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Water-Soluble and Exchangeable Components of Vietnam Acid Sulfate Soils

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Water-soluble and exchangeable components of Vietnam acid sulfate soils were analyzed. Large amounts of water-soluble Fe, Al, Ca and Mg sulfates and sulfuric acid were found. Their amount and the ratio of the amounts of water-soluble ions to those of the exchangeable ions increased with the decreasing pH. The strong acidity at low pH (<2.7) was due to water-soluble Fe and Al sulfates. At pH 12.8. water-soluble Fe^{3+} disappeared and the contribution to the acidity of exchangeable Al^{3+} and Al sulfate increased. The amount of water-soluble $Ca^{2+}+Mg^{2+}$ (17-44 me/100g) was higher than that of acid sulfate soils from other countries.

The treatment with H_2O_2 caused the remarkable increase of water-soluble Fe^{3+}, Al^{3+}, H^+ and SO_4^{2-} especially in subsoil layers. This indicates the high potential acidity derived from sulfides and the liberation of Al from organic matter.

INTRODUCTION

Acid sulfate soils are derived usually from marine and estuarine sediments high in sulfides (mainly pyrite, FeS_2). The marine sediments are usually neutral to slightly alkaline when submerged. Upon drainage and aeration, large amounts of sulfides are oxidized to sulfuric acid, resulting in extremely strong acidity. Acid sulfate soils cover large areas in tropical and subtropical regions (Moormann, 1963). They occupy about 2 million hectares in the southern part of the Mekong delta in Vietnam (Pham-huu-Anh et *al.*, 1961).

Acid sulfate soils have drawn considerable attention recently. Bloomfield (1972) studied the oxidation of iron sulfides in soils and stated that aerating pyritic soils causes acidification and the formation of acid sulfate soils, or cat-clay. Calvert and Ford (1973) investigated acid sulfate soils from Florida marshland and recognized that the high potential for developing acid sulfates is due to the unoxidized S. A high S level is confirmation that low pH values of 3.0 or below after oxidation with H_2O_2 are caused by pyrite. Horn *et al.* (1967) investigated coastal alluvial soils of the Republic of Guinea and stated that drainage of acid sulfate soils permits oxidation and the formation of H_2SO_4, resulting low pH values in the range of 2.5 to 4.0. The data on their chemical properties showed considerable amounts of water-soluble components, especially Na, Mg, Cl and SO, (Horn and Chapman, 1968). Murakami (1968a) investigated the characteristics and improvement of acid sulfate soils from Naka-umi, Japan and reported that S is oxidized and produces high acidity, and that consequently a large amount of water-soluble Al, Fe, Mn and free acid are formed. Allbrook (quoted from Bloomfield and Coulter (1973)) extracted Al from acid sulfate soils in Malaysia using a 1 : 1 soil water ratio and reported 8.5 me/100 g of soluble Al from a soil which had 3 % S. Lefebre-Drouet (quoted from Bloomfield and Coulter, 1973) found that the destruction of organic matter in acid soils with H_2O_2 liberates large quantities of Al. Sompatpanit (quoted from Bloomfield and Coulter, 1973) quoted 3.5–5.0 me/100 g exchangeable Ca and 3.0–3.2 me/100 g exchangeable Mg in the top 35cm of an acid sulfate soil in Thailand. Amounts of this order were also given by Mai-thi-my-Nhung and Ponnamperuma (1966) for a soil from Vietnam. Pham-huu-Anh et al. (1961) gave 3.0 me/100 g exchangeable Ca in the O-35cm horizon, 2.9 in the "cat" clay horizon, and 3.6 in the reduced horizon; corresponding figures for Mg were 4.1, 5.7 and 9.0.

In the previous paper (Huynh-tong-Tho and Egashira, 1976), some chemical, physical and mineralogical properties of Vietnam acid sulfate soils were investigated. They contained large amounts of extractable Fe^{3+}, Al^{3+} and H^+ and considerable amounts of extractable Ca^{2+}, Mg^{2+} and SO_4^{2-}. These components show an important role in the soil acidity and affect seriously the crop production. Therefore, the present investigation was carried out to identify their water-soluble and exchangeable components and to elucidate the potential acidity of these soils. It is hoped that the obtained result helps the reclamation of such infertile soils.

MATERIALS AND METHODS

Soil samples

Acid sulfate soil samples used in this investigation were collected from 2 sites of a paddy field at the experimental farms of Cantho University in Vietnam and the same as those of the previous study (Huynh-tong-Tho and Egashira, 1976). Some of their mechanical and chemical properties are shown in Table 1. The sampling sites are located near the Bassac river, and flooded once a year in rainy season but not influenced by sea water intrusion (Fig. 1). The dotted line of 0.4 g NaCl/l shows the sea water intrusion.

Extraction and determination of water-soluble and extractable components

Duplicate 5 g air-dried soil samples ($<$2 mm) were placed in polyethylene bottles (60 ml in volume) with 50ml of distilled water or 1 M KCl. Solution of 1 M $NaNO_3$ was used to extract Cl^- and 1 M NH_4Cl for K+. The soil suspensions were shaken for 3 hours followed by centrifugation and filtration.
The soil extracts were then analyzed for the following components :

1. Total acid by titration with 0.1 M NaOH
2. Fe^{3+} and Al^{3+} by atomic absorption spectrophotometer
3. Ca^{2+} and Mg^{2+} by titration with 0.01 M EDTA
4. Na^+ and K^+ by flame photometer
5. NH_4^+, Cl^- and NO_3^- by ionmeter
6. SO,"- based on the Versene chelation of the excess Ba remaining after

Table 1. Some mechanical and chemical properties of Vietnam acid sulfate soils.

Layer	Depth (cm)	Content (%)			Texture	Organic matter (%)	pH (H_2O)	Exchange acidity (y_1)
		Sand	Silt	Clay				
				Profile 1				
1	0- 40	8.8	48.0	43.2	HC	2.6	3.0	68
2	40- 80	4.6	38.7	56.7	HC	4 5	3.4	48
3	80-120	1.0	35.7	G3.3		15.7	3.1	83
4	120-130	3.3	45.1	51.6	HC	7.1	2.7	321
				Profile 2				
1	0- 40	4.6	43.1	52.3	HC	4.3	3.7	24
2	40- 80	2.9	51.2	45.9	HC	4.0	5.8	2
3	80-120	1.0	36.3	62.7		16.5	2.8	88
4	120-140	2.7	43.9	53.4	HC	6.9	2.5	256

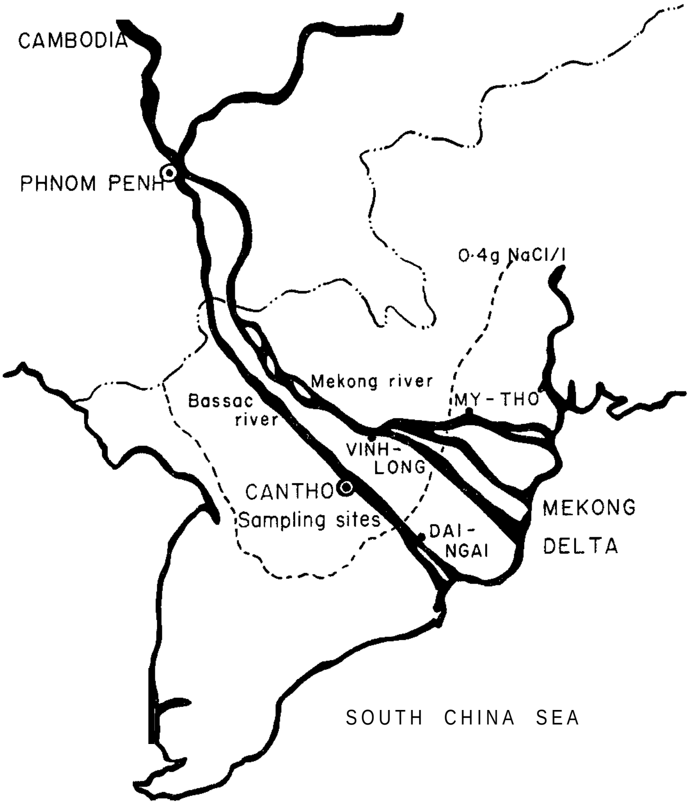

Fig. 1. Location of sampling sites of Vietnam acid sulfate soils.

$BaSO_4$ precipitation by addition of $BaCl_2$ (Jackson, 1958).

Single and 5-time extractions of KCl-extractable components gave similar results (Table 2). Therefore, the data of single extraction were reported in this paper.

Table 2. Comparison of single and five-time extractions of KCl-extractable components (Profile 2).

Layer	Number of extraction	Total acid	Fe^{3+}	Al^{3+}	$Ca^{2+} + Mg^{2+}$	SO_4^{2-}
				me/100 g		
1	1	8.0	0.4	5.4	29.3	19.2
	5	a.0	0.7	5.2	29.4	18.3
2	1	0.0	0.0	0.0	35.1	16.7
	5	0.0	0.0	0.0	36.9	16.5
3	1	31.4	0.7	24.3	49.9	60.6
	5	33.7	1.4	27.5	50.9	60.5
4	1	61.2	28.1	30.0	36.0	74.0
	5	62.9	30.0	29.7	35.9	74.0

Duplicate 2g air-dried soil samples were treated for 3 times with 10 ml of 35% H_2O_2. Water-soluble and KCI-extractable components were extracted for 3 times with distilled water or 1 M KC1 and determined as described above.

RESULTS AND DISCUSSION

The amounts of water-soluble and exchangeable components of air-dried soil samples are shown in Table 3. The amounts of exchangeable components were calculated by subtracting the amounts of water-soluble ones from those of KCI-extractable ones. The main cations were Fe^{3+}, Al^{3+}, H^+, Ca^{2+} and Mg^{2+} and the main anion was SO_4^{2-}. Other cations (Na+, K+ and NH_4^+) and anions (Cl^- and NO,-) were present in amounts of less than 1 me/100 g, respectively. So, they are not presented here. There were large amounts of water-soluble ions. Their amount and the ratio of the amounts of water-soluble ions to those of the exchangeable ions increased with the decreasing pH. The total amount of water-soluble Fe^{3+}, Al^{3+}, H+, Ca^{2+} and Mg^{2+} showed similar values with the amount of water-soluble SO_4^{2-}. Therefore, these cations are considered to be present in the soil under the form of sulfates.

Fe^{3+},Al^{3+} and H+ are responsible for the soil acidity. The amount of H+ was calculated by subtracting the amount of $Fe^{3+} + Al^{3+}$ from the total amount of titratable acid. The soil acidity was derived from water-soluble and exchangeable components. Water-soluble acid components are iron and aluminum sulfates and free sulfuric acid. The strong acidity at low pH(<2.7) was due to water-soluble iron and aluminum sulfates. At pH>2.8 water-soluble Fe^{3+} disappeared and the contribution to the acidity of exchangeable Al^{3+} and aluminum sulfate increased. Water-soluble Al^{3+} at pH less than 3 varied from 6

Table 3. Water-soluble and exchangeable components of air-dried Vietnam acid sulfate soils.

Layer (pH)		Fe^{3+}	Al^{3+}	$H^{+1)}$	$Ca^{2+}+Mg^{2+}$	Total cations$^{2)}$	SO_4^{2-}
		me /100 g					
				Profile 1			
1	WS	0.5	6.1	2.2	31.4	40.2	40.8
(3.0)	Ex	0.2	6.4	2.5	6.5	15.6	2.2
	WS	0.1					
(324)	Ex	0.1	2.4 6.6	3.0 1.5	26.2 9.3	31.7 17.5	32.6 2.6
3	WS	0.a	13.3	0.a	43.7	58.6	54.3
(3.1)	Ex	0.3	7.3	5.0	7.1	19.7	2.5
4	WS	37.4	25.a	2.5	33.6	99.3	89.8
(2.7)	Ex	4.a	5.7	0.0	3.3	13.8	0.0
				Profile 2			
	w s	0.2	1.1	2.2	19.2	22.7	19.2
(3.17)	Ex	0.2	4.3	0.0	10.1	14.6	0.0
	w s	0.0	0.0	0.0	16.7	16.7	16.7
(528)	Ex	0.0	0.0	0.0	18.4	18.4	0.0
3	w s	0.4		6.5			
(2.8)	Ex	0.2	13.0 11.3	0.0	42.7.8 1	60.21.0 3	59.1.4 2
4	WS	28.1	19.4	2.3	33.1	82.9	74.0
(2.5)	Ex	0.0	10.6	0.a	2.9	14.3	0.0

WS : Water-soluble.
Ex : Exchangeable (KCl-extractable—water-soluble).
[1] Calculated by [Total acid—($Fe^{3+}+Al^{3+}$)].
[2] Total of Fe^{3+}, Al^{3+}, H^+, Ca^{2+} and Mg^{2+}.

to 25 me/100 g and kept the same as or higher than that of acid sulfate soils from Malaysia (8.5 me/100 g) (Allbrook, quoted from Bloomfield and Coulter (1973)) and from Naka-umi, Japan (<7 me/100 g) (Murakami, 1968a).

Water-soluble $Ca^{2+}+Mg^{2+}$ were present in considerable amounts. Their values were 17–44 me/100 g throughout the profiles and higher than those of other acid sulfate soils (<10 me/100 g) from the Guinea coast (Horn and Chapman, 1968), from Naka-umi, Japan (Murakami, 1968b) and from Thailand (Breemen and Harmsen, 1975). Acid sulfate soils located in the coastal areas under conditions of periodic salt water intrusion often contain considerable amounts of water-soluble ions, mainly Na+ and Cl- (Horn and Chapman, 1968; Breemen and Harmsen, 1975). The soil samples used in this investigation, containing very small amounts of water-soluble Na+ and Cl^-, were not influenced by sea water intrusion and had no application of lime. Therefore, so large amounts of water-soluble $Ca^{2+}+Mg^{2+}$ seem to be due to the intrusion of the Bassac river water in rainy season. Water analyses of the Bassac and Mekong rivers are shown in Table 4. The amount of exchangeable $Ca^{2+}+Mg^{2+}$ was less than 10 me/100 g throughout the profiles and showed the same level as that of other acid sulfate soils (Sompatpanit, quoted from Bloomfield and Coulter,

Table 4. Water analyses of the Bassac and Mekong rivers (Mekong Committee, Saigon).

River	Location	Sampling date		pH	Ca	Mg	Al	Fe	Cl	SO,	HCO_3
					ppm						
Bassac	Cantho[1]	April	1963	7.9	17. 2	4. 1			6. 1	16. 5	
	Dai-Ngai	Sept	1971	7. 2	16. 8	1.9	6.2	1.7		3.7	64
Mekong	Vinh-Long	May	**1963**	a. 0	***24.8***	***6.6***			15.1	14.4	
		July	1963	8.0	17. 2	2. 9			tr	7. 4	
	My-Tho	May	1971	n. a	31.3	5.8	19.2	0.9	36.6	11.0	
		July	1963	7. 6	19. 2	4.9			7. 6	24. 7	
		Sept	1971	1.9	16. 4	1. 4	5. 3	4.2	45.8	6.2	61

n.a : Not available. tr : Trace. [1] Sampling sites.

1973; Mai-thi-my-Nhung and Ponnamperuma, 1966; Pham-huu-Anh ***et al.,*** 1961), except the second layer of profile 2 with pH 5.8 where the amount of exchangeable $Ca^{2+}+Mg^{2+}$ (18.4 me/100 g) exceeded that of water-soluble $Ca^{2+}+Mg^{2+}$ (16.7 me/100 g).

The soil samples were oxidized by treating with H_2O_2 and analyzed for water-soluble and exchangeable components in order to know their potential acidity. The data are shown in Table 5. The amounts of water-soluble Fe^{3+}, Al^{3+}, H+ and SO,,- were remarkably increased after treating with H_2O_2, especially at the third and fourth layers. But there was almost no change in the amounts of the exchangeable components. The potential acidity of acid sulfate soils is due to sulfides, mainly pyrite (Bloomfield, 1972; Calvert and Ford, 1973; Murakami, 1961). If pyrite is completely oxidized by H_2O_2, ferric sulfate and sulfuric acid will be produced as follows: $2FeS_2+H_2O+15O \rightarrow Fe_2(SO_4)_3+H_2SO_4$. In this experiment, $Fe^{3+}+H^+$ increase was proportional to SO_4^{2-} increase but usually kept higher than SO,‘- increase. And the increase of Fe^{3+} was 4-6 times higher than that of H^+ at the third layers, but the increase of H^+ was far exceeded that of Fe^{3+} at the fourth layers. These results show the incompleteness of the oxidation of S to SO, (Murakami, 1961) and the presence of other sulfides.

Water-soluble Al^{3+} was also increased by the H_2O_2-treatment, especially at the third layers with high organic matter content. This agrees with the result of Lefebre-Drouet who found that the destruction of organic matter in acid soils with H_2O_2 liberates large quantities of Al (quoted from Bloomfield and Coulter, 1973). This supports the contention that Al forms stable complexes with organic matter.

There was almost no change of both water-soluble and exchangeable $Ca^{2+}+Mg^{2+}$ after treating with H_2O_2, except the second layer of profile 2 where the increase of water-soluble $Ca^{2+}+Mg^{2+}$ (16.9 me/100 g) was nearly equal to the decrease of exchangeable $Ca^{2+}+Mg^{2+}$ (−14.4 me/100 g). This indicates that the exchangeable Ca^{2+} and Mg^{2+} adsorbed on the organic matter became water-soluble after treating with H_2O_2.

Table 5. Water-soluble and exchangeable components of air-dried Vietnam acid sulfate soils after treating with H_2O_2.

Layer		Fe^{3+}	Al^{3+}	H^+	$Ca^{2+}+Mg^{2+}$	SO_4^{2-}
		me /100 g				
				Profile 1		
1	WS	0.7 (0.2)	11.1 (5.0)	9.3 (7. 1)	31.7(0.3)	42.5(1.7)
	Ex	1.0 (0.8)	7.0 (0.6)	0.0 (-2.5)	7.7(1.2)	2.8(0.6)
2	w s	0.7 (0.6)	13.3 (10.9)	13.9 (10.9)	27.0(0.8)	36.7(4.1)
	Ex	0.0 (−0.1)	5.5 (-1.1)	0.7 (-0.8)	10.3(1.0)	2.9(0.3)
3	WS	35.8 (35.0)	35.1 (21.8)	6.6 (5.8)	46.6(2.9)	87.5(33.2)
	Ex	1.0 (0.7)	5.2 (−2.1)	3.4 (−1.6)	6.3(-0.8)	0.0(−2.5)
4	w s	39.5 (2.1)	28.1 (2.3)	55.3 (52.8)	32.8(−0.8)	134.3(44.5)
	Ex	2.7 (−2.1)	13.1 (7.4)	1.0 (1.0)	1.9(−1.4)	0.2(0.2)
				Profile 2		
1	WS	2.8 (2.6)	7.6 (6.5)	4.4 (2.2)	20.5(1.3)	28.5(9.3)
	Ex	0.0 (-0.2)	2.8 (−1.5)	2.3 (2.3)	10.2(0.1)	1.4(1.4)
2	WS	4.4 (4.4)	3.8 (3.8)	6.8 (6.8)	33.6(16.9)	38.9(22.2)
	Ex	0.3 (0.3)	4.4 (4.4)	0.3 (0.3)	4.0(−14.4)	6.2(6.2)
3	WS	27.6 (27.2)	32.0 (20.7)	14.5 (8.0)	49.0(6.9)	85.7(26.3)
	Ex	5.5 (5.3)	7.1 (−5.9)	0.0 (0.0)	3.0(-4.8)	0.9(−0.3)
4	WS	30.4 (2.3)	24.7 (5.3)	39.5 (37.2)	36.1(3.0)	112.2(38.2)
	Ex	2.8 (2.8)	9.1 (-1.5)	3.0 (2.2)	0.8(−2.1)	6.2(6.2)

WS : Water-soluble. Ex : Exchangeable (KCl-extractable—water-soluble).
Values in the parentheses are increase or decrease by the H_2O_2-treatment.

CONCLUSION

Vietnam acid sulfate soils contained large amounts of water-solubleions of Fe^{3+}, Al^{3+}, H^+, Ca^{2+}, Mg^{2+} and SO_4^{2-}. The strong acidity at low pH(<2.7) was due to water-soluble Fe and Al sulfates. At pH >2.8 water-soluble Fe^{3+} disappeared and the contribution to the acidity of exchangeable Al^{3+} and Al sulfate increased. Considerable amounts of water-soluble Ca^{2+} and Mg^{2+} were ascribed to the intrusion of river water.

These soils showed the high potential acidity derived from sulfides especially in subsoil layers. The treatment with H_2O_2 caused the liberation of Al from organic matter.

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