www.thaiagj.org *Thai Journal of Agricultural Science 2015, 48(3): 133-146*

Forms of Acidity in Potential, Active and Post-Active Acid Sulfate Soils in Thailand

T. Sukitprapanon[1], A. Suddhiprakarn[1,*], I. Kheoruenromne[1],
S. Anusontpornperm[1] and R.J. Gilkes[2]

[1] *Department of Soil Science, Faculty of Agriculture, Kasetsart University, Bangkok 10900, Thailand*
[2] *School of Earth and Environment, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia*

**Corresponding author, Email: agrals@ku.ac.th*

Abstract

Acidity generated by the oxidation of sulfides, especially pyrite, during development of acid sulfate soils (ASS) has adverse impacts on soil quality and ecosystems. Agricultural use of ASS in Thailand has resulted in widespread development of ASS and associated soil acidity. It is necessary to understand the nature of acidity and change in other properties that occur during the several stages of ASS development. In the present study, we determined the forms of acidity in potential (PASS), active (AASS) and post-active (PAASS) acid sulfate soils from the Lower Central Plain and the Southeast Coast regions of Thailand. The complete suspension peroxide oxidation combined acidity and sulfur method (SPOCAS) was used to measure acidity fractions (actual acidity, sulfidic acidity and retained acidity), reduced-inorganic sulfur and acid-neutralizing capacity (ANC). These ASS do not contain ANC due to the absence of carbonate minerals. pH buffering capacity is provided by the dissolution of phyllosilicate minerals, organic carbon and (hydr)oxide minerals. The amounts of reduced sulfur in PASS and AASS are above the threshold criterion for ASS management planning (300 mg kg^{-1}), but amounts are smaller for PAASS because of their longer history of management. A positive relationship exists between reduced sulfur and sulfidic acidity and a large amount of this acidity is liberated when the soils become oxidized by natural or human-induced drainage. The AASS contain larger amounts of actual acidity compared to PASS and PAASS. Jarosite retains acidity where sulfide oxidation has occurred, especially in the partly oxidized layer of AASS. This research concludes that the soil acidity has been ameliorated by the long term management of ASS which includes liming and periodic flooding.

Keywords: acidity forms, sulfidic materials, SPOCAS, acid sulfate soil development, Thailand

Introduction

Acid sulfate soils (ASS) in a broad sense are soils where sulfuric acid may be produced, is being produced or has been produced by oxidation in amounts which have affected soil characteristics (Pons, 1973).These soils develop under reducing conditions and contain sulfur and iron sulfides especially pyrite. Where these reduced materials are near the soil surface, the soils are considered to be potential acid sulfate soils (PASS). When the materials are exposed to oxidizing conditions by natural (e.g. land uplift, climate change, hydrological environmental change) or human-induced drainage (commonly for farmland or building), oxidation causes sulfuric acid (H_2SO_4) to be produced which decreases the pH of the soil to below 4, creating active acid sulfate soils (AASS) (Fanning, 2012). Post-active acid sulfate soils (PAASS) no longer have sulfidic and sulfuric materials in the solum and have pH values above 4 (Fanning, 2012).

Worldwide ASS occupy approximately 17 million hectares (Andriesse and van Mensvoort, 2006), and are located mostly around the coast under tropical (e.g. Thailand, Vietnam, Malaysia), mediterranean (e.g. Australia) and temperate (e.g. Finland, USA) climates. These soils have been extensively drained and utilized for agricultural purposes (Attanandana and Vacharotayan, 1986; Auxtero and Shamshuddin, 1991; Boman et al., 2010; Gröger et al., 2011; Yvanes-Giuliani et al., 2014). Drainage for agricultural uses has induced the oxidation of pyrite and sulfur and extreme soil acidification may occur. Consequently, potentially toxic elements including Al, As, Cd, Co, Mn, Ni and Zn dissolve and leach into groundwater thereby contaminating drinking water resources with consequent health hazards (Åström, 2001; Sohleniusand Öborn, 2004; Burton et al., 2008; Boman et al., 2010; Nystrand and Österholm, 2013; Yvanes-Giuliani et al., 2014). Acidification kills fish and other biota (McCarthy et al., 2006; Toivonen and Österholm, 2011), damages engineering infrastructures (Dent and Pons, 1995), reduces plant growth (Moore and Patrick 1991) and may adversely affect human health and well-being (Ljung et al., 2009).

Acid sulfate soils in Thailand occupy approximately 8,800 km^2 in the Lower Central Plain with small areas in the Southeast Coast and Peninsular regions (Land Development Department, 2006) (Figure 1). Extensive areas of Thai ASS have been developed over 140 years of agricultural management by drainage, liming, irrigated agriculture and paddy rice cultivation with periodic flooding. This management has caused the transformation of PASS into AASS and eventually into PAASS which may be considered as the mature equilibrium state of the developed ASS (Attanandana and Vacharotayan, 1986). The occurrence of associated PASS, AASS and PAASS in a landscape leads to complex spatial distributions of soil acidity.Soil acidity trends can be consideredwith respect to changes of total actual acidity, potential sulfidic acidity and retained acidity. Total actual acidity is defined as the pool of available acidity (soluble + exchangeable H$^+$) in ASS (Ahern et al., 2004; Vithana et al., 2013; Johnston et al., 2015), while potential sulfidic acidity represents the acidity that would be generated by the oxidation of inorganic sulfur and sulfides by natural or man-made drainage (Ahern et al., 2004; Vithana et al., 2013). Retained acidity is the acidity stored in poorly soluble secondary Fe and Al sulfate minerals such as schwertmannite ($Fe_8O_8(OH)_{4.6}(SO_4)_{1.7}$), jarosite ($KFe_3(SO_4)_2(OH)_6$) and basaluminite ($Al_4(OH)_{10}SO_4.4H_2O$), this acidity is not considered to be readily available but is released slowly by hydrolysis of these minerals (Ahern et al., 2004; Vithana et al., 2013, 2015).

Globally, the area occupied by PAASS is increasingand PAASS will probably become the dominant form of ASS in some regions. Therefore, it is necessary to better understand the forms of acidity present in PAASS and their ASS precursors. This publication identifies forms of soil acidity for the several stages of ASS development. The particular aim of this research is to determine the acidity fractions in potential, active and post-active acid sulfate soils in Thailand as an aid to land management.

Materials and Methods

Soil Sampling

Soils on the Lower Central Plain and the Southeast Coast of Thailand under tropical savanna and tropical monsoon climates, respectively have formed on estuarine sediments deposited during the Holocene epoch (Sinsakul, 2000) (Figure 1). Large areas adjacent to Chao Phraya River were drained for paddy rice cultivation between 1870 and 1889 (Attanandana and Vacharotayan, 1986). Large amounts of lime (mostly dolomitic limestone) has been applied to these soils.

Eighteen study sites representing PASS, AASS and PAASS, situated in these areas, were investigated (Figure 1). The PASS of this study were collected from the Southeast Coast because this type of soils in the Lower Central Plain has been replaced by fish and shrimp ponds as well as rice-based cropping on drained land. The partly oxidized AASS and PAASS study sites are mostly used for paddy rice cultivation which involves drainage and several periods of flooding each year, a process that affects soil properties (Luster et al., 2014). The soil samples were collected in the dry

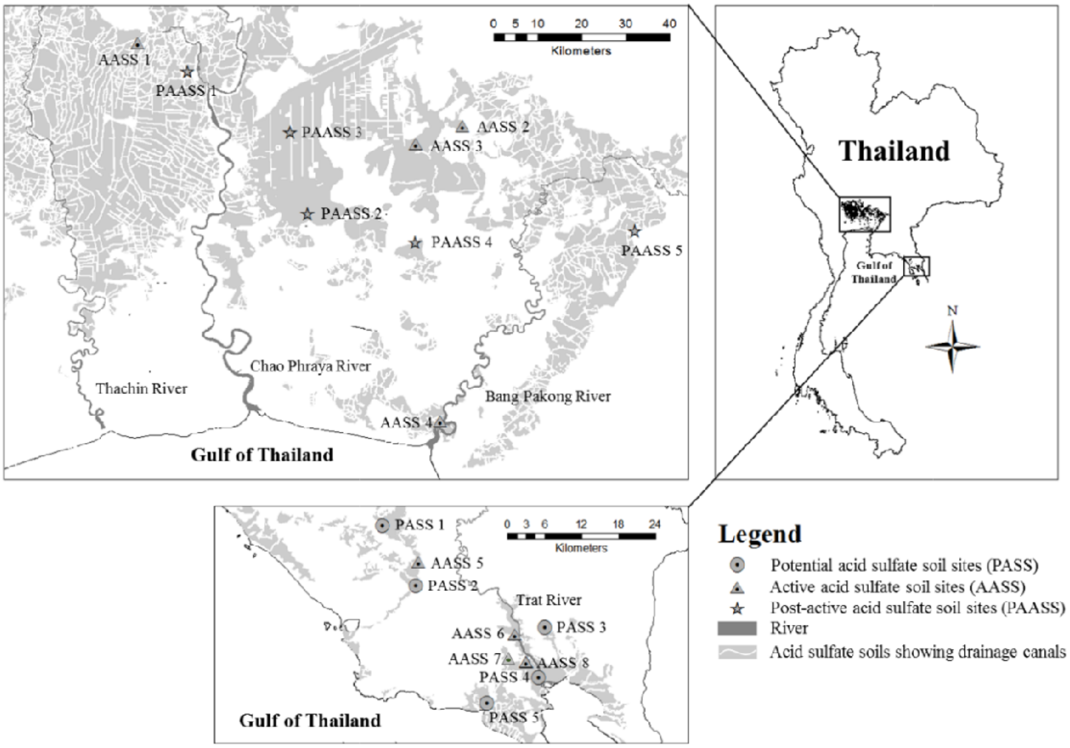

Figure 1 Study sites for potential, active and post-active acid sulfate soils in the Lower Central Plain and the Southeast Coast regions, Thailand.

season between October 2012 and January 2013. They were collected by hand auger to a depth of 2 meters where reduced sediments persist for each type of ASS. The water table for AASS and PAASS was located at approximate 80-100 cm depth in contrast to PASS where the water table is near the soil surface. Soil profiles were classified based on Soil Taxonomy (Soil Survey Staff, 2014). Soil texture ranges from clay to sandy clay loam in the Southeast Coast and clay to silty clay in the Lower Central Plain (Table 1). Soil samples were kept in plastic containers cooled to 4°C to prevent the oxidation of sulfidic materials. The classification of soil profiles into PASS, AASS and PAASS in this research is based on the definition of Fanning (2012). Soil profiles may be divided into distinct layers: topsoil, partly oxidized and reduced layers with only topsoil and reduced layers occurring in PASS.

General Methods

All reagents were analytical grade. Solutions were prepared using deionized (Milli-Q, 18.2 mΩ cm^{-1}) water. Cleaning of all plastic and glassware was in 10% (v/v) nitric acid for at least 24 hours, followed by triplicate rinsing with Milli-Q water. The water content of each sample was determined by measuring weight loss after 24 hours at 105°C, with sample parameters being reported on an oven dry basis.

Analytical Methods

Pore water analysis

The pore water was extracted from the field-moist soil samples with Milli-Q water using 1:2.5 soil to solution (Frankenberger et al., 1996). The pore water was filtered through a syringe driven 0.45 μm filter. The soluble (dissolved) Cl and SO_4 in pore water were determined by ion chromatography (Lachat Instruments Model 8500 Quickchem series 2). Another sample of pore water was acidified with HNO_3 to a pH slightly below 2 and analyzed by ICP-AES for soluble Ca, K, Mg and Na.

Table 1 Site descriptions for Thai potential, active and post-active acid sulfate soils.

ASS type[1]	Location[2]	Classification	Texture[3]	Land Use	Elevation (m) MSL[4]
PASS1	SE	TypicSulfaquent	SCL	Swamp forest	9
PASS2	SE	TypicSulfaquent	C	Swamp forest	1
PASS3	SE	TypicSulfaquent	SCL	Swamp forest	6
PASS4	SE	TypicSulfaquent	SCL	Mangrove, Nipa	8
PASS5	SE	TypicSulfaquent	L	Mangrove forest	2
AASS1	LCP	HydraquenticSulfaquept	C	Paddy rice	6
AASS2	LCP	HydraquenticSulfaquept	SiCL	Paddy rice	3
AASS3	LCP	HydraquenticSulfaquept	SiC	Paddy rice	3
AASS4	LCP	HydraquenticSulfaquept	C	Weeds	2
AASS5	SE	HydraquenticSulfaquept	C	Paddy rice	1
AASS6	SE	HydraquenticSulfaquept	C	Swamp forest	7
AASS7	SE	HydraquenticSulfaquept	L	Paddy rice	5
AASS8	SE	HydraquenticSulfaquept	SL	Paddy rice	2
PAASS1	LCP	SulficEndoaquept	C	Paddy rice	6
PAASS2	LCP	SulficEndoaquept	C	Paddy rice	8
PAASS3	LCP	SulficEndoaquept	SiCL	Paddy rice	3
PAASS4	LCP	SulficEndoaquept	C	Paddy rice	4
PAASS5	LCP	SulficEndoaquept	C	Paddy rice	11

Sampling in the dry season during October 2012 to January 2013; [1]PASS = potential acid sulfate soils; AASS = active acid sulfate soils; PAASS = post-active acid sulfate soils; [2]SE = the Southeast Coast; LCP = the Lower Central Plain; [3]SL = sandy loam, SCL = sandy clay loam, SiCL = silty clay loam,SiC = silt clay, L = loam, C = clay; [4]MSL = mean sea level.

Soil sample analysis

All analyses were determined on field-moist soil samples. Soil color was measured in a field-moist condition using a Munsell Soil Color Chart (Munsell Color, 2000).The redox potential (Eh) of PASS was measured with a calibrated electrode relative to a standard hydrogen electrode and is reported in mV once a steady state value was obtained. The Eh of partly oxidized layers in AASS and PAASS was not measured because they had been partly and inhomogeneously oxidized by drainage for agriculture. Soil pH and electrical conductivity (EC) of saturated paste were measured in the laboratory within 24 hours of collection from the field. pH H_2O was measured in water using a 1:1 soil to water extract (National Soil Survey Center, 2004). pH H_2O_2 was measured in 30 % hydrogen peroxide solution adjusted to pH 5.5 using 1:5 soil to solution (Ahern et al., 2004). Total organic carbon (OC) was determined using a CN analyzer (Elementar, Vario Macro).

The acidity fractions and reduced-inorganic sulfur in soil samples were measured by the complete suspension peroxide oxidation combined acidity and sulfur (SPOCAS) method (Ahern et al., 2004). Titratable potential acidity (TPA) was measured after peroxide oxidation (Ahern et al., 2004). Total actual acidity representing currently available acidity in soils was measured as titratable actual acidity (TAA) by titrating a 1 M KCl suspension of a soil sample using 1:40 soil to solution with NaOH to pH 6.5. Titratable sulfidic acidity (TSA) is the difference between TPA and TAA. The retained acidity (RA), representing the amounts of acidity stored in insoluble sulfate minerals, was determined on the residue after 1 M KCl extraction. The acid-neutralizing capacity (ANC) of soils was determined by a titrimetric method (Ahern et al., 2004). Net acidity is the latent acid-producing capacity of the soils due to the presence of sulfidic materials (Hall et al., 2006; Vithana et al., 2013). Ahern et al. (2004) introduced an approach to calculate the net acidity generating capacity of ASS using the following equation (Eq. 1).

$$\text{Net acidity} = \text{potential sulfidic acidity (TSA)} + \text{actual acidity (TAA)} + \text{retained acidity (RA)} - \text{acid neutralizing capacity (ANC)} \quad (1)$$

Peroxide-oxidizable sulfur (SPOS) is considered to represent reduced inorganic sulfur oxidized when a soil sample is oxidized by a strong oxidizing agent, namely 30 % hydrogen peroxide, adjust to pH 5.5 with dilute NaOH (Ahern et al., 2004).

The pH buffering capacity was determined on field-moist soil by batch titration to produce a titration curve (Prakongkep et al., 2012). Briefly, 25 mL of water or NaOH solution ranging from 0.00001, 0.0006, 0.0018, 0.0048, 0.0072, 0.0144, 0.0432, 0.0576, 0.0720, 0.0864 M were added to 2.5 g field-moist soil sample. Initially, soil samples in centrifuge tubes were treated with 30 % H_2O_2 adjusted to pH 5.5 to oxidize sulfide minerals, sulfur and organic matter. Samples in the batch titration were shaken for 15 minutes and pH was measured immediately. The alkali required to change the pH of H_2O_2oxidized soil to its original pH H_2O value is a measure of the acidity produced by oxidation. Finally, pH buffering capacity was calculated from the slope of the plot of OH^- added versus soil pH H_2O_2. All data were log transformed to meet the requirement of normality for regression analysis ($P < 0.05$).

Mineralogical analysis

X-ray diffraction of hand-picked materials was performed on randomly oriented powder samples on a low background holder in order to detect if jarosite and other minerals that contribute to retained acidity. Patterns were scanned between 3 and 70° 2θ with 0.02° 2θ step size at scan speed 0.02° 2θ per second using CuKα radiation. The morphology and composition of minerals occurring in hand-picked materials was determined by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS; TESCAN VEGA3, 15kV) on specimens on aluminum stubs coated with carbon.

Results and Discussion

Soil Characteristics

Acid sulfate soils in the Lower Central Plain and the Southeast Coast of Thailand which have been utilized for farmland are similar in morphology and properties to comparable ASS in other countries including Australia, Finland, Sweden, Vietnam, Malaysia and USA (Auxtero and Shamshuddin, 1991; Sohlenius and Öborn, 2004; Boman et al., 2010; Gröger et al., 2011; Yvanes-Giuliani et al., 2014).

Soil profile characteristics are shown in Table 2. The study sites have been mainly utilized for paddy rice growing, apart from PASS sites which are in waterlogged swamps or mangrove environments. The PASS were classified as Typic Sulfaquents, whereas the AASS and PAASS were classified as Hydraquentic Sulfaquepts and Sulfic Endoaquepts, respectively (Table 1).

Table 2 Morphology and typical chemical properties of Thai potential, active and post-active acid sulfate soils

Type[1]	Layer	Depth (cm)[2]	pH H_2O	pH H_2O_2	Eh (mv)	Munsell color (moist)
PASS	Topsoil	0-20	5.1	2.3	149	2.5Y 4/2 (dark grayish brown)
	Reduced	20-200	5.8	1.7	-33	Gley1 4/10Y (dark greenish gray)
AASS	Topsoil	0-21	3.6	2.1	-	2.5Y 2.5/1 (black); 2.5Y 5/3 (light olive brown)
	Partly oxidized	21-170	3.7	2.3	-	2.5Y 5/3 (light olive brown); 2.5Y 6/8 (olive yellow); 2.5Y 7/8 (yellow)
	Reduced	170-200	4.7	2.3	-203	2.5Y 4/1 (dark gray)
PAASS	Topsoil	0-17	4.5	2.4	-	10YR 3/2 (very dark grayish brown); 5YR 4/4 (reddish brown)
	Partly oxidized	17-170	4.1	2.4	-	2.5Y 5/1 (reddish gray); 10R 3/6 (dark red); 10R 4/8 (red); 2.5Y 8/8 (yellow)
	Reduced	170-200	5.0	1.8	-73	2.5Y 4/1 (dark gray)

[1] PASS = potential acid sulfate soils; AASS = active acid sulfate soils; PAASS = post-active acid sulfate soils.

[2] The reduced layer in PASS, AASS and PAASS is located well below the water table at approximately 80-100 cm

The PASS profiles consist of a partly oxidized topsoil layer and a waterlogged reduced layer, while AASS and PAASS profiles contain three distinct layers. The topsoil layer of all three types of ASS is dark grayish brown to very dark grayish brown and is OC rich (median 39, 27 and 24 g kg^{-1} for PASS, AASS and PAASS, respectively) (Table 3). The partly oxidized layer in AASS and PAASS is characterized by yellow and red redox concentrations due to jarosite and iron (hydr)oxides, respectively. The AASS contain more yellow redox concentrations in the upper horizon than do the PAASS which contain more red redox concentrations. The waterlogged reduced layer situated below approximately 80-100 cm depth in AASS and PAASS and below 20 cm in PASS consists of gray sediment with an Eh value ranging from -203 to -33 mV.

Soil and Pore Water Chemical Properties

The pH H_2O of PASS, AASS and PAASS increases with depth to where a highly reducing condition is dominant in the waterlogged layer (Table 2).The pH H_2O_2 for these three types of soil is lower than the pH H_2O because of the oxidation by H_2O_2 of iron sulfides, sulfur and organic matter (Table 2).The pH H_2O of soils varies with the extent of soil development. The lowest pH H_2O values down to 3.6 in the topsoil of the AASS and above 4 for the PAASS are due to acidity derived from the oxidation of pyrite and sulfur or the hydrolysis of iron (hydr)oxides. Some acidity in AASS and PAASS has been neutralized by liming and drainage, this management extending over many years for PAASS.

The change of soil pH with inputs of acidity depends on the pH buffering capacity and ANC of soils which together control the dynamics of acidification (Hartikainen, 1996). Most Thai ASS do not contain ANC from carbonate but the soils have a significant pH buffering capacity (Table 3) which can be attribute to the dissolution of clay minerals and ion exchange by clay minerals and organic matter (Totsche et al., 2003; Khawmee et al., 2013; Bibi et al., 2014; Whitworth et al., 2014). Bibi et al. (2014) suggested that dissolution of clay minerals could be the most significant contributor to ANC in those wetland sediments with little or no carbonate mineral content. Weber et al. (2005) reported that dissolution of Al and Fe from clay minerals and oxides did not provide ANC because of the possibility that acidity would be released via hydrolysis of these elements. However, the complete hydrolysis of Al and Fe would take place in the pH range 4-5 and above 4, respectively (Weber et al., 2005; Bibi et al., 2014). The pH of topsoil and partly oxidized layers of the AASS is less than 4, whereas in the PAASS, it ranges from 4-5 (Table 2) which indicates that the acidity released by the hydrolysis of Al and Fe (hydr)oxides is low. Therefore, it is suggested that the pH buffering capacity of Thai ASS, especially PAASS which have been managed for a long period of time, is not due to native carbonate but is derived from the dissolution of silicates and exchange onto clay minerals, organic carbon and some (hydro)oxide minerals. However, addition of lime to topsoil is commonly used in the management of ASS thereby providing ANC.

The median EC of topsoil and reduced layers of the PASS is 26 and 29 dS m^{-1}, respectively. The EC values of topsoil, partly oxidized and waterlogged reduced layers of the AASS are 4.8, 7.5 and 12 dS m^{-1}, values for the PAASS are about one third those of AASS (Table 3). The concentration of Cl declines with the extent of ASS development from PASS through AASS to PAASS (Table 3).The amounts of soluble SO_4, Na, K, Mg and Ca in pore water normalized to the Cl concentration can be used to distinguish the influence of land management practices involving drainage and addition of lime and to indicate pyrite oxidation and pedogenic processes (Vuai et al., 2003; Mosley et al., 2014a). The ratios of soluble elements to the concentration of Cl are presented in Table 4.

The median SO_4/Cl ratio in the PASS is less than 0.50 indicating that the major source of sulfate is seawater, while the ratio for the AASS and the PAASS is greater than 0.50 indicating that sulfate may have originated from the oxidation of iron sulfides (Mulvey, 1993), the dissolution of jarosite (Mosley et al., 2014b) or the dissolution of gypsum (Bolan et al., 1991) (Table 4). The SO_4/Cl ratio value follows the sequence PAASS < AASS < PASS which is a result of the higher degree of soil development reducing the residual effect of seawater.

Table 3 Median and range (in parenthesis) of chemical properties of topsoil, partly oxidized and reduced layers of PASS, AASS and PAASS

Property[1]	PASS[b]		AASS[b]			PAASS[b]		
	Topsoil n = 5	Reduced n = 20	Topsoil n = 8	Partly oxidized n = 24	Reduced n = 8	Topsoil n = 5	Partly oxidized n = 16	Reduced n = 4
OC	39	23	27	7.5	9.1	24	4.9	14
(g kg^{-1})	(18-45)	(8.3-66)	(15-54)	(3.2-23)	(1.5-20)	(13-27)	(2.1-14)	(12-18)
EC	26	29	4.8	7.5	12	1.8	2.4	9.2
(dS m^{-1})	(1.7-74)	(1.1-59)	(1.1-13)	(1.1-20)	(2.8-28)	(1.0-4.3)	(0.92-4.9)	(6.7-11)
Soluble Cl	1,922	3,493	1,117	1,022	1,795	47	98	111
(mg kg^{-1})	(885-4,784)	(408-6,183)	(14-2,712)	(12-3,003)	(32-3,605)	(21-279)	(17-353)	(17-189)
Soluble Na	2,581	2,693	568	711	1,374	159	225	621
(mg kg^{-1})	(94-10,096)	(70-7,504)	(64-2,646)	(68-3,463)	(115-4,866)	(72-424)	(89-652)	(389-798)
Soluble K	158	94	40	38	67	7.7	26	80
(mg kg^{-1})	(21-680)	(3.8-433)	(14-113)	(12-159)	(34-324)	(5.5-29)	(10-60)	(21-137)
Soluble Mg	395	500	158	106	346	49	55	576
(mg kg^{-1})	(49-1,806)	(25-1,455)	(51-446)	(33-1,248)	(46-2,332)	(20-130)	(25-384)	(228-709)
Soluble Ca	240	277	160	95	227	146	76	767
(mg kg^{-1})	(54-882)	(30-851)	(73-344)	(25-2,575)	(39-2,058)	(53-189)	(54-2,385)	(308-1,267)
Soluble SO_4	841	1,484	588	701	1,197	359	438	904
(mg kg^{-1})	(310-4,218)	(101-5,560)	(234-1,772)	(315-4,005)	(404-6,222)	(187-530)	(186-1,034)	(81-1,859)
ANC	0	0	0	0	0	0	0	0
(% $CaCO_3$)								
Net acidity	2,100	16,097	2,710	2,325	4,618	577	1,635	10,133
(mg S kg^{-1})	(160-3,239)	(577-62,017)	(1,058-6,221)	(609-5,147)	(834-2,469)	(385-2,325)	(90-5,131)	(465-18,663)
pH Buffer	54	50	66	24	37	58	17	48
	(48-68)	(25-205)	(48-131)	(14-62)	(26-135)	(42-87)	(10-30)	(30-126)

[1] OC = organic carbon; EC = electrical conductivity, ANC = acid neutralizing capacity, pH Buffer = pH buffering capacity (mmol OH$^-$ kg^{-1} pH^{-1}).

[2] PASS = potential acid sulfate soils, AASS = active acid sulfate soils, PAASS = post-active acid sulfate soils.

Table 4 Median and range (in parenthesis) of water soluble ion ratios for topsoil, partly oxidized and reduced layers of PASS, AASS and PAASS.

Type[1]	Layers	SO_4/Cl	Na/Cl	K/Cl	Mg/Cl	Ca/Cl
PASS	Topsoil	0.31	1.4	0.09	0.17	0.09
	(n = 5)	(0.17 - 2.2)	(0.11 - 3.0)	(0.02 - 0.16)	(0.06 - 0.45)	(0.05 - 0.23)
	Reduced	0.48	0.73	0.03	0.17	0.10
	(n = 20)	(0.15 - 5.9)	(0.10 - 8.2)	(0.00 - 0.39)	(0.05 - 1.4)	(0.02 - 0.61)
AASS	Topsoil	1.6	1.1	0.05	0.26	0.17
	(n = 8)	(0.09 - 34)	(0.40 - 8.1)	(0.03 - 1.0)	(0.11 - 4.9)	(0.06 - 24)
	Partly oxidized	1.4	0.78	0.07	0.26	0.19
	(n = 24)	(0.25 - 69)	(0.30 - 7.9)	(0.02 - 2.9)	(0.03 - 21)	(0.02 - 203)
	Reduced	1.3	1.1	0.07	0.25	0.20
	(n = 8)	(0.21 - 29)	(0.58 - 3.6)	(0.03 - 2.1)	(0.03 - 6.6)	(0.02 - 17)
PAASS	Topsoil	8.4	3.4	0.26	1.3	3.1
	(n = 5)	(1.5 - 13)	(0.39 - 19)	(0.02 - 1.3)	(0.17 - 5.8)	(0.47 - 8.5)
	Partly oxidized	4.5	2.4	0.26	0.54	0.83
	(n = 16)	(2.4 - 49)	(1.1 - 13)	(0.10 - 2.3)	(0.16 - 21)	(0.30 - 124)
	Reduced	6.4	10	1.6	4.9	6.1
	(n = 4)	(2.1 - 76)	(3.2 - 23)	(0.11 - 3.6)	(3.2 - 32)	(4.1 - 74)
Seawater[2]		0.14	0.56	0.02	0.07	0.02

[1] PASS = potential acid sulfate soils; AASS = active acid sulfate soils; PAASS = post-active acid sulfate soils.

[2] Data from Holland (1978). In ion ratio calculation, ion concentrations were expressed as mg kg^{-1}

The median Ca/Cl and Mg/Cl values for the PASS are slightly higher than for seawater, while for the AASS and PAASS values are much greater than for seawater (Table 4). This suggests that the elevated concentrations of Ca and Mg in both AASS and PAASS are derived from the addition of dolomiticlime and the dissolution of gypsum ($CaSO_4.2H_2O$) which is present in the partly oxidized layer of soil profiles (Figure 2).

The ratio of soluble Na to Cl in the PASS, AASS and PAASS increases relative to seawater. Two possible processes by which additional Na can be contributed to soil solution are desorption from clay minerals and dissolution of natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) (Vuai et al., 2003; Mosley et al., 2014a). When Ca is added to soil by liming, Ca can replace some exchangeable Na on clay minerals (Vuai et al., 2003). The SEM/EDS analysis shows that Na is present in clay minerals (Figure 2) and jarosite (Figure 8). Potassium (K) in the jarosite structure has been substituted to about 15 mole% by Na to produce Na-substituted jarosite ($Na_{0.1}K_{0.9}Fe_3(SO_4)_2(OH)_6$) (Figure 8).Mosley et al. (2014a) suggested that natrojarosite could dissolve at low pH and released Na into soil solution.

The soluble K/Cl ratio in the PASS, AASS and PAASS is higher than that of seawater because K is released from dissolution of illite in acidic conditions (Bibi et al., 2014) and from dissolution of jarosite (Smith et al., 2006).The concentrations of soluble Na, K, Mg and Ca in the reduced layer of the AASS and PAASS are higher than in the overlying partly oxidized horizon because of downward diffusion and leaching.

Distribution of Sulfidic Materials in Thai Acid Sulfate Soils

The distribution of sulfidic materials in the PASS, AASS and PAASS as indicated by peroxide-oxidizablesulfur (SPOS) is shown in Figure 3. The concentrations of SPOS in the topsoil and partly oxidized layers of the PASS, AASS and PAASS are in the sequence PASS > AASS > PAASS indicating that a long period of soil oxidation induced by man-made regional drainage, together with liming and cyclical drainage for paddy rice cultivation can significantly affect the pyrite content of these soil profiles (Figure 3). The soluble sulfate concentration has a positive relationship with SPOS for the waterlogged reduced layer ($R^2 = 0.43$) but there is no systematic relationship for the topsoil and partly oxidized layer (Figure 4). The occurrence of soluble sulfate in an anoxic horizon indicates that it was derived from seawater or from the upper oxic horizon as mentioned above. A concentration of SPOS higher than 300 mg kg^{-1} is considered to be indicative of ASS in coastal plain systems (Stone et al., 1998), while a more conservative value (200 mg kg^{-1}) for SPOS has been proposed for the presence of sulfidic sediments in inland ASS (Hall et al., 2006).According to the requirements of management and development planning, the risk threshold for coastal ASS has been established at 300 mg kg^{-1} SPOS which represents 18 mol H^+ if 1 tonne of soil is fully oxidized (Stone et al., 1998). In this study, we found that the PASS and AASS contain more than 300 mg kg^{-1} SPOS which will result in substantial acidification of the soils. Although the PAASS have experienced a long period of management, the soils retain amounts of oxidizeablesulfur up to 300 mg kg^{-1} in the topsoil and 100 mg kg^{-1} in the partly oxidized layer (Figure 3). Additionally, this study clearly demonstrates that the reclamation of ASS does not affect sulfidic materials in the underlying reduced layer of the AASS and PAASS. (Figure 3).

Variation of the Forms of Acidity in Thai Acid Sulfate Soils

Titratable actual acidity

The various acidity forms in the PASS, AASS and PAASS are shown in Figure 5. The titratable actual acidity (TAA) in surface soil of PASS (median 241 mg kg^{-1}) is interpreted as being due to the oxidation of sulfide minerals induced by lowering of water table by natural processes. Willett and Walker (1982) and Smith et al. (2003) reported that the acidity of floodplain ASS in New South Wales, Australia was influenced by oxidation controlled by topography and natural drainage. In addition, the oxidation of sulfidic materials may occur due to the lowering of water table due to evapotranspiration during extreme drought. The presence of much TAA in surface soil of the PASS clearly indicates that considerable acidity was present in the PASS before drainage of the land for agricultural uses produced AASS and PAASS.

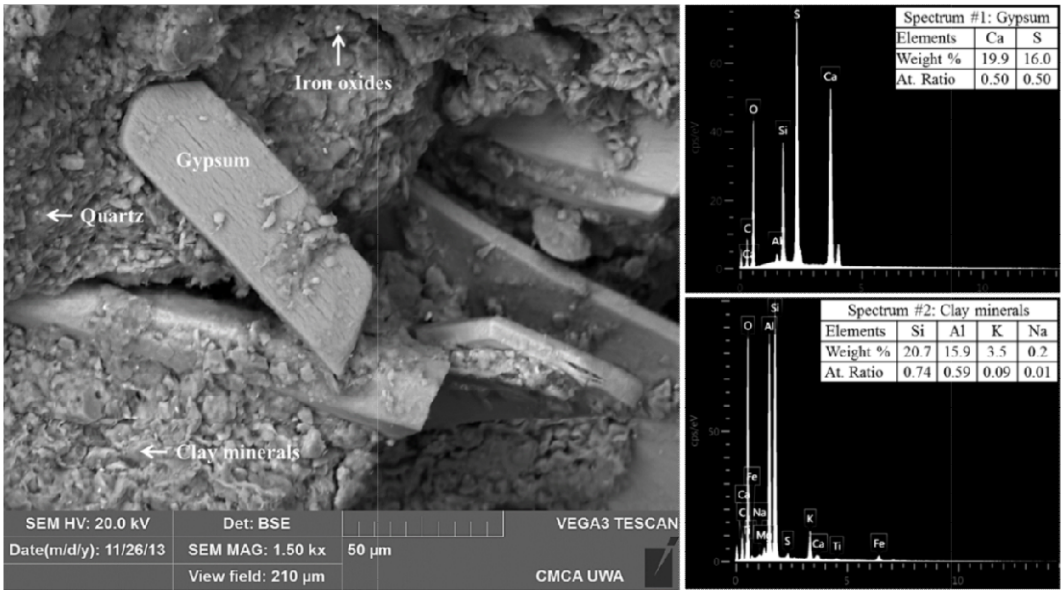

Figure 2 Backscattered electron micrograph with energy dispersive spectra showing large euhedral crystals of gypsum (spectrum 1) with small quartz (Si) crystals on their surfaces in a matrix of clay minerals (spectrum 2) and iron oxides in the partly oxidized layer of an active acid sulfate soil

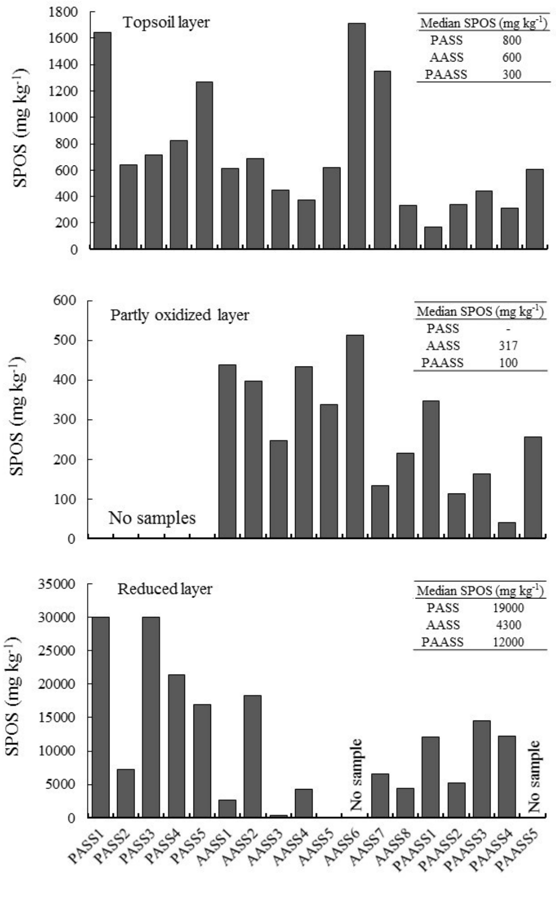

Figure 3 Peroxide-oxidizable sulfur (SPOS) (mg kg^{-1}) in topsoil, partly oxidized and reduced layers of potential (PASS), active (AASS) and post-active (PAASS) acid sulfate soils in Thailand

The concentrations of TAA in the surface soil of the AASS are about three times greater than for the PASS and are about two times higher than for the PAASS. The TAA in topsoil of the PAASS (median 417 mg kg^{-1}) is about half that for the AASS because the PAASS have been managed by liming and drainagefor a long period of time.The greater TAA in the reduced horizons of the PASS (median 1,090 mg kg^{-1}) and PAASS (median 1,619 mg kg^{-1}) are due to the downward flow of oxidation products from topsoil to deeper horizons. The particular management of AASS in Thailand has included liming, drainage and periodic flooding for paddy rice for over a century and this management has affected the amounts of actual acidity including soluble and exchangeable acidity in the PAASS. In the future, as developed ASS become more mature under appropriate management, the potential toxicity due to actual acidity may decline.This will be a worldwide phenomenon where similar land management regimes are applied to ASS.

Titratablesulfidic acidity

The concentrations of titratablesulfidic acidity (TSA) in the surface soil (median 1,315 mg kg^{-1}) and waterlogged reduced layer (median 15,232 mg kg^{-1}) of the PASS are greater than values for the AASS and PAASS indicating that the PASS will

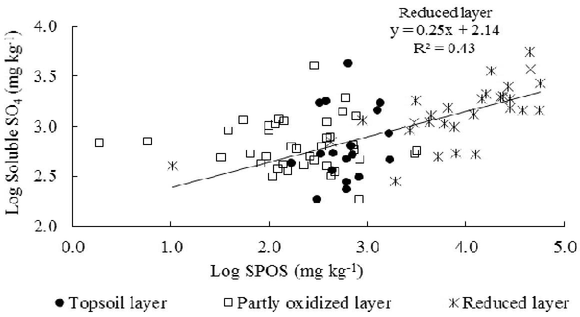

Figure 4 A plot of log soluble SO_4 (mg kg^{-1}) versus log peroxide-oxidizable sulfur (SPOS) (mg kg^{-1}) for topsoil (no relationship), partly oxidized (no relationship) and reduced (regression line shown) layers of potential, active and post-active acid sulfate soils.

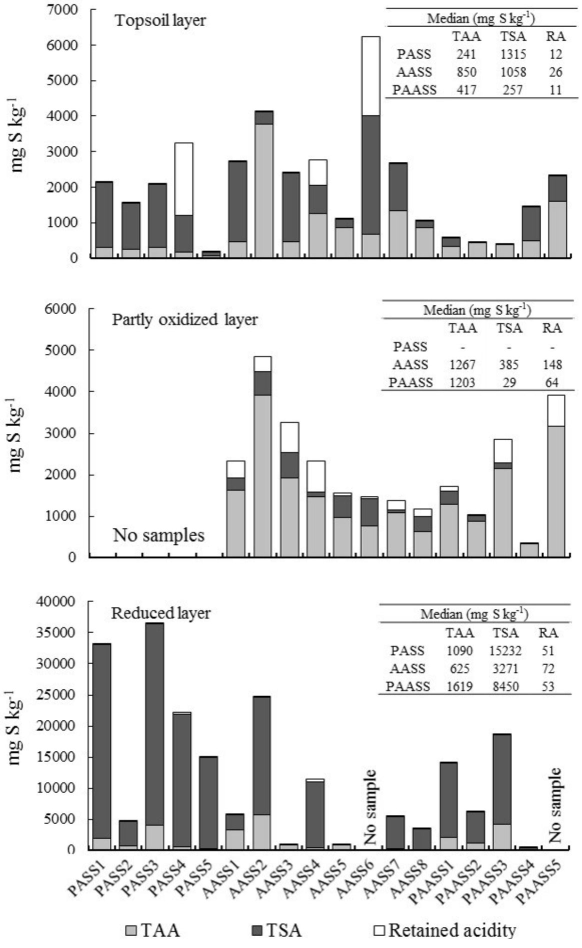

Figure 5 Distribution of titratable actual acidity (TAA), titratablesulfidic acidity (TSA) and retained acidity (RA) in potential (PASS), active (AASS) and post-active (PAASS) acid sulfate soils of Thailand

produce more acidity than the AASS and PAASS as the soils are developed. The TSA value of the PASS, AASS and PAASS is strongly associated with SPOS (R^2 = 0.80) (Figure 6). Although, the surface soil of the AASS and PAASS has been disturbed and managed for a long period of time, the TSA content of this layer (median 1,058 and 257 mg kg^{-1} for AASS and PAASS, respectively) is higher than that of the underlying partly oxidized layer. Ahern et al. (2004) reported that SPOCAS gives a measurement of the maximum oxidizable sulfur, usually predominantly sulfides, present in a soil sample using a chemical oxidizing condition, consequently the TSA and SPOS results may include some acidity and sulfur from the organic fraction in surface soil with its considerable organic matter content. The acidity and sulfate can be released from schwertmannite and jarosite during peroxide oxidation. However, natural schwertmannite and jarosite seem to be more stable during this procedure compared to synthesized minerals (Vithana et al., 2013).

According to this research, the surface soil in the AASS and PAASS in agricultural and swamp forest areas, respectively, contain higher amounts of TSA than is present in the partially oxidized layer indicating that the TSA in surface soil does not mainly originate from sulfidic materials. It is predominantly due to oxidation of soil organic matter derived from swamp vegetation and crop residues added into agricultural surface soils. The amount of acidity derived from the oxidation of sulfide in topsoil and partly oxidized layers of the PAASS is less than 300 mg kg^{-1} (18 mol H^+ t^{-1}) indicating that the risk of additional acidification of mature PAASS by drainage is low.

Retained acidity

The median values of retained acidity (RA) of the AASS are 26, 148 and 72 mg kg^{-1} for topsoil, partly oxidized and reduced layers, respectively and are greater than for the PASS and PAASS.The elevated concentrations of RA in the AASS are associated with yellow redox concentrations of jarosite ($KFe_3(SO_4)_2(OH)_6$) which was identified by XRD (Figure 7) and SEM/EDS (Figure 8). Additionally, PASS4 has elevated values of RA in surface soil because of oxidation induced by partial drainage or

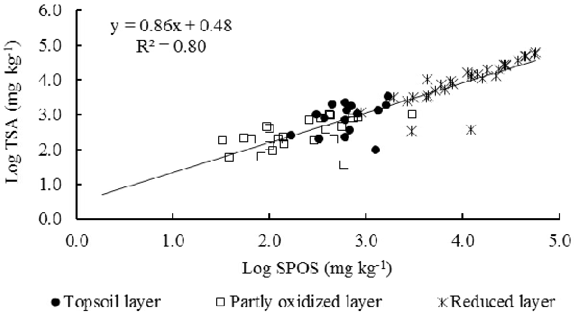

Figure 6 Bivariate relationship between log peroxide-oxidizable sulfur (SPOS) (mg kg^{-1}) and log titratablesulfidic acidity (TSA) (mg kg^{-1}) in topsoil, partly oxidized and reduced layers of Thai potential, active and post-active acid sulfate soils

drying. Jarosite appears to be a major source of retained acidity in the ASS on the Lower Central Plain and the Southeast Coast regions of Thailand.

The dissolution rate of jarosite in sulfuric acid solution at pH 3 and in water is approximately 0.25 and 1.1 μmol g^{-1} day^{-1}, respectively (Welch et al., 2008). Jarosite is stable under oxic, acidic (pH 1-3) and sulfate rich conditions (Smith et al., 2006) but under other conditions acidity will be generated by the dissolution and hydrolysis of jarosite (Eq. 2), especially when pH is raised by lime addition (Hall et al., 2006; Welch et al., 2007, 2008; Mosley et al., 2014b) or by flooding in order to prevent further oxidation of pyrite (Eq. 3) (White et al., 1997).

$$\underset{\text{Jarosite}}{KFe_3(SO_4)_2(OH)_6 + 3H_2O} \longrightarrow \underset{\text{Iron hydroxides}}{3Fe(OH)_3 + K^+ + 3H^+ + 2SO_4^{2-}} \qquad (2)$$

$$\underset{\text{Pyrite}}{FeS_2 + 14Fe^{3+} + 8H_2O} \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (3)$$

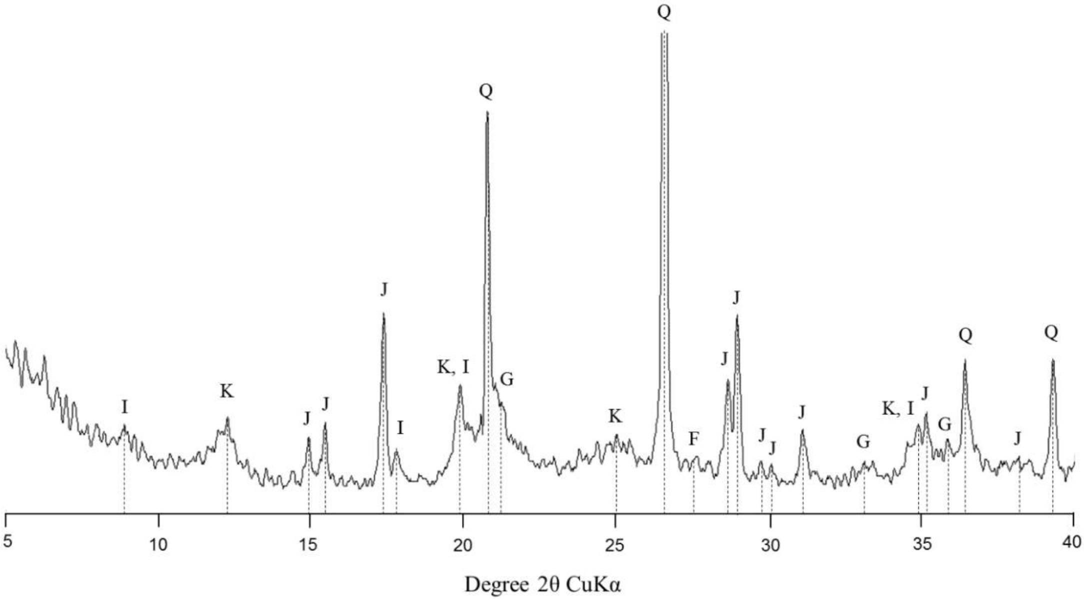

Figure 7 Random powder X-ray diffraction pattern of a yellow redox concentration on a low background holder. The material is from the partly oxidized layer in an active acid sulfate soil, F = Feldspars, G = Goethite, I = Illite, J = Jarosite, K = Kaolinite, Q = Quartz

Singer and Stumm (1970) suggested that release of dissolved ferric iron can be a vital factor in controlling the oxidation of sulfides and the acidity generated under reducing conditions as it contributes more acidity than the reaction with oxygen (Eq. 3). This study indicates that periodic flooding for paddy rice growing combined with liming of ASS, especially the AASS where jarosite is dominant, will stimulate the dissolution of jarosite and induce the oxidation of residual sulfides.

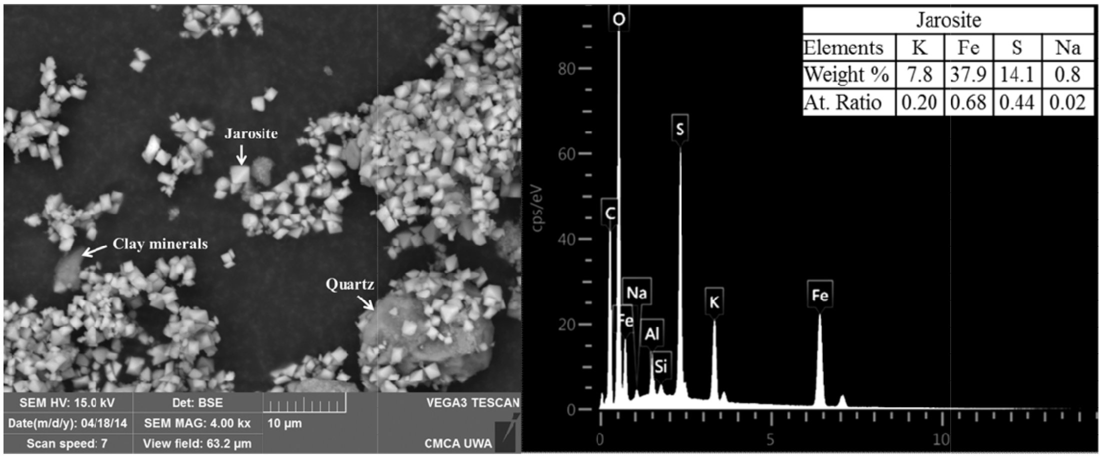

Figure 8 Backscattered electron micrograph of crystals of jarosite, clay minerals and quartz in a yellow redox concentration in the partly oxidized layer of an active acid sulfate soil and energy dispersive spectrum for jarosite which contains minor Na substitution for K

Management Implications

This research provides a better understanding of the nature of acidity in potential, active and post-active acid sulfate soils. Thai ASS have been drained and periodically flooded over one hundred and forty years for paddy rice production which has generated a large area of PAASS which is expected to increase. This is likely to be a global phenomenon. Our results show that the PASS, AASS and PAASS in the Lower Central Plain and the Southeast Coast of Thailand have amounts of net acidity exceeding 300 mg kg^{-1} (18 mol H^{+} t^{-1}) which is the criterion for acidification risk used in ASS management planning where soils are oxidized by natural or human-induced drainage. The elevated amounts of reduced-sulfur in the PASS can result in a significant acidification when they become oxidized. There are large amounts of TAA in the AASS, especially in the partly oxidized layer. The long term management of Thai AASS and PAASS has changed the oxidizing layers of the soil profile but has not materially affected the underlying reduced zone. Jarosite retains acidity in Thai ASS and it is dissolved during the soil management regime that involves liming, drainage and cyclical flooding. It is likely that further drainage and liming to increase pH to approximately 6 in the AASS and PAASS will decrease the acidity generated from the dissolution of jarosite and the oxidation of residual sulfides. This particular management practice causes the dissolution of bright yellow jarosite which transforms to goethite and hematite in orange/red redox concentrations in the partly oxidized layer.

Acknowledgments

The authors acknowledge the Royal Golden Jubilee Ph.D. Program under Thailand Research Fund and Kasetsart University for financial support. We sincerely acknowledge the kind assistance from Rathanon Jaroenchasri and Rachan Leotphayakkarat from the Department of Soil Science, Kasetsart University, Michael Smirk and Kim Duffecy from the School of Earth and Environment and staff from the Center for Microscopy, Characterisation and Analysis, the University of Western Australia.

References

Ahern, C.R., A.E. McElnea and L.A. Sullivan. 2004. Acid Sulfate Soils Laboratory Methods Guidelines. Queensland Department of Natural Resources, Mines and Energy: Indooroopilly, Queensland.

Andriesse, W. and M.E.F. van Mensvoort. 2006. Acid sulfate soils: distribution and extent, pp. 14-19. In R. Lal, ed., Encyclopedia of Soil Science. CRC Press: Boca Raton, Florida.

Åström, M. 2001. Effect of widespread severely acidic soils on spatial features and abundance of trace elements in streams. J. Geochem. Explor. 73: 181-191.

Attanandana, T. and S. Vacharotayan. 1986. Acid sulfate soils: their characteristic, genesis, amelioration and utilization. Southeast Asian Studies. 24: 154-180.

Auxtero, E.A. and J. Shamshuddin. 1991. Growth of oil palm (*Elaeisguineensis*) seedling on acid sulfate soils as affected by water regime and aluminium. Plant and Soil 137: 243-257.

Bibi, I., B. Singh and E. Silvester. 2014. Dissolution kinetics of soil clays in sulfuric acid solutions: ionic strength and temperature effects. Appl. Geochem. 51: 170-183.

Bolan, N.S., J.K. Syers and M.E. Sumner. 1991. Dissolution of various sources of gypsum in aqueous solutions and in soil. J. Sci. Food. Agric. 57: 527-541.

Boman, A., S. Fröjdö, K. Backlund and M.E. Åström. 2010. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. Geochim. Cosmochim. Acta. 74: 1268-1281.

Burton, E.D., R.T. Bush, L.A. Sullivan, S.G. Johnston and R.K. Hocking. 2008. Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. Chem. Geol. 253: 64-73.

Dent, D.L. and L.J. Pons. 1995. A world perspective on acid sulphate soil. Geoderma 67: 263-276.

Fanning, D.S. 2012. Acid sulfate soils, pp. 26-30. In S.R. Jorgensen, ed., Encyclopedia of Environmental Management. Taylor and Francis, New York.

Frankenberger, W.T., M.A. Tabatabai and D.C. Adriano. 1996. Bromine, chloride, and fluorine, pp. 449-493. In D.L. Spark, P.A. Helmke, R.H. Poeppert, P.N. Soltanpour, M.A. Tabatabai, C.T. Johnston, M.E. Summer, eds., Methods of soil analysis, part 3: chemical methods. SSSA Book Series, Madison, Wisconsin.

Gröger, J., U. Proske, T.J.J. Hanebuth and K. Hamer. 2011. Cycling of trace metals and rare earth elements (REE) in acid sulfate soils in the Plain of Reeds, Vietnam. Chem. Geol. 288: 167-177.

Hartikainen, H. 1996. Soil response to acid percolation: acid-base buffering and cation leaching. J. Environ. Qual. 25: 638-645.

Hall, K.C., D.S. Baldwin, G.N. Rees and A.J. Richardson. 2006. Distribution of inland wetlands with sulfidic sediments in the Murray-Darling Basin, Australia. Sci. Total Environ. 370: 235-244.

Holland, H.D. 1978. The Chemistry of The Atmosphere and Ocean. A Wiley-Interscience Publication, John Wiley & Sons.

Johnston, S.G., E.D. Burton, R. Hagan, T. Aaso and G. Tuckerman. 2015. A revised method for determining existing acidity in re-flooded acid sulfate soils. Appl. Geochem. 52: 16-22.

Khawmee, K., A. Suddhiprakarn, I. Khworuenromne, I. Bibi and B. Singh. 2013. Dissolution behavior of soil kaolinites in acidic solutions. Clay Miner. 48: 447-461.

Land Development Department. 2006. Acid Sulfate Soil Distribution Map of Thailand, 1:2 500 000, Land Development Department, Ministry of Agriculture and Cooperatives, Bangkok.

Ljung, K., F. Maley, A. Cook and P. Weinstein. 2009. Acid sulfate soils and human health-amillennium ecosystem assessment. Environmen International 35: 1234-1242.

Luster, J., K. Kalbitz, B. Lennartz and J. Rinklebe. 2014. Properties, processes and ecological functions of floodplain, peatland, and paddy soils. Geoderma 228-229: 1-4.

McCarthy, B., A. Conallin, P. D'Santos and D.S. Baldwin. 2006. Acidification, salinization and fish kills at an inland wetland in south-eastern Australia. Ecol. Manage. Restor. 7: 221-223.

Moore, P.A. and W.H. Patrick. 1991. Aluminum, boron and molybdenum availability and uptake by rice in acid sulfate soils. Plant and Soil 136: 171-181.

Mosley, L.M., P. Shand, P. Self and R. Fitzpatrick. 2014a. The geochemistry during management of lake acidification caused by the rewetting of sulfuric (pH < 4) acid sulfate soils. Appl. Geochem. 41: 49-61.

Mosley, L.M., R.W. Fitzpatrick, D. Palmer, E. Leyden and P. Shand. 2014b. Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought. Sci. Total Environ. 485-486: 281-291.

Mulvey, P.J. 1993. Pollution prevention and management of sulfidic clays and sands, pp. 116-129. In R. Bush, ed., Proceeding of The National Conference on Acid Sulfate Soils. Wollongbar, New South Wales.

Munsell Color. 2000. Munsell Soil Color Charts. GretagMacbeth, New Windsor, New York.

National Soil Survey Center. 2004. Soil survey field and laboratory methods manual: soil survey investigation. United States Department of Agriculture, Natural Resources Conservation Service, Washington DC.

Nystrand, M.I., P. Österholm. 2013. Metal species in a Boreal river system affected by acid sulfate soils. Appl. Geochem. 31: 133-141.

Pons, L.J. 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils, pp. 3-27. In H. Dost, ed., Proceeding of The International symposium on Acid Sulfate Soil. ILRI Publication, Wageningen, the Netherlands.

Prakongkep, N., R.J. Gilkes, B. Singh and S. Wong. 2012. Pyrite and other sulphur minerals in giant aquicspodosols, Western Australia. Geoderma 181-182: 78-90.

Singer, P.C. and W. Stumm. 1970. Acidic mine drainage: rate-determining step. Science 167: 1121-1124.

Sinsakul, S. 2000. Late Quaternary geology of the Lower Central Plain, Thailand. J. Asian Earth Sci. 18: 415-426.

Smith, A.M.L., K.A. Hudson-Edwards, W.E. Dubbin and K. Wright. 2006. Dissolution of jarosite [$KFe_3(SO_4)_2(OH)_6$] at pH 2 and 8: insights from batch experiments and computational modelling. Geochim. Cosmochim. Acta 70: 608-621.

Smith, J., P. van Oploo, H. Marston, M.D. Melville and B.C.T. Macdonald. 2003. Spatial distribution and management of total actual acidity in an acid sulfate soil environment, McLeods Creek, northeastern NSW, Australia. Catena 51: 61-79

Sohlenius, G. and I. Öborn. 2004. Geochemistry and partitioning of trace metals in acid sulphate soils in Sweden and Finland before and after sulphide oxidation. Geoderma 122: 167-175.

Soil Survey Staff. 2010. Key to Soil Taxonomy. United State Department of Agriculture, Natural Resource Conservation Service, Washington DC.

Stone, Y., C.R. Ahern and B. Blunden. 1998. Acid sulfate soils manual. Wollongbar, New South Wales.

Toivonen, J. and P.Österholm. 2011. Characterization of acid sulfate soils and assessing their impact on a humic boreal lake. J. Geochem. Explor. 110: 107-117.

Totsche, O., R. Pothig, W. Uhlmann, U. Buttcher and C.E. Steinberg. 2003. Buffering mechanisms in acidic mining lakes-a model-based analysis. Aquat. Geochem. 9: 343-359.

Vithana, C.L., L.A. Sullivan, E.D. Burton and R.T. Bush. 2015. Stability of schwertmannite and jarosite in an acidic landscape: prolonged field incubation. Geoderma 239-240: 47-57.

Vithana, C.L., L.A. Sullivan, R.T. Bush and E.D. Burton. 2013. Acidity fractions in acid sulfate soils and sediments: contributions of schwertmannite and jarosite. Soil Res. 51: 203-214.

Vuai, S.A., K. Nakamura and A. Tokuyama. 2003. Geochemical characteristics of runoff from acid sulfate soils in the northern area of Okinawa Island, Japan. Geochem. J. 37: 579-592.

Weber, P.A., E.J. Thomas, W.M. Skinner and R.S.C. Smart. 2005. A method to determine the acid-neutralization capacity of rock samples. The Canadian Mineralogist 43: 1183-1192.

Welch, S.A., A.G. Christy, D. Kirste, S.G. Beavis and F. Beavis. 2007. Jarosite dissolution I-trace cation flux in acid sulfate soils. Chem. Geol. 245: 183-187.

Welch, S.A., D. Kirste, A.G. Christry, F.R. Beavis and S.G. Beavis. 2008. Jarosite dissolution II – reaction kinetics, stoichiometry and acid flux. Chem. Geol. 254: 73-86.

White, I., M.D. Melville, B.P. Wilson and J. Sammut. 1997. Reducing acid discharges from coastal wetlands in eastern Australia. Wetlands Ecol. Manage. 5: 55-72.

Whitworth, K.L., E. Silvester and D.S. Baldwin. 2014. Alkalinity capture during microbial sulfate reduction and implications for the acidification of inland aquatic ecosystems. Geochim. Cosmochim. Acta 130: 113-125.

Willett, I.R. and P.H. Walker. 1982. Soil morphology and distribution of iron and sulfur fractions in a coastal floodplain toposequence. Soil Res. 20: 283-294.

Yvanes-Giuliani, Y.A.M., T.D. Waite and R.N. Collin. 2014. Exchangeable and secondary mineral reactive pools of aluminium in coastal lowland acid sulfate soils. Sci. Total Environ. 485-486: 232-240.

Manuscript received 27 January 2016, accepted 31 March 2016