation analysis, a correlation coefficient (r) table and Pearson correlation were used to determine the strength of correlation between different between groups on a single variable. The 29 variables of

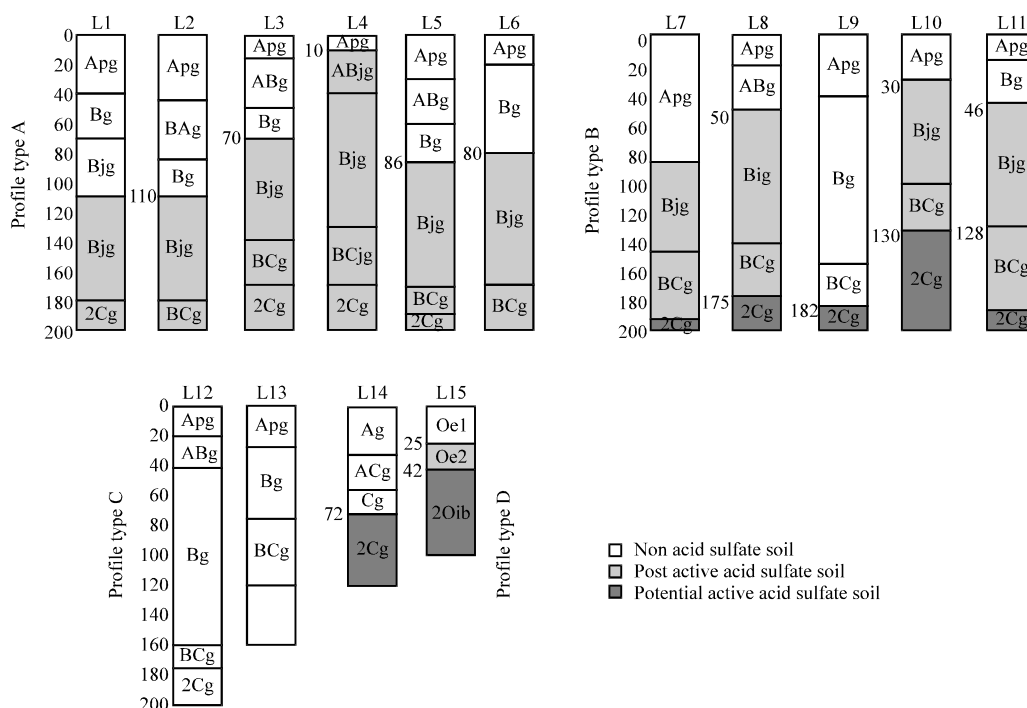


Fig. 2: A model of 15 soil profiles: profile type A (L1-L6), profile type B (L7-L11), profile type C (L12 and L13) and profile type D (L14 and L15)

physicochemical and chemical composition analyses data with 4 cases (profile types A, B, C and D) were considered for each variable at a significance level of $p < 0.05$.

RESULTS

Morphological of soils: The field morphological properties of the soil samples were examined to obtain characteristics of soils in the profiles. The soils had significant characteristics in each profile type (Table 1).

The soils of profile type A show dark surface overlying brown and gray surface with common color mottles including jarosite mottles. Most of the horizons had an angular blocky structure in the upper parts and structureless as massive in the lower parts of the profiles. Decayed roots and iron pipes normally appeared in the horizons containing jarosite and continued further below. Wood fragments were accumulated in the lower parts of L1, L3, L4 and L5. Additionally, common gypsum crystals accumulated near the surface in the profiles of L1 and L2. Field pH was low and slightly decreased to 3.6-5.3 in the horizon containing jarosite (Table 1).

The soils in profile type B generally had characteristics similar to those of profile type A. On the other hand, most had fewer jarosite mottles than profiles of type A, with the exception of the profile of L9, which had no jarosite mottles in its profile. Decayed roots and iron pipes were commonly found, but there was an absence of wood fragments. Additionally, a few gypsum crystals were observed in near surface of the profiles of L7 and L9. Field pH varies from 4.3-7.8 and 4.3-6.7 in the horizon containing jarosite.

The soils in profile type C were characterized by very gray and dark greenish gray surfaces overlying brown to gray and greenish gray surfaces with common color mottles but were missing

Table 1: Morphology of the study soils in the lower central plain

		Color				
Genetic horizon	Depth (cm)	Matrix	Mottles	Structure ^e	Field pH	Distinct ^d features
Profile type A: L1						
Apg	0-40	10YR3/1	10R4/6, 10YR5/8	1-2 ABK	5.0-5.3	-
ABg	40-70	10YR4/1	10YR3/6, 2.5YR6/6	1-2 ABK	5.1	1 gyp
Bg	70-110	Mixed 10YR2/1 and 10YR3/1, 10YR4/1, 6/2	10YR5/8, 7.5YR5/8, 10R4/8	1 ABK	4.8	2 gyp
Bjg	110-180	10YR6/2, 5/2	10R4/6, 6/8, 7.5YR5/8, 2.5YR4/8, 2.5Y6/6, 8/8	1 ABK	4.7-5.1	1 dr
2Cg	180-200	10YR4/2-3	-	M	4.6	1 pf
Profile type A: L4						
Apg	0-10	Mixed 10YR3/1 and 5/2	10YR4/6, 7.5YR5/8 and 2.5Y7/8	2 SBK	4.4	2 r
ABj	10-40	Mixed 10YR5/2 and 3/1	10YR4/6, 5/8, 6/8, 7.5YR5/8, 2.5Y8/4, 8/8	1 semi-ABK	4.4	2 r
Bjg	40-130	10YR4/2	10YR4/6, 2.5Y8/8	1 ABK to M	4.2-4.5	1 ip
BCj	130-170	Mixed 10YR3/1 and 5/2	5YR5/8	M	4.7	3 ip and dr, 1 pf
2Cg	170-200+	Mixed 10YR3/1 and 5/2	5YR5/8	M	4.4	3 dr, 2 pf
Profile type B: L8						
Apg	0-20	10YR4/2	-	2 ABK	5.9	-
ABg	20-50	Mixed 10YR4/2 and 5/1	10YR6/8, 2.5YR3/4	2 ABK	5.9	-
Bjg	50-140	Mixed 10YR5/1 and 3/1, 10YR5/2	10YR6/8, 7/8, 2.5YR4/6, 2.5Y8/6, 6/6, 8/6, 10R4/6	1-2 ABK	5.1	2 ip, dr
BCg	140-175	10YR5/1-2, 5/2	10R4/8	1 ABK	4.3-4.6	1 dr, very thin sand layers
2Cg	175-250	5GY5/1-2, 10Y5/1	-	M	5.3	1 dr, tsl
Profile type B: L11						
Apg	0-18	10YR4/1	10YR3/4, 7.5YR5/8	2 ABK	5.5	-
Bg	18-46	10YR6/2	10YR6/8, 7/6, 10R4/6-8	2 ABK	4.9	-
Bjg	46-128	10YR6/1, 6/2	10YR6/8, 2.5YR5/8, 2.5Y7/6, 10R4/4, 4/6-8	1 ABK	4.9-5.0	2 ip
Bcg	128-185	Mixed 10YR6/1 and 5/2, Mixed 10YR5/2 and 10Y5/1	-	M	5.0-5.1	2-3 dr
2Cg	185-200	Mixed 10YR5/2, 10Y5/1 and 5GY3/1	-	M	5.7	2-3 dr, om
Profile type C: L12						
Apg	0-20	Mixed 10YR3/1 and 10Y3/1	-	1 ABK	7.8	-
ABg	20-40	Mixed 10Y4/1 and N3/0	-	1 ABK	7.8	-
Bg	40-160	Mixed 10YR5/2 and 5GY-10Y5/1, 10YR5/2	10YR4/4, 5/3-4, 5/6, 6/6, 7.5YR5/8, 2.5Y5/6	1 ABK	7.8-8.0	2 sf, mn, 1 ip
BCg	160-175	10GY4-5/1	7.5YR5/6	M	7.8	tsl, ip and mn
2Cg	175-200	5GY4/1	-	M	7.7	2 sf, 1 ip
Profile type C: L13						
Apg	0-28	10YR4/2	5YR5/8, 2.5YR3/6	2 ABK	7.4	-
Bg	28-76	10YR5/1, 6/2	10YR5/8, 6/4-6, 7.5YR5/8, 2.5YR3/4, 5GY4/1	1-2 ABK	7.3	-
BCg	76-120	10YR4/1, 5/2	7.5YR5/6, 5GY4/1	1 ABK	7.6-7.8	2 sf, dr 1 ip
2Cg	120-160	10Y4/1, 5/1	-	M	8.3-8.5	2-3sf, 1 ip, dr

Table 1: Continued

		Color				
Genetic horizon	Depth (cm)	Matrix	Mottles	Structure ^e	Field pH	Distinct ^d features
Profile type D: L14						
Ag	0-32	10YR3/1, Mixed 10YR4/2 and 5/2,	7.5YR5/8, 10Y-5GY5/1	M	7.4	-
ACg	32-55	10Y4-5/1	7.5YR4/4	M	7.1	3 dr
Cg	55-72	10Y4/1	7.5YR3/3, 5/6	M	7.3	2 ip and dr
2Cg	72-120	Mixed 10Y3/1 and 5G4/1	-	M	7.8-8.1	2 ip and dr 2 pf at 95-120+cm
Profile type D: L15						
Oe	0-42	Mixed 10YR4/2 and 10Y3/1	7.5YR5/8, 2.5YR4/8, 2.5Y8/8	1 ABK	4.7-4.8	3 om
2Oib	42-100	10Y5-4/1	-	M	6.9-7.1	3 pf

^aC: Clay, SiC: Silty clay, SiCL: Silty clay loam, ^b1: Weak, 2: Moderate, ABK: Angular blocky structure, SBK: Subangular blocky structure, M: Massive, ^d1: Few, 2: Common, 3: Many, r: Roots, dr: Decomposed roots, pf: Plant fragments, ip: Iron pipes, gyp: Gypsum crystals, tsl: Thin sand layers, sf: Shell fragments, mn: Marl nodules, om: Organic matter

any jarosite mottles. Most of the horizons had an angular blocky structure in the upper parts and a massive structure in the lower parts of profile. A variety of materials that accumulated in some of the profiles, such as iron pipes and shell fragments, were found in the lower parts of profiles. Marl nodules were found only in the profile of L12 and decayed roots were found in the profiles of L13. The field pH ranged from 7.3-8.5.

The soils that match profile type D had a color and structure similar to profiles of type C, but plenty of wood fragments were observed in the middle of both profiles. Additionally, decayed roots and iron pipes were found in the profile of L14. The field pH ranges from 4.7-8.1.

Observation of pyrite and jarosite in micromorphological properties: Pyrite was observed in the lower parts of some soils of all profile types. Of the soils of profile type A, pyrite was found in the 2Cg of L3 and the BCg and 2Cg of L4. Of the soils of profile type B, pyrite was found in the 2Cg of L9, L10 and L11. Of the soils of profile type C, pyrite was found in the 2Cg of L13. Of the soils of profile type D, pyrite was found in the 2Cg of L14 and the 2Oib of L15. For the most part, pyrite accumulated as framboidal shapes associated with decomposed plant fragment. Another accumulated feature was single/cluster pyrite particles, which scattered in the soil matrix; Fig. 3 shows accumulation of pyrite in soil samples.

Jarosite was observed in the upper parts of profile types A, B and D. Jarosite was observed in the B₁g and BC₁g of all soils in profile type A and in the B₁g of L3 as well as the A₁g and the B₁g of L5. Jarosite was observed in the B₁g of L7, L8, L10 and L11 and the B₁g of L11 in profile type B. Jarosite was observed in the Oe₁ of the profile of L15 in profile type D. However, jarosite was not observed in the profiles of L9 in profile type B, L14 in profile type D and all soils of profile type C. Jarosite mostly accumulated in the soils as mixed material with iron oxides and clay mineral in cracks and soil pores, Fig. 4 shows the accumulation of jarosite in soil samples.

Physicochemical properties of soils: Most of the soils were fine to moderately fine texture soils (Fig. 5), soils of profile types A-D are mineral soils, which predominantly contain clay (25.32-75.53%) and silt (21.33-59.92%) particles but few sand (0.52-25.17%) particles. The 2Cg

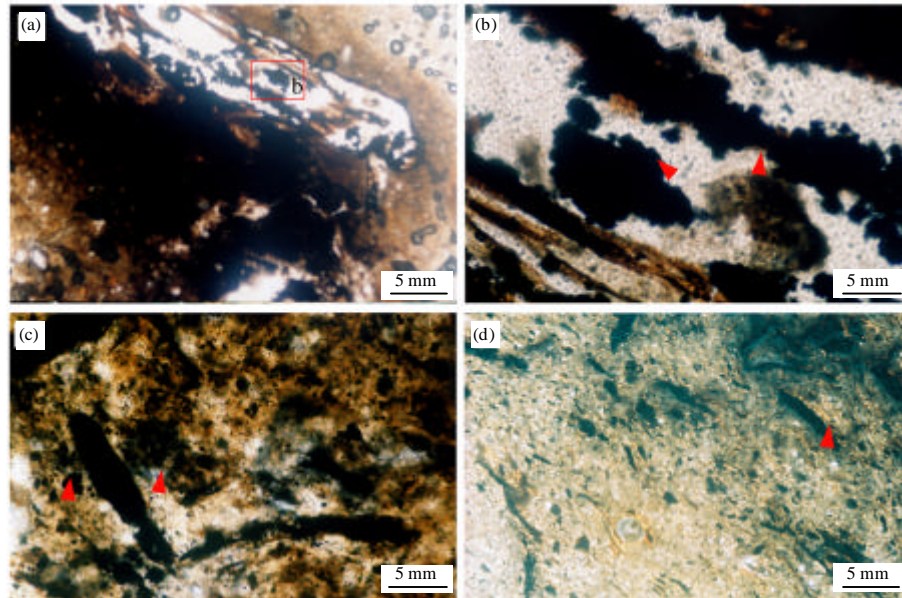


Fig. 3: An optical micrograph of a selected horizon showing pyrite accumulation in the soils: a) Framboidal pyrite associate with decayed a plant fragment at 170-200 cm-2Cg in L3 (plane light); b) Framboidal pyrite in an enlarged view of the same horizon (plane light); c) Pyrite associated with plant fragments distributed in a matrix and mixed clay and iron oxide at the same horizon (plane light); d) Pyrite associated with plant fragments and transformed into jarosite, which appears as yellow mottles around the plant fragments in their boundaries areas at 130-170 cm-BCjg in L4 (plane light)

horizon of the profiles of L8 and L14 had a slightly coarser textural class, like silt loam. Additionally, the profile of L15 is organic soil that has mucky clay in the surface and peaty clay in the subsoil.

Chemical properties of the soils are shown as graphs in Fig. 6, soils of profile type A had ultra-acidic to very strongly acidic soil, with pH values ranging from 3.0-4.7. Commonly, the pH values were lowest in the B_{jg} and BC_{jg} horizons. Most of soils of profile type B had ultra-acidic to strongly acidic conditions (pH 2.5-5.4). Except for the L9 and L10 profiles, which had higher pH values, specifically in the upper parts of the profile (pH 5.3-6.7). Generally, the bottom parts of profile type B, the 2C_g horizons, had the lowest values in the profiles (pH 2.5-4.6). Soils of profile type C had moderately acidic to neutral conditions (pH 5.7-6.9) and showed stable pH levels throughout their profiles. As for the soils of profile type D, the L14 profile was similar to the L9 and L10 profiles, which had moderately acidic to neutral conditions (pH 5.6-6.7) in the upper parts and very strongly acidic conditions (pH 4.5) in the bottom parts of profiles, whereas the L15 profile had ultra-acidic to extremely acidic conditions (pH 3.0-4.3). For the most part, the soils had a similar pattern of pH-KCl values to 1:1 H₂O pH-KCl values, but 1:1 H₂O pH values of the soils were slightly higher than pH-KCl values about 0.7 units on average. The difference in pH was a result of the displacement of OH⁻ ions by Cl⁻ ions. This result means that all profile types had a net positive charge, except for the 2C_g of L8 and the 2O_{ib} (70-100 cm) of L15. They had air-dried pH values lower than pH-KCl in 0.3 and 0.7 units, respectively which show a negative charge property.

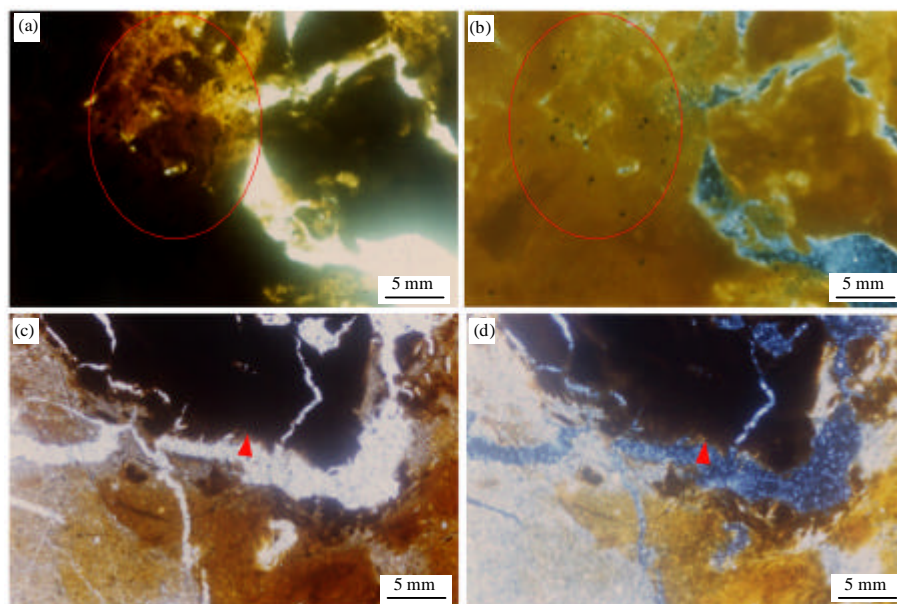


Fig. 4: An optical micrograph of selected horizons showing jarosite accumulation in the soils: a) pyrite Pyrite particles appearing as black spots distributed in the jarosite nodule. The concentrated part appears as an opaque area at 90-110 cm-Bjg2 in L3 (plane light). b) Jarosite appears as a yellow nodule with small black particles of pyrite (x-nicol). c) An amorphous organic material appearing as dark brown nodule and goethite and hematite mixed clay at 80-100 cm-Bjg3 in L10 (plane light). d) The same horizon in x-nicol

Most of the soils had a similar pattern of the depth of organic carbon, which is high ($4.19-41.59 \text{ g } 100 \text{ g}^{-1}$) at the surface, low ($1.91-12.89 \text{ g } 100 \text{ g}^{-1}$) in the middle and high ($10.94-30.98 \text{ g } 100 \text{ g}^{-1}$) again in the lower part of profiles. Organic carbon in the subsoil mainly concentrated in the BCg and 2Cg horizons of the type A-C profiles. Except for the L2 and L6 profiles, other profiles had large amounts of organic carbon in the bottom of profiles ($2.73-11.28 \text{ g } 100 \text{ g}^{-1}$). On the other hand, organic carbon accumulated in large quantities throughout profiles of type D, ranging from $13.17-39.26 \text{ g } 100 \text{ g}^{-1}$. The soils had moderately high to very high CEC.

Most of the type A, B and D profile soils had medium to very high extractable Na ($0.57-8.37 \text{ cmol kg}^{-1}$). Except for L14, which had a high amount of extractable Na-as much as the type C profile soils,-the amount of extractable Na ranged from $3.88-21.36 \text{ cmol kg}^{-1}$ and increased toward the bottom of the profiles. For the most part, extractable Mg was contained in the type A, B and D profile soils varied from low to high ($0.26-5.16 \text{ cmol kg}^{-1}$) and maintained a stable concentration throughout the whole profile. Except for the L10 and L14 profiles, which had a larger amount extractable Mg, like the type C profile soils, the amount of extractable Mg ranged from $5.25-13.54 \text{ cmol kg}^{-1}$ and increased toward the bottom parts of profiles. Type A and B profile soils had very low to high extractable K ($0.04-0.73 \text{ cmol kg}^{-1}$). Except for the L9 and L10 profiles, which had extractable K in amounts similar to type C profile soils, the amount of extractable K ranged from $0.54-1.76 \text{ cmol kg}^{-1}$. Type D profile soils had the highest amount of extractable K, ranging

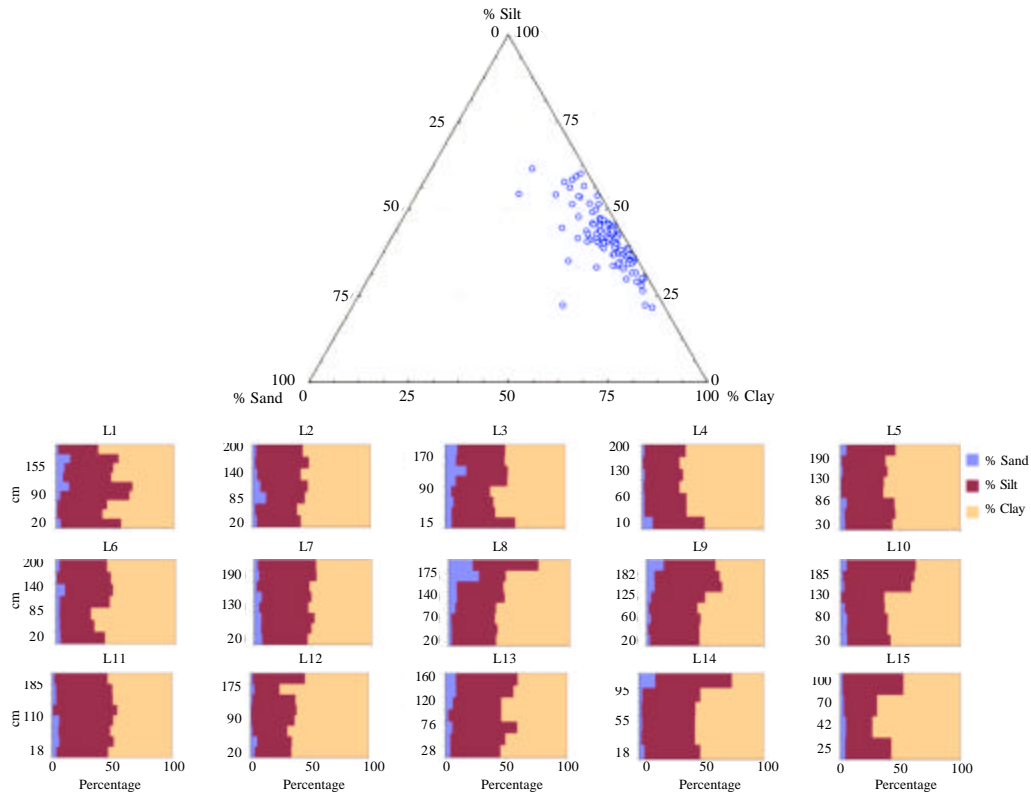


Fig. 5: The particle-size distribution of the studied soils plotted on the texture triangle

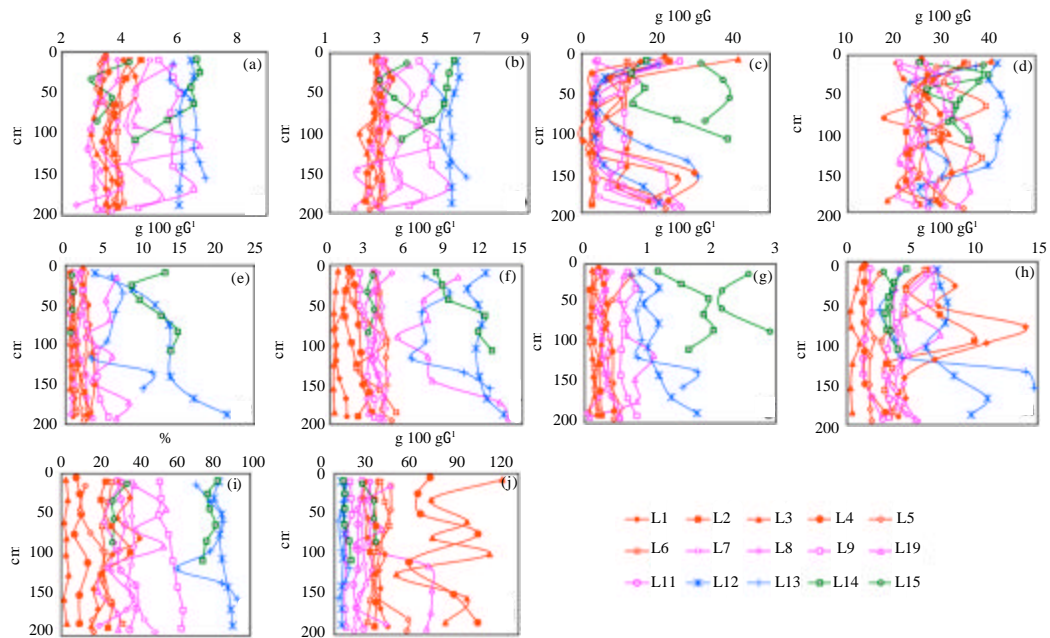


Fig. 6: The depth function diagrams of some chemical properties for each soil profiles. (a) Air-dried pH, (b) pH KCl, (c) Organic carbon, (d) CEC, (e) Extractable sodium, (f) Extractable magnesium, (g) Extractable potassium, (h) Extractable calcium, (i) Base saturation and (j) EA

from 1.15-2.91 cmol kg⁻¹. Most of the type A, B and D profile soils had low to medium extractable Ca (0.28-7.01 cmol kg⁻¹). Except for the profiles of L1, L2, L9 and L10 had high concentrations of extractable Ca (5.67-14.80 cmol kg⁻¹) in the upper parts but dropped to low concentrations in the bottom parts as the others in the types. Profile type C had low to medium extractable Ca (2.54-7.90 cmol kg⁻¹) in the upper part and increasing to medium to high (9.78-14.78 cmol kg⁻¹) in the lower parts of profiles. Most of types A, B and D profile soils had low to medium base saturation (1.54-64.43%), except for L14 and profile type C, which had a higher amount of base saturation ranging from medium to high (61.22-93.19%). For the most part, the soils of profile type A had high EA values throughout their profiles (18.53-109.4 cmol kg⁻¹), especially, the profiles of L3, L4 and the lower part of L10, which had an EA ranging from 40.3-109.4 cmol kg⁻¹. Soils of profile types B and D had Eas similar to those of profile type A. The EA values range from 12.35-36.50 cmol kg⁻¹ and showed stable trends across all depths. Except for the profiles of L9 and L14, which had an EA as low as in profile type C, ranging from 2.85-11.24 cmol kg⁻¹.

Chemical composition: The graphs of the amount of elements with respect to depth are shown in Fig. 7. Silicon, Al and Fe were the major elements in the soils. There was no distinct pattern of accumulated Si in any of the soil profiles at any depth. The amounts of total Al and Ti were slightly more concentrated in soils of profile type A (Al: 8.33-12.64% and Ti: 0.37-0.62%) than soils of profile type B, C and D (Al: 7.90-10.96% and Ti: 0.43-0.56%). Fe concentrations varied to a small degree in all soils of all profile types; however, some horizons in profile types A and B (e.g., L1: B₁g₁, L2: B₁Ag, L3: B₁g₃, L6: B₁g₂ and L11: B₁g) had higher amounts of Fe than other horizons in the profiles. The total amount of Ca in profile types A, B and D was much lower than in profile type C. The amount of Ca in the soils of profile types A, B and D ranged from 0.01-0.58%. Soils of profile type C had a high total Ca, especially in the 2C_g horizon. The amounts ranged from 0.17-1.75%. It was not notably different in K levels among soils of all profile types, the amounts ranged from 1.04-2.19%. Most soils of profile types A and B had lower concentrations of total Na, Mg, Mn, P and Cl than soils of profile types C and D. The profiles of L9 and L10 had higher total Na, Mg and Mn than others in profile type B and remarkably high amounts of Mg and Mn. For the most part, the total S of soils was low even as the depth increases, but it sharply increased in the bottom parts, like the 2C_g horizon, except for the profiles of L2 and L6. Additionally, total S was highly concentrated in the B₁g₂ horizon of L3 (8614 mg kg⁻¹) and the B₁g and BC₁g horizons of L4 (9343 and 10616 mg kg⁻¹). The total amount of Cu in soil had a pattern similar to that of Fe. It existed in even amounts in most profiles, from 19-45 mg kg⁻¹. With the exception of the 2C_g horizon of L1 and the BC₁g horizon of L4, this had higher amounts of Cu than other horizons in their profiles, 73 and 74 mg kg⁻¹, respectively.. Most of the soils had no difference in total Zn; the amounts ranged from 31-130 mg kg⁻¹. The 2C_g of L7 had dramatically higher levels of Zn, 301 mg kg⁻¹ than others. All of the soil profile types had pyrite in the same pattern. It was very low from the surface to the middle of the profile and then dramatically increased in the bottom part of profiles. The amount of pyrite ranged from 0.77-3.14 % in bottom parts of profiles. Except for the L2 and L6 profiles, this had low pyrite levels throughout the profiles, ranging from 0-0.029%.

Mineralogical characteristics: The summary of the XRD result is shown in Table 2. In the clay fraction, smectite and kaolinite were the major clay minerals with a minor amount of illite and

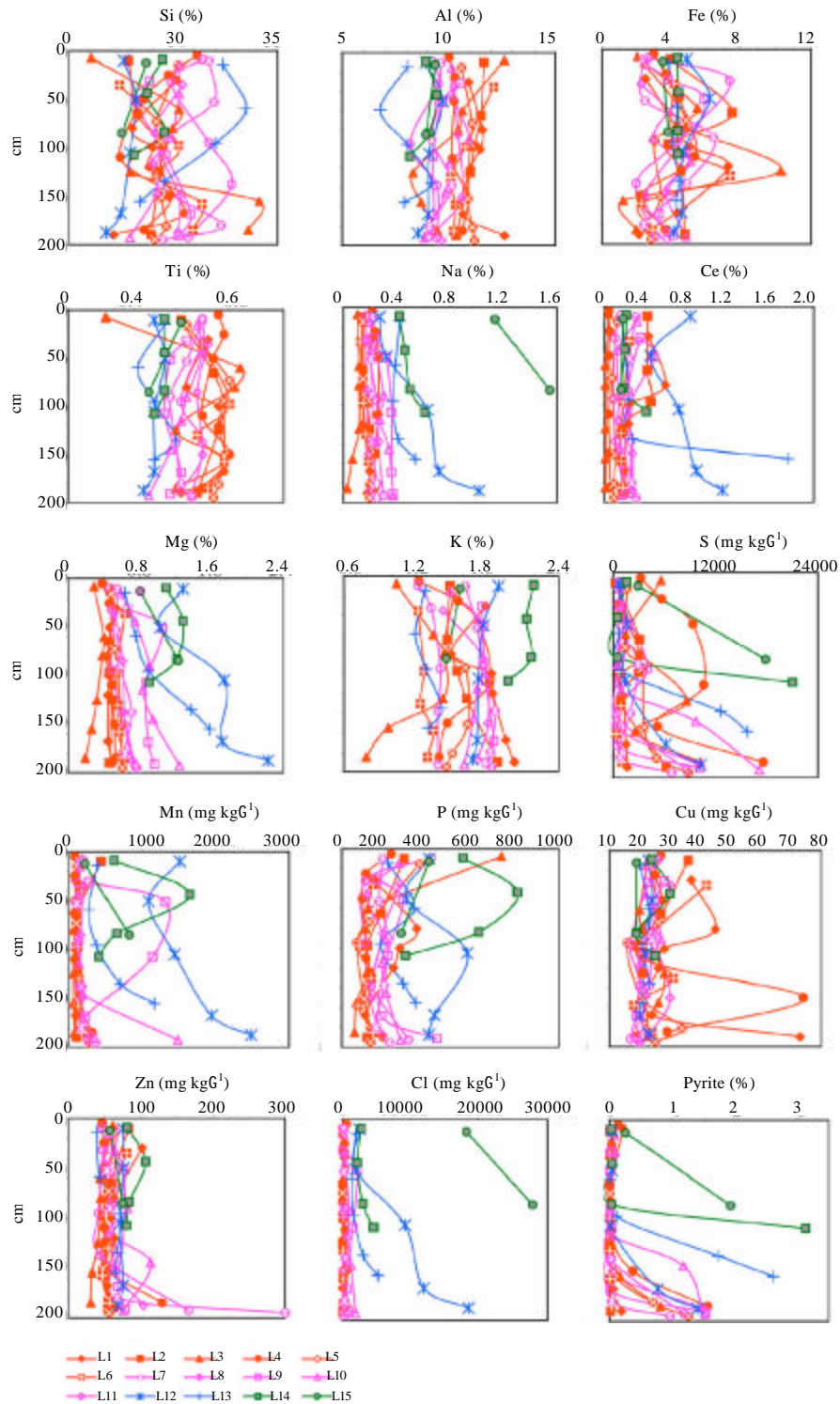


Fig. 7: The depth function trends for some chemical composition for each soil profiles

Table 2: Mineralogical composition of clay and silt fractions based on XRD

No.	Site	Horizon	Depth (cm)	Clay fraction				Silt fraction	
				Large	Moderate	Small	Trace	Dominant	Trace
1	L1	Apg2	20-40	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel
2		Bg2	90-110	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel
3		Bjg1	110-130	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz, Jr	Qtz	Fel, Mic
4		Bjg3	155-180	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
5		2Cg	180-200	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
6	L2	Apg1	0-20	-	Kao, Smec	Ill	Chl, Qtz	Qtz	Fel
7		Bg	85-110	-	Kao, Smec	Ill	Chl, Qtz	Qtz	Fel
8		Bjg1	110-140	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz, Jr	Qtz	Fel
9		BCjg	190-200	-	Kao, Smec	Ill	Int10 and 14, Qtz, Jr	Qtz	Fel, Jr
10	L3	Ag	0-15	-	Kao	Mont	Ill, Int10 and 14, Qtz	-	-
11		Bg	50-70	-	Kao	Mont	Ill, Chl, Int10 and 14, Qtz	Qtz	Fel
12		Bjg1	70-90	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz, Jr	Qtz	Fel
13		Bjg3	110-140	-	Kao, Smec	Ill	Int10 and 14, Qtz	Qtz	Fel, Jr
14		BCg	140-170	-	Kao, Smec	-	Ill, Int10 and 14, Qtz	-	-
15		2Cg	170-200	-	Kao, Smec	-	Ill, Int10 and 14, Qtz	Qtz	Fel
16	L4	Apg	0-10	-	Kao, Smec	Ill	Int10 and 14, Qtz	-	-
17		ABjg	10-40	-	Kao, Smec	Ill	Int10 and 14, Qtz, Jr	Qtz	Fel, Mic
18		Bjg2	60-90	-	Kao, Smec	Ill	Int10 and 14, Qtz, Jr	Qtz	Fel, Jr
19		BCjg	130-170	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz, Jr	Qtz	Fel
20		2Cg	170-200	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	-	-
21	L5	Apg	0-30	-	Kao, Smec	Ill	Int10 and 14, Qtz	Qtz	Fel
22		Bg	48/60-86	-	Kao	Mont, Ill	Int10 and 14, Qtz	Qtz	Fel
23		Bjg1	86-102	-	Kao, Smec	Ill	Int10 and 14, Qtz	Qtz	Fel
24		Bjg3	130-172	-	Kao, Smec	Ill	Qtz	Qtz	Fel, Jr
25		BCg	172-190	-	Kao, Smec	Ill	Qtz	Qtz	Fel
26		2Cg	190-200	-	Kao, Smec	Ill	Chl, Qtz	Qtz	Fel
27	L6	Bg1	20-40/50	-	Kao, Smec	-	Ill, Chl, Int10 and 14, Qtz	Qtz	Fel
28		Bjg1	80-115	-	Kao, Smec	-	Ill, Int10 and 14, Qtz	Qtz	Fel
29		Bjg3	145-170	-	Kao, Smec	-	Ill, Int10 and 14, Qtz, Jr	Qtz	Fel
30		BCjg	170-200	-	Kao, Smec	-	Ill, Chl, Qtz, Jr	Qtz	Fel
31	L7	Apg2	20-45	-	Kao, Smec	Ill	Qtz, Jr	Qtz	Fel, Mic
32		Bjg1	85-95	-	Kao, Smec	Ill	Qtz	Qtz	Fel, Mic
33		BCg2	170-190	-	Kao, Smec	Ill	Int10 and 14, Qtz	Qtz	Fel, Mic
34		2Cg	190-200	-	Mont	Kao, Ill	Int10 and 14, Qtz	Qtz	Fel, Mic
35	L8	ABg	20-50	-	Kao, Smec	Ill	Int10 and 14, Qtz	Qtz	Fel
36		Bjg2	70-100	-	Kao, Smec	Ill	Int10 and 14, Qtz	Qtz	Fel, Mic
37		BCg1	140-160	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
38		2Cg1	175-200	-	Kao, Smec, Ill	-	Int10 and 14, Qtz	Qtz	Fel, Mic
39	L9	Apg2	20-42	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
40		Bg1	42-60	Smec	Kao	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
41		Bg3	90-125	Smec	Kao	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel
42		BCg	155-182	Smec	Kao	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
43		2Cg	182-200	-	Kao, Smec	Ill	Chl, Qtz	Qtz	Fel, Mic
44	L10	Apg	0-20/30	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	-	-

Table 2: Continued

No.	Site	Horizon	Depth (cm)	Clay fraction				Silt fraction	
				Large	Moderate	Small	Trace	Dominant	Trace
45		Bjg1	30-58	Smec	Kao	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
46		Bjg3	80-100	Smec	Kao	Ill	Int10 and 14, Qtz, Jr	Qtz	Fel, Mic
47		BCg	100-130	Smec	Kao	Ill	Int10 and 14, Qtz	Qtz	Fel, Mic
48		2Cg3	185-200	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel
49	L11	Apg	0-18	Smec	Kao	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
50		Bg	18-46	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel
51		Bjg2	80-110	-	Kao, Smec	Ill	Qtz, Jr	Qtz	Fel
52		BCg1	128-148	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel
53		2Cg	185-200	-	Kao, Smec	Ill	Chl, Int10 and 14, Qtz	Qtz	Fel
54	L12	Apg	0-20	Smec	Ill	Kao	Int10 and 14, Qtz	-	-
55		Bg1	40-60	Smec	-	Kao, Ill	Chl, Int10 and 14, Qtz	Qtz	Fel
56		Bg3	90-120	Smec	-	Kao, Ill	Chl, Qtz	Qtz	Fel
57		BCg	160-175	Smec	-	Kao, Ill	Int10 and 14, Qtz	Qtz	Fel
58		2Cg	175-200	Smec	-	Kao, Ill	Int10 and 14, Qtz	Qtz	Fel
59	L13	Apg	0-28	Smec	-	Kao, Ill	Int10 and 14, Qtz	Qtz	Fel
60		Bg2	42-76	Smec	-	Kao	Ill, Int10 and 14, Qtz	Qtz	Fel
61		BCg1	76-98/115	Smec	-	Kao	Ill, Chl, Int10 and 14, Qtz	Qtz	Fel
62		2Cg1	120-150	Smec	-	Kao	Ill, Chl, Int10 and 14, Qtz	Qtz	Fel, Mic
63	L14	Ag1	0-18	Smec	Kao, Ill	-	Int10 and 14, Qtz	-	-
64		ACg	32-55	Smec	Kao, Ill	-	Int10 and 14, Qtz	Qtz	Fel, Mic
65		2Cg2	72-95	-	Kao, Smec	Ill	Qtz	Qtz	Fel
66		2Cg3	95-120	-	Kao, Smec, Ill	-	Qtz	-	-
67	L15	Oe1	0-25	-	Kao, Smec	Ill	Int10 and 14, Qtz	-	-
68		2Oib2	70-100	Smec	Kao	Ill	Int10 and 14, Qtz	Qtz	Fel

Dominant: >60%, Large: 40-60%, Moderate: 20-40%, Small: 5-20%, Trace: <5%, -: Not detected, Kao: Kaolinite, Smec: Smectite, Ill: Illite, Ver: Vermiculite, Chl: Chlorite, Int10 and 14: Interstratified clay 1.0 and 1.4 nm, Qtz: Quartz, Mic: Mica, Jr: Jarosite

traces of chlorite interstratified at 1.0 nm and 1.4 nm clay and quartz. Most of the soils of profile types A, B and D consisted of similar minerals. They contained moderate to large amounts of smectite and kaolinite with small traces of illite and chlorite interstratified at 1.0 nm and 1.4 nm clay and quartz. Nevertheless, trace amounts of jarosite observed only in the soils of profile type A and B (Fig. 8). Generally, jarosite occurred in Bjg horizons of profiles. Profile type C consisted of moderate to large amounts of montmorillonite and small amounts of kaolinite with small traces of illite and traces of interstratified at 1.0 nm and 1.4 nm clay and quartz. The trace of chlorite was investigated only in lower part of profile of L13. There was no jarosite in profiles of type C.

Quartz was the dominant mineral of the silt fraction with small amounts of feldspar in all profiles. Traces of mica could be found in soils of profile type B and some of the horizons of profiles type A, C and D. Traces of jarosite were found only in the horizons of profile type A.

Correlation analyses: Due to the large size of the 29 variable correlation matrix, the interesting correlations of the four soil profile types are shown in Table 3. The correlated soil properties are analyses of field pH, EA, base saturation, organic carbon, extractable Ca, S, Fe and pyrite.

Field pH had a negative relationship ($r = -0.48$) with EA in soils of profile type A. EA was correlated with base saturation in all soils. They were strongly negatively correlated in soils of

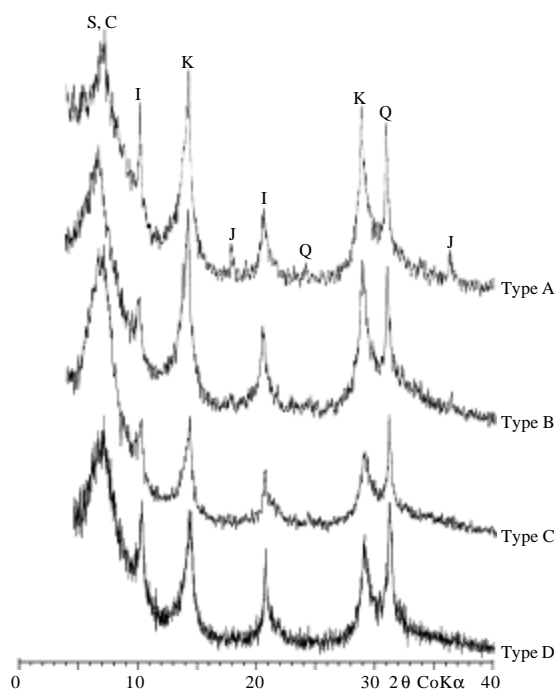


Fig. 8: The X-ray diffraction patterns of the oriented clay fraction of profile type A (Bjg1 40-60 cm of L4), profile type B (Bjg2 80-110 cm of L11), profile of type C (Bg3 90-120 cm of L12) and profile type D (ACg 32-55 cm of L14). The patterns of type A and B show weak board jarosite reflection

profile types A and D, with correlation coefficients of $r = -0.82$ and -0.96 , respectively and were less negatively correlated in soils of profile types B and C, with correlation coefficients of $r = -0.64$ and -0.68 , respectively. EA was correlated with organic carbon and S in soils of profile types A and B. Soils of profile type A had slightly higher coefficient values than soils of profile type B in both correlations. EA also was correlated with extractable Ca in soils of profile type A as shown by the negative correlation value of -0.54 . Fe had no significant correlation with S and pyrite in all soil profile types. On the other hand, pyrite had a positive relationship with S in soils of all profile types, with correlation coefficients of $r = 0.72, 0.94, 0.99$ and 0.98 in soils of profile types A, B, C and D, respectively. Moreover, pyrite also had positive correlation with organic carbon in all soils. Soils of profile type A had the smallest coefficient value, with $r = 0.52, 0.78, 0.82$ and 0.82 for profile types A, B, C and D, respectively. Pyrite had a positive correlation with EA in soils of profile types A and B. Soils of profile type A had a slightly greater correlation than soils of profile type B, with $r = 0.48$ and 0.39 , respectively. Nevertheless, pyrite had a positive correlation with extractable Ca only in soils of profile type C and with a correlation coefficient of 0.88 .

DISCUSSION

Relation of pyrite and jarosite in soil profiles: The results from the micro morphology and chemical compositional analyses revealed that pyrite existed in the lower parts of the soils of all profile types, mainly in the 2Cg and with the exception of the type A profiles, L2 and L6. This result indicated that sulfidic material, mainly pyrite, accumulated extensively in the Lower Central Plain

Table 3: Correlation matrix of some chemical properties in the soil profile types A-D; n = 76. Correlations significant at p<0.05 are in bold

Variable	Field pH	EA	OC	extCa	BS	Fe	S	Pyrite
Soil profile type A								
Field pH	1.00							
EA	-0.48	1.00						
OC	-0.03	0.62	1.00					
extCa	0.58	-0.54	-0.13	1.00				
BS	0.54	-0.82	-0.38	0.81	1.00			
Fe	0.04	-0.28	-0.51	0.14	0.04	1.00		
S	-0.23	0.53	0.20	-0.33	-0.43	0.02	1.00	
Pyrite	-0.19	0.48	0.52	-0.22	-0.29	-0.30	0.72	1.00
Soil profile type B								
Field pH	1.00							
EA	0.13	1.00						
OC	0.27	0.43	1.00					
extCa	0.41	0.13	0.27	1.00				
BS	0.56	-0.68	-0.16	0.23	1.00			
Fe	0.20	0.08	-0.18	-0.08	-0.01	1.00		
S	0.28	0.48	0.73	-0.03	-0.22	0.14	1.00	
Pyrite	0.24	0.39	0.78	-0.01	-0.15	0.00	0.94	1.00
Soil profile type C								
Field pH	1.00							
EA	-0.08	1.00						
OC	0.56	0.06	1.00					
extCa	0.85	-0.06	0.74	1.00				
BS	0.51	-0.64	0.21	0.66	1.00			
Fe	0.17	0.06	-0.44	0.08	0.21	1.00		
S	0.75	-0.21	0.80	0.91	0.65	-0.22	1.00	
Pyrite	0.75	-0.28	0.82	0.88	0.64	-0.26	0.99	1.00
Soil profile type D								
Field pH	1.00							
EA	-0.39	1.00						
OC	-0.06	0.61	1.00					
extCa	0.52	-0.39	-0.21	1.00				
BS	0.64	-0.96	-0.52	0.48	1.00			
Fe	0.86	-0.79	-0.42	0.47	0.93	1.00		
S	0.31	0.53	0.81	0.20	-0.35	-0.11	1.00	
Pyrite	0.37	0.40	0.82	0.21	-0.22	0.00	0.98	1.00

OC: Organic carbon; extCa: Extractable Ca; BS: Base saturation

of Thailand. This observation is in agreement with a study by Van Breemen, 1976 that found that soils in the plain had an unmottled pyritic substratum.

The pyrite containing horizons had remarkable, increasing concentrations of organic carbon in their profiles. Moreover, pyrite has a strong relationship with organic matter (Table 3). Thus, pyrite in the Lower Central Plain of Thailand was formed under the condition of a tidal flat with mangrove vegetation to salt grass swamp in the Holocene period. Therefore, when we observed pyrite containing horizon, it was usually rich in plant fragments and other organic matter forms (Janjirawuttikul *et al.*, 2010).

Field morphological, micromorphological and XRD analyses revealed the presence of jarosite in the soils. Results from the field morphological and micromorphological analyses indicated that

jarosite occurred in most of the soils of the type A, B and D profiles, except for the profiles of L9 (profile type B) and L14 (profile type D), which are transitional acid sulfate soil profiles. Jarosite was detected by XRD in all of the type A profiles including L2 and L6. The occurrence of jarosite in the soil of the L2 and L6 profiles confirmed the existence of pyrite by indicating that the horizon containing pyrite should lie below 200 cm. Jarosite was detected in trace amount in these soils and they had pH values higher than 4. Van Breemen (1976) reported that a pH between 1.7 and 4 is an appropriate condition for jarosite formation. These results indicated that the soils were post-active acid sulfate soil in which oxidation and acidification had already occurred. The remaining jarosite in the soil was due to the pH condition, which was higher than appropriate for its formation. However, remaining jarosite was important evidence that the soil had been developed under extremely acidic conditions, specifically conditions of high sulfuric acid. The amounts of total Fe and S were slightly higher in the horizons containing jarosite.

Nevertheless, jarosite was not observed in type C profile soils (L12 and L13 profiles) and the transitional acid sulfate soils (type B profile L9 and type D profile L14). This observation revealed that the jarosite formation in non-acid sulfate soil and transitional soil occurred differently than in the acid sulfate soil. Jarosite formation occurred in a very short period and was then neutralized with an excess of alkaline ions. Under these conditions, jarosite was temporary formed, which explains the absence of jarosite in these soils. Upon neutralization, jarosite was commonly transformed to gypsum. Gypsum crystals were investigated in the L9 profile. However, the absence of gypsum crystal in the L12, L13 and L14 profiles may be because the gypsum was leached out from these soil bodies by water due to the shallow groundwater level.

Acidification and neutralization: According to the results of the chemical analysis, the EA values showed a trend opposite to those of the pH values. The EA was high in most of the profiles of types A and B, which are acid sulfate soils, especially in the L3 and L4 profiles. Conversely, the EA was low in the L9 and L14 profiles, which are transitional soils and type C profiles, which is a non-acid sulfate soil. The differences in the EA values are the result of acidification and neutralization in the soil. High EA values indicate that acidification occurred at a greater rate than neutralization.

The soils that have insufficient neutralizing agents to react with acidic agents will become acid sulfate soils, whereas the soils that have sufficient neutralizing agents to react with most of the acidic agents will become non-acid sulfate soils. Upon oxidation, most of the type A, B and D profile soils (profiles L1-L8, L10-L11 and L15) had more sulfuric acid than neutralizing agents. Consequently, because intensive sulfuric acid remained the soils became acid sulfate soils. In comparison, the L9 and L14 profiles, which are transitional soils, had more neutralizing agents than other type A, B and D profile soils. However, the neutralizing agents were insufficient to react with all of the sulfuric acids. The remaining sulfuric acid resulted in a notable drop in the pH of the soil upon oxidation but not lower than 4.0. This observation is characteristic of transitional acid sulfate soil. The L12 and L13 profiles were rich in neutralizing agents because very little acid remained in the soil and the soil developed into non-acid sulfate soil.

The neutralizing agents that reacted with acid compounds were alkaline ions, for example, Ca, Na, Mg and K. The soils that had a high EA and a high amount of extractable Ca, like soils of profile type C, will not become acid sulfate soils because Ca will react with a large portion of the acid. Conversely, the soils that had a high EA and low amount of extractable Ca but high values of other alkaline cations, Na, K, Mg, as profiles of L9 and L14 will become transitional soils.

Although Na, K and Mg react with acid, they do so less efficiently than Ca. Therefore, since sulfuric acid exists in the soil body, it decreases the pH in acid sulfate soil profiles. However, the amount of acid is not sufficient to drive pH below 4.0; thus, the soils cannot be categorized as acid sulfate soils. This result supports a study by Dent (1986) that found that Ca was the most important alkaline ion that reacts with sulfuric acid in soils. Some acidity is also neutralized rapidly by exchangeable bases in soils. One part mass of pyrite sulfur is neutralized by three parts of calcium carbonate. The remainder is gradually lost by leaching or by slow reaction with aluminosilicate minerals. It can be expected that soils without carbonates show a sharp drop in pH upon pyrite oxidation, even when the oxidation of pyrite has started recently (Ritsama *et al.*, 1992).

It is important to consider the clay minerals in all soils. Most of the neutralizing agents in the soils may be derived from minerals: K was derived from illite and mica; Na was derived from montmorillonite and feldspar; Ca was derived from montmorillonite, feldspar (gypsum crystals and calcium carbonate nodules were observed in the field) and Mg was derived from montmorillonite and chlorite.

Mineralogical analysis of all profile types revealed that acid sulfate soil and non-acid sulfate soil have similar clay mineralogy, except for higher kaolinite levels in acid sulfate soil and higher levels of smectite and total alkaline elements in non-acid sulfate soil. These observations offer clues to the environment for soil development and the quantity of neutralizing agents. We think that most of neutralizing agents belong to components in clay minerals. Weathered smectite gives many more alkaline ions to the soil than weathered kaolinite. Therefore, acid sulfate soil contained kaolinite more often than non-acid sulfate soil. And the acidified condition led to more alkaline ions dissolved in the soil solution. The alkaline ions may have reacted with sulfuric acid and may have been leached from soil body. In our opinion, most of the alkaline ions may have worked as neutralizing agents because the low-lying and flat area has poor drainage conditions.

Pons and van der Kevie (1969) studied acid sulfate soil in the Lower Central Plain of Thailand and reported that the reduced subsoil of non-acid sulfate soil contained green minerals, whereas green minerals were absent in the reduced subsoil of acid sulfate soil. The main green mineral was probably chlorite ($10(\text{Mg,Fe}) \cdot 0.2\text{Al}_2\text{O}_3 \cdot 6\text{SO}_2 \cdot 8\text{H}_2\text{O}$), which is known to be present in sea bottom sediments before the coast. Pyrite clay with green minerals will yield normal marine clay soil or non-acid sulfate soil. Pyrite clay without green minerals and sufficient amount of carbonates will develop into acid sulfate soil after ripening. Contrary to, the work of Van Breemen (1969), which found that chlorite was essentially absent in non-acid sulfate soil from the Lower Central Plain, our study found traces of chlorite in every soil profile, indicating that chlorite could be developed in both acid sulfate soil and non-acid sulfate soil. Occurrence of chlorite in soils in the Lower Central Plain of Thailand indicates that the plain were formed in a relatively marine condition. These explained by Velde (1995) that the conditions permitting 0.7 nm chlorite formations occur at times near the sediment-seawater interact or in shallow burial.

According to Brady and Weil (2002), Si is an important element of silicon sheets and Al is an important element of aluminum sheets. Silicon, Al and K are the elements that compose kaolinite. Acidification may occur because of the leaching away of non-acid cations that the H^+ ions from acids displace from the exchange complex. Aluminum is the other principal acid cation beside hydrogen. From the results of mineralogical analyses, all profiles contained similar clay minerals but in different amounts. There were similar quantities of kaolinite and smectite in type A, B and D profile soils, which are acid sulfates soil and transitional soils. In contrast to the type C profile soils, they

consisted of large amount of smectite and a small of kaolinite. This discrepancy indicated that acidity affects the kinds of clay mineral in the soil because kaolinite was developed more in acid sulfate soil than in non-acid sulfate soil.

The amount of Al was highest in the type A profile soils and most of the type B profile soils. This high amount of Al caused the soils to be dominated by kaolinite because Al formed aluminum sheets in the kaolinite structure. This supports a study by Pons (1973) that found that, in acid sulfate soils, the Al-clay was the result of the acids attacking the clay minerals and thereby liberating Al-cations in such concentrations that they not only replace originally absorbed cations but also remain in the soil solution.

Relationships of soil properties: The results of correlation analysis were considered to estimate the correlation between features of the soils' properties. Field pH was correlated with EA only in the soils of profile type A since the soils were already oxidized and sulfuric acid was generated, whereas the other soils still kept sulfidic material under reducing EA conditions. An increasing EA decreased the field pH value.

Base saturation had a strong relationship with EA in all soils. Bases in soils reacted with acid upon oxidation as neutralizing agents. The type A and D profile soils exhibited a strong relationship between base saturation and EA. This indicates that the amount of base influenced the acidity of the soils. The soils that had a low concentration of base reacted with acids, so small changes in the amount of base were more sensitive to changes in the acidity of the soils. Conversely, the type B and C profile soils had a lower correlation coefficient for this factor because they had a moderately high to high base saturation and a low EA. The basic cations in the strong acid condition were dissolved into the soil solution. Some reacted with acids while others were leached out from the profiles. Therefore, the acid sulfate soil in type A, B and D profiles had very low alkaline ions compared with the type C profile soils, which is a non-acid sulfate soil.

The extractable form of bases easily reacted with acid in the soils. The most important base that reacted with sulfuric acid was Ca. There was a high correlation between EA and extractable Ca in the type A profile soils because the soils lacked bases to react with the acid. The increase of Ca resulted in a strong decrease of the EA in the soil.

EA only had a correlation with organic carbon in the type A and B profile soils. The result from the correlation matrix analysis showed that the horizons containing sulfidic material (mainly pyrite) were closely related to organic material in the subsoils of all of the profile types. However, type D profile soils were rich in organic materials not only in the horizons containing sulfidic material, especially L15 profile soils, but also throughout the whole profile. This explanation has support from a report by Tabatabai (1982) that maintained that sulfur occurs in soils in organic and inorganic forms. The inorganic S fraction in soils may occur as sulfate and compounds of lower oxidation state such as sulfide and elemental S.

A stronger relationship between pyrite and S occurred in soils of the type B, C and D profile than of the type A profile since a portion of S in soils of type A profile was oxidized and changed from pyrite to jarosite. Figure 9 shows a bivariate plot of the two variables of the correlations. Each dot on the plot represents an individual value of the soil horizon. Only the significant correlation of each soil profile type is presented. In each graph, a straight line through the group of data points presents the pattern in the bivariate plot. This figure shows how we could estimate the amount of pyrite from the amount of total S in each profile type as follows:

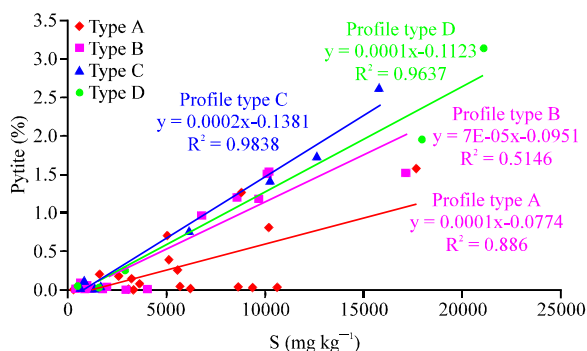


Fig. 9: A Bivariate plot of pyrite and S concentration in soils

Profile type A	$y = 7273.2x + 938.91$	$R^2 = 0.886$
Profile type B	$y = 7557.5x + 2627.3$	$R^2 = 0.5146$
Profile type C	$y = 6130.8x + 929.08$	$R^2 = 0.9838$
Profile type D	$y = 7015.4x + 1056.7$	$R^2 = 0.9637$

where, x = pyrite and y = total S

Fe is a component of pyrite, FeS_2 , along with S. Additionally, iron usually forms with many elements in soil. Therefore, pyrite has no correlation with Fe but a very strong correlation with S. Nevertheless, pyrite and jarosite are not the only compounds that form with iron in soil. The excess of Fe in soils presumably exist in chlorite and iron oxides such as goethite and lepidocrosite (FeOOH). However, the iron oxide was not formed as a crystalline mineral but as a mixture occurring with clay mineral in an amorphous form; therefore, we could not observe the iron oxide clearly in the XRD pattern. This result is also in agreement with Van Breemen (1969) who found that during pyrite oxidation, essentially all ferrous iron is ultimately oxidized to ferric iron, which precipitates as jarosite, poorly crystallized goethite or amorphous ferric oxide.

CONCLUSION

This study has shown the relationship between morphological, physical, chemical and mineralogical properties of soils in the Lower Central Plain of Thailand.

The results revealed that pyrite was accumulated in the lower part of all profile types, A-D and was associated with plant fragments. Moreover, the development of acid sulfate soil was dependent on the result of the acidification and neutralization. Upon oxidation in soils, pyrite was oxidized and transformed into jarosite.

Jarosite remained in type A, B and D profile soils due to the low amount of neutralizing agents present to react with acidic compounds. In contrast, L9 and L14 profiles, which are transitional soils that have characteristics similar to type C profile soils in that they have low acidity and high alkalinity, did not contain jarosite because any acidic compounds were neutralized and leached out of their soil bodies. However, pyrite in these soils was oxidized and transformed into jarosite temporarily, until it reacted with sufficient neutralizing agents. The most important neutralizing agent was Ca. Excess Ca led to the development of non-acid sulfate soils, whereas relatively low levels of Ca led to the development of transitional soil. Most of the neutralizing agents were derived from the soil solution and clay minerals. Type A, B and D profile soils had high EA, Si, Ti, Al, K and

Cu, which was related to the leaching of alkaline and kaolinite formation. The acidity and alkalinity in soil affected clay mineral formation. The strong acid conditions of acid sulfate soil (types A, B and D profile soils) increased kaolinite formation. Conversely, the alkaline conditions of non-acid sulfate soil (type C profile soils) resulted in the dissolution of Fe, S, Ca, Na, Mg, Mn, Cl, P and Zn into the soil solution and elevated smectite formation. Pyrite had no correlation with the amount of total Fe in soils but had a strong correlation with the total amount of S. Moreover, in each profile type, pyrite was able to be estimated from the total amount of S.

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