The evaporation and acidification process in an acid sulphate soil

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1 Summary

Fourteen undisturbed soil columns of 20 cm in diameter and 70 cm length from an acid sulphate soil in Mijdrecht, Netherlands were used to study the acidification process upon drying. Two groundwater levels: 40 cm and 65 cm below the soil surface, 5 different durations of evaporation and 2 agronomic practices were imposed.

Among treatments, averaged total acidity over 14 layers in the soil profile did not show much variation as the cumulative evaporation increased. The depth of the acidity maximum in the soil profile with low groundwater varied with the presence or absence of peat on the surface. Without peat, the total acidity maximum in the soil profile was about 35 – 40 cm below the surface, with a thin peat layer, they remained about 10 cm deeper.

The presence of peat layer on the surface reduced the rate of acidification, presumably mainly by reducing evaporation rate and perhaps by reducing the input of oxygen in the soil profile.

The average pH value over 14 layers along the soil profile decreased as the depth of groundwater increased from 40 to 65 cm. In treatments with a low groundwater table, the average pH decreased sharply with increasing evaporation: to about 3.5 after 140 mm of evaporation. The decrease was less drastic where groundwater remained high. Mulching or plowing at the start of a dry season to reduce the flux of solutes by capillary movement and maintaining the water table as high as possible to reduce oxidation may be a good management practices in acid sulphate soils.

Résumé

14 Colonnes des sols en structure naturelle, d'un diamètre de 20 cm et une longueur de 70 cm ont été prélevés d'un sol sulfaté-acide de Mijdrecht, Pay-Bas, dans le but d'étudier les processus d'acidification consécutifs au séchage.

Deux profondeurs de la nappe aquifère (à 40 cm et à 65 cm), cinq différentes durées d'évaporation et deux pratiques agricoles ont été expérimentées.

Parmi ces traitements, l'acidité totale moyenne des 14 colonnes, n'a pas montré beaucoup de variation avec l'augmentation de l'évaporation cumulative. La profondeur de l'acidité maximale dans le profil à nappe aquifère profonde, a varié en fonction de la présence ou de l'absence d'une couche de tourbe à la surface. Sans tourbe, le maximum de l'acidité totale a été jusqu'à environ 35-40 cm de profondeur. Avec un couche mince de tourbe elle s'est résumée à rester seulement à environ 10 cm de profondeur.

135

La présence de la couche de tourbe à la surface réduit la vitesse d'acidification, vraisemblablement surtout par le réduction de la vitesse de l'évaporation et peut-être aussi par la réduction de l'intrant de l'oxygène dans le profil du sol. La valeur pH moyenne sur les quatorze couches le long du profil du sol a été diminuée si la profondeur de la nappe aquifère a augmente de 40 à 65 cm. Dans les traitements à nappe aquifère profonde, la moyenne des valeurs pH a diminué d'une manière tranchante avec l'augmentaion de l'évaporation (jusqu'à 3,5 après 140 mm d'évaporation). La diminution a été moins drastique si la nappe aquifère est restée élevée. Le mulch ou le labour au début de la saison sèche, éffectués dans le but de reduire le flux de sels par ascension capillaire ainsi que la maintenance de la nappe aquifère à une profondeur aussi haute que possible, peuvent être des pratiques d'améliorations valables dans les sols sulfaté-acides.

2   Introduction

The formation of acid sulphate soils results from the presence of sulphides, the introduction of aerobic conditions, and the lack of bases, usually calcium carbonate, to neutralize the acidity. Soils may become aerobic when they are drained for agriculture but also when there are seasonal changes in soil drainage, e.g. by a lowering of the groundwater table. Evaporation from bare soils may have the same effect owing to the loss of soil water. Evaporation may also cause accumulation of toxic salts in surface horizons because of upward capillary movement. Low pH, high acidity and accumulation of toxins can degrade the productivity of the soils. Results of field experiments about the effects of changes in groundwater level on the acidity of acid sulphate soils and on crop yields were reported by Beye (1973), Kanapathy (1973) and Yin and Chin (1982), but basic information about the effect of evaporation in the dry season is lacking. Field observation in Vietnam indicate that plowing in the dry season followed by leaching of salts accumulated just below the surface soil may depress the toxicity to crops in acid sulphate soils (Vo tong Xuan, personal communication).

The objective of this study was to determine the effects of groundwater levels and other factors related to the evaporation rate on the acidification process of an acid sulphate soil.

3   Materials and methods

An acid sulphate soil from Mijdrecht Polder in the Netherlands was used for this study.

The soil profile consisted of a thin (10 cm) peat layer, somewhat compacted, over 35 cm jarositic material, with a half ripe pyritic substratum. Before the experiment, the peat layer was removed except where stated.

In spite of the artificial drainage in the polder the acid sulphate soil has remained in its poorly drained condition, being protected by a 35 cm thick man-made soil cover. This was removed before sampling. Undisturbed soil columns were collected in 14 PVC pipes with 20 cm inside diameter and 70 cm length (Figure 1). One end of the PVC pipe was sharpened in order to have a good cutting edge. The procedure used
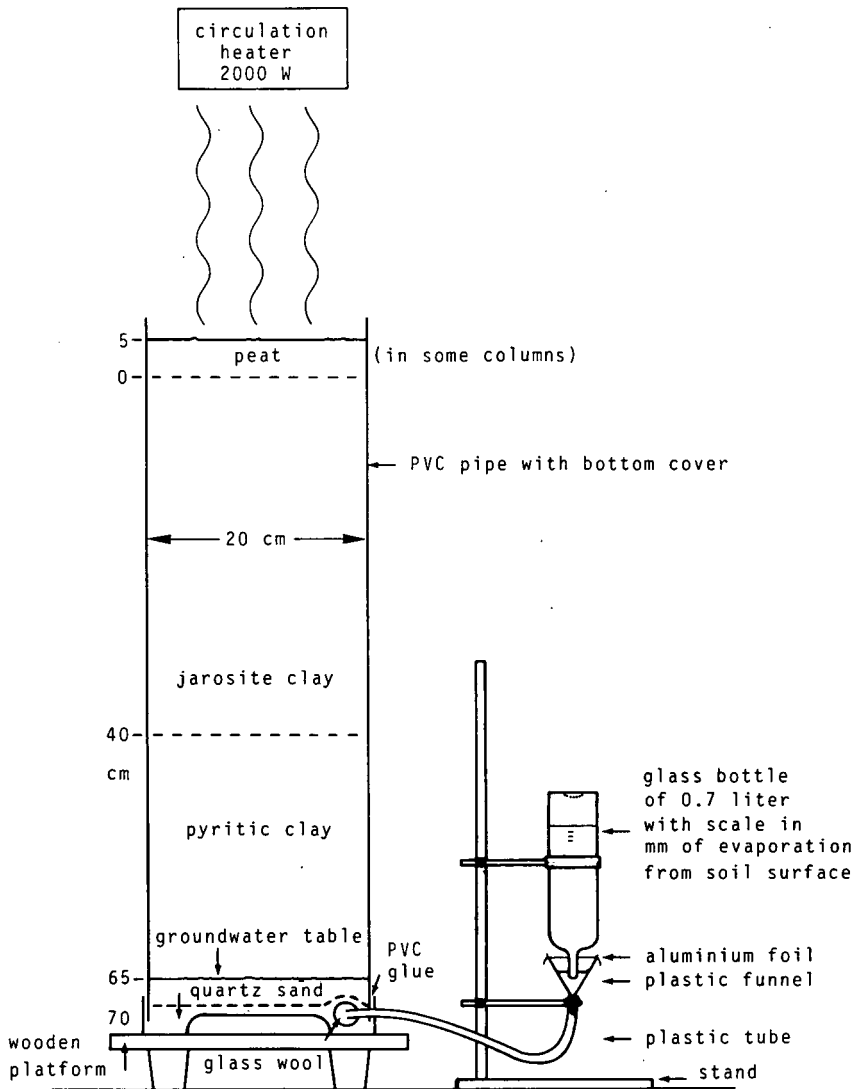
Figure 1 Cross-section of a soil column with low groundwater

in obtaining the columns was similar to that described by Le Ngoc Sen (1982). The columns were excavated in two rows close to each other in an area of 0.5 × 2 m (Figure 2). The filled PVC pipes were tied with rope, turned 45 degrees and dragged up to the ground surface along the sloping side of the pit. The excess soil material at the bottom was trimmed level with the cutting edge. A PVC cover placed over the top of the column, which was then inverted and kept wet during transport. In the laboratory, a 1.5 cm layer of soil was removed from the bottom of the pipe, replaced by quartz sand and connected with a plastic tube through a bored hole at the side. The end of the plastic tube inside the pipe was covered with glass wool and the other
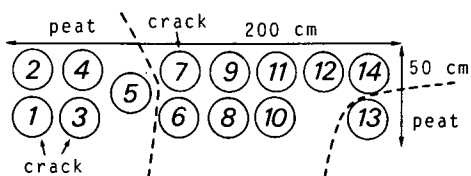
137

Figure 2 Place of soil columns in the original soil

end connected with a source of water to regulate the groundwater table in the profile (Figure 1). A PVC cover was then sealed to the bottom of the pipe with PVC glue, the column replaced in its original position and the top cover was removed. Two of the fourteen columns were used as controls and were sampled at the beginning of the experiment. The remaining ones were arranged at random (Figure. 3). Two electrical circulation heaters of 2000 watts placed at 0.50 meter above the surface of the columns increased the evaporation rate.

The depths of ground water were maintained at 40 and 65 cm below the soil surface. Different combinations of treatments were imposed (Table 1). The high groundwater level, 40 cm below the surface was chosen to saturate the pyritic horizons, which started at about that depth. The low groundwater level, 65 cm, should allow some oxidation in the upper part of the pyritic horizons.

Table 1 Characteristics of different soil columns

Column number	Groundwater level (cm)	Duration of evaporation (weeks)	Plowing surface soil	Presence of peat on surface	Presence of jarositic crack
1	65	14	yes	yes	yes
2	65	10	no	yes	no
3*	–	–	no	yes	yes
4	65	15	no	yes	no
5	40	7	no	yes	no
6	65	10	no	no	no
7	40	14	no	no	yes
8	65	5	no	no	no
9	65	14	yes	no	no
10	65	15	no	no	no
11	40	14	no	no	no
12*	–	–	no	no	no
13	40	7	no	yes	no
14	65	5	no	no	no

* control column

At the end of a run, the bottom of each pipe was removed and the pipe itself cut into two along the profile by electric saw. The columns were then sectioned into 5 cm segments. In each segment, two samples of 25 ml were taken with the aid of a PVC auger of 5 cm diameter and placed in plastic bottles, then mixed with 100 ml demineralized water, shaken for one hour and centrifuged for 30 minutes at 3000 rpm.

138

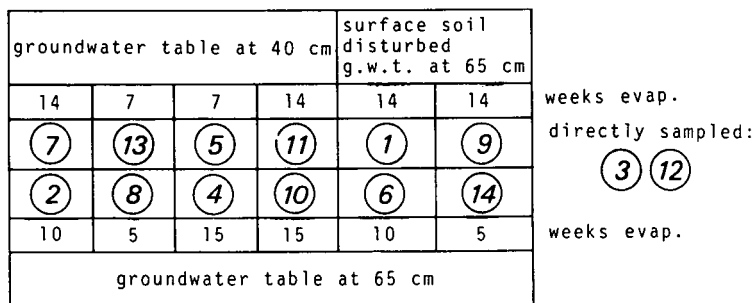| groundwater table at 40 cm				surface soil disturbed g.w.t. at 65 cm		
14	7	7	14	14	14	weeks evap.
⑦	⑬	⑤	⑪	①	⑨	directly sampled: ③ ⑫
②	⑧	④	⑩	⑥	⑭	
10	5	15	15	10	5	weeks evap.
groundwater table at 65 cm						

Figure 3 Arrangement of soil columns in the laboratory

In the supernatant EC and pH were determined electrometrically.

Total acidity was determined by titration with 0.1 N NaOH to the end point by phenolphtaleine as indicator. Total acidity comprises three kinds of acid: H^+, Al^{3+} and Fe^{2+}. The former is neutralized directly during titration, Al^{3+} is hydrolyzed to $Al(OH)_3$ releasing $3H^+$; and Fe^{2+} is oxidized in the mechanically stirred solution during titration, producing $Fe(OH)_3$ and $2H^+$. Vertical moisture distribution was determined along all profiles except for the control columns 3 and 12. Bulked samples over 10 cm depth increments were freeze-dried for sulphur fractions and other chemical analyses, according to Begheijn (1980). Samples of columns 4 and 10 were collected in 100 ml aluminium rings for bulk density determination. In supernatants of columns 4, 10 and 11, determinations of Ca, Mg, Na, K, Fe, Cl, NO_3, SO_4 and HCO_3^- were made additionally. Except for HCO_3^-, which was determined by organic carbon analyzer after centrifugation, these determinations were made on solutions stored in the refrigerator for 2 weeks after adding a few drops concentrated HCl.

Some of the water samples from columns 4, 10 and 11 were also analyzed for Ca, Fe, Mg by atomic spectrophotometer; Na and K by atomic emission spectrometer; Al by spectrophotometer with pyrocatechol violet; Fe, Cl, NO_3 and SO_4^{2-} by ion-chromatography.

Freeze-dried samples of columns 3, 4, 10 and 12 were used to determine CEC, Ca, Mg, Al and total acidity, and freeze-dried samples of columns 2, 3, 8, 12 and 10 for sulphur fractions.

4 Results and discussion

4.1 Evaporation

The evaporation rate appeared to be influenced by the level of the groundwater table, by disturbance of the surface soil and by the presence of peaty layer on the surface. The evaporation rate was about 1.5 to 2.1 mm per day with a high groundwater table and about 0.7 to 1.5 mm per day with a low groundwater table (Table 2). This amounts to about 30 – 60 percent of the evaporation from a free water surface measured in the experiment (3 mm/day). The presence of a peaty layer on the surface decreased the evaporation rate by about 50 percent compared with the columns without peat. Disturbance of the upper 10 cm decreased the rate by about 20 percent.

139

Table 2 Evaporation rate, average soil moisture, EC, pH, total acidity and basic cations of different soil columns

Column number	Evaporation rate (mm/day)	Averaged* soil moisture (mass %)	Averaged EC (ms/cm)	Averaged pH	Averaged total acidity (mol/cm^3)	Averaged basic cations (mol/m^3)
1	0.82	85	0.93	3.95	1.71	11.5
2	0.66	102	1.02	3.97	2.07	12.8
3	0.00	–**	0.79	3.78	1.04	9.2
4	0.73	94.	1.11	3.96	2.50	14.0
5	1.47	88	1.03	4.19	2.12	12.9
6	1.37	92	1.16	3.77	3.01	14.4
7	1.69	93	0.97	3.90	1.78	12.0
8	1.28	87	1.28	4.04	3.44	16.2
9	0.99	88	1.60	3.70	11.84	13.8
10	1.19	85	1.89	3.61	16.96	14.0
11	1.61	92	1.11	3.93	4.56	11.9
12	0.00	–**	0.82	4.25	1.74	10.0
13	2.14	92	0.97	4.15	1.77	12.2
14	1.54	95	1.06	4.16	2.16	13.3

* Averaged value of 7 layers in the soil column
** Not determined

4.2 Sulphur fractions

Four columns subjected to different durations of evaporation were selected for sulphur fraction analysis. Total S, pyrite, jarosite and water-soluble S are shown in Figure 4. In general, total S and pyrite of the four columns showed similar trends along the soils profile: both total S and pyrite increased with depth. The difference in total S and pyrite trends between the treated columns and a control (column 3) may be attributed to the strong microvariability of soil in the field. The lower pyrite content in column 3 is related to oxidation along a deep crack with a concentration of jarosite in this column; the low average jarosite and water-soluble S contents must have been the result of preferential leaching. Because of the variability between columns, even taken adjacent to each other, no quantitative calculation was made about the rate of oxidation and the results were studied by inividual columns.

4.3 The distribution of pH, total acidity, non-acid cations and soil moisture in different soil columns

The distribution of pH, total acidity, non-acid cations and soil moisture in water extracts of different soil columns is presented in Figure 5.
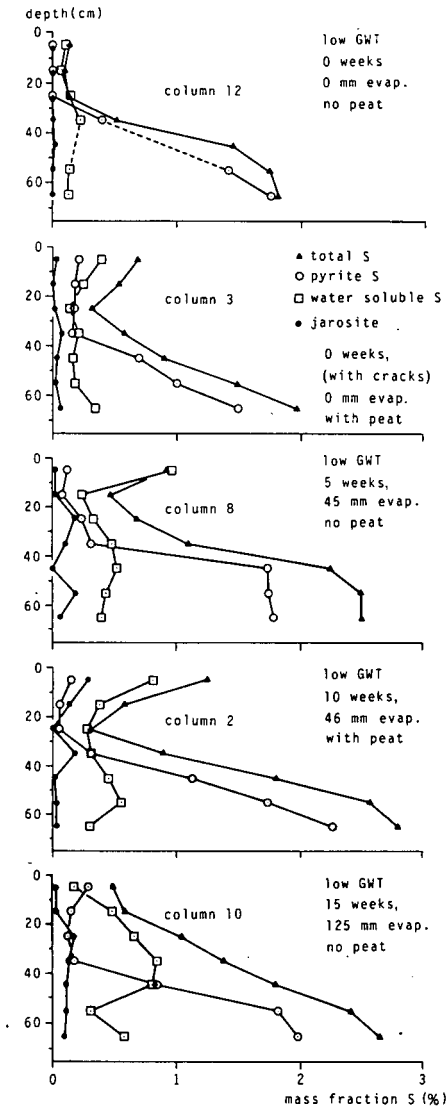
depth(cm)

column 12 — low GWT / 0 weeks / 0 mm evap. / no peat

column 3 — ▲ total S / ○ pyrite S / □ water soluble S / ● jarosite / 0 weeks, (with cracks) / 0 mm evap. / with peat

column 8 — low GWT / 5 weeks, / 45 mm evap. / no peat

column 2 — low GWT / 10 weeks, / 46 mm evap. / with peat

column 10 — low GWT / 15 weeks, / 125 mm evap. / no peat

mass fraction S (%)

Figure 4 Sulphur fractions of five soil columns with low groundwater table

4.3.1   pH

In general, the pH of the water extract of samples from all columns showed the same trend along the soil profile (Figure 4): a slight decrease in pH during the first 50 mm of evaporation only in the 40 cm surface soil, followed by a drop of half a pH unit throughout the profile as evaporation increased. For columns with a low groundwater
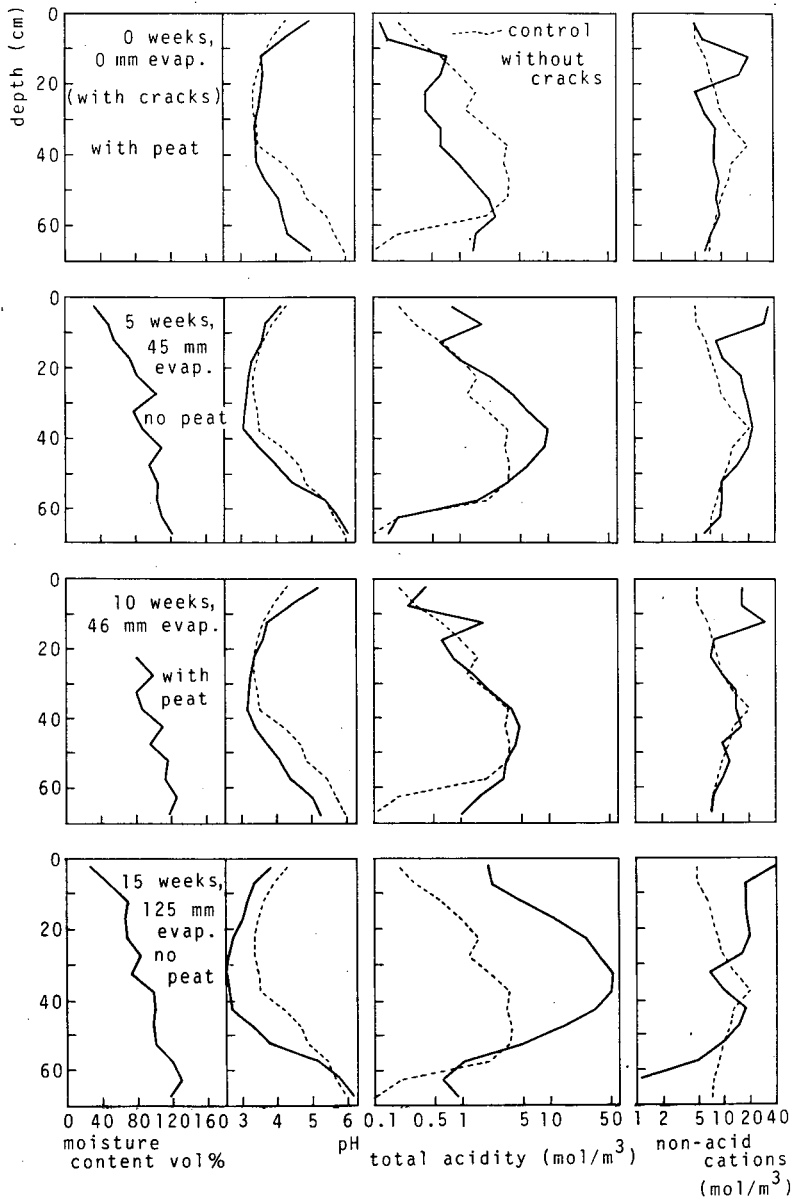
141

Figure 5 The distribution of soil moisture content and pH, total acidity, basic cations in water extracts of selected soil columns with groundwater at 65 cm depth

level the lowest pH values were observed at the pyrite-jarosite boundary at 35 to 40 cm; with high groundwater, about 5 cm higher (Table 4). This difference is attributed to the upward movement of acidity from the oxidation products of pyritic layers.

142

4.3.2   Total acidity

The total acidity of water extracts along the soil profile shows a clear picture with relatively small variations (Figure 5). Acidity maxima were found at 45 – 50 cm depth, just below the pyrite-jarosite boundary, in columns with low groundwater and a peaty layer on the subsurface; about 10 cm higher without peat (Table 4).

The position of total acidity maxima for both high and low groundwater treatments were higher in the profile compared with the control (Table 4). As the evaporation increased, more acidity was developed in the profile and the position of the total acidity maximum moved upward. The frequency distribution of the acidity maxima is shown in Figure 7 for low and high groundwater levels separately. Although there are few data points only, the peak concentrations of soluble acidity in the low groundwater treatments whithout peat appear to be far higher than with high groundwater. The total acidity of surface soil in treatments with a thin layer of peat was less than without peat.

For both groundwater levels, the average soluble acidity over the whole profile is about 3 mol/m$_3$ (s = 0.3).

A comparison between the controls with a jarositic crack and without cracks respectively shows that the subsoil in the column with a crack has a lower pH, but less total dissolved acid than the column without cracks; this may be ascribed to preferential movement of both oxygen and leaching water into the subsoil along the crack under field conditions before the experiment.

Table 3 Averaged pH. EC, total acidity of the first 30 cm in the profile of different columns

Column number	pH	EC mS/cm	Average total acidity mol/m^3
1	4.05	0.95	0.75
2	3.90	1.05	0.89
3	3.92	0.76	0.38
4	4.00	1.15	0.99
5	3.59	1.24	1.27
6	3.49	1.16	1.19
7	3.54	1.08	1.13
8	3.51	1.36	1.77
9	3.31	1.50	5.57
10	3.10	1.98	13.88
11	3.37	1.26	2.94
12	3.64	0.64	0.79
13	3.79	1.14	0.83
14	3.62	1.08	1.04

4.3.3   Basic cations

In general, the soluble basic cations did not show much variation between treatments at depths of 25 to 55 cm (Figure 4). An increase in soluble non-acid cations was found in surface soil only as the evaporation increased. A sharp decrease in concentrations

Table 4 Depths of total acidity maximum and pH minimum

| Column number | Groundwater table | Presence of peat | Depths, cm | |
			Total acidity maximum	pH minimum
1	low	+	45 – 50	35 – 40
2	low	+	40 – 45	35 – 40
4	low	+	45 – 50	40 – 45
Average	low	+	45 – 50	35 – 40
14	low	–	40 – 45	25 – 30
6	low	–	40 – 45	40 – 45
8	low	–	35 – 40	35 – 40
9	low	–	35 – 40	35 – 40
10	low	–	30 – 35	30 – 35
Average	low	–	35 – 40	35 – 40
13	high	+	45 – 50	25 – 30
7	high	–	50 – 55	30 – 35
5	high	+	40 – 45	25 – 30
11	high	–	30 – 35	35 – 40
Average	high	+ and –	40 – 45	30 – 35
3	control	+	55 – 60	30 – 35
12	control	–	45 – 50	25 – 30
Average	control	+ and –	50 – 55	30 – 35

of non-acid cations was found in soil horizons below 55 cm (Figure 4). Among the control columns, the surface soil of the cracked core has a higher concentration of basic cations; this is probably due to less leaching water passing through the surface soils near a crack than further away (short circuiting).

4.3.4   Soil moisture

As expected, the soil moisture contents of different layers along the profile increased with depth. In the half ripe subsoil the gravimetric soil moisture content of the lower layers exceeded 100 percent. The moisture distribution showed little variation among treatments. Disturbance of the surface layer allowed this layer to dry out (Figure 5), but did nor appreciably change the soil moisture distribution along the profile. The disturbed layer may not have been thick enough to decrease drastically the evaporation from lower horizons.

4.4   Changes of pH and total acidity of water extracts with cumulative evaporation
4.4.1   Average pH and total acidity over the profile

As the evaporation increased, the average pH of water extracts along the profile de-

creased (Figure 6a). In columns with a high groundwater table, the pH decreased slowly with increasing cumulative evaporation. It decreased sharply in columns with low groundwater. About 140 mm of evaporation in low groundwater treatments resulted in an average pH about 3.5. Except in three columns (9, 10 and 11), the average total acidity of water extracts over the profile did not show much variation with time (Figure 6b).
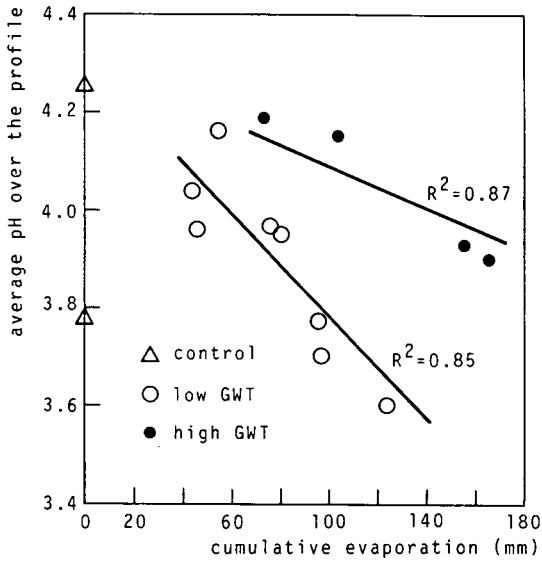

Figure 6a Average pH of extract over the profile in relation to cumulative evaporation
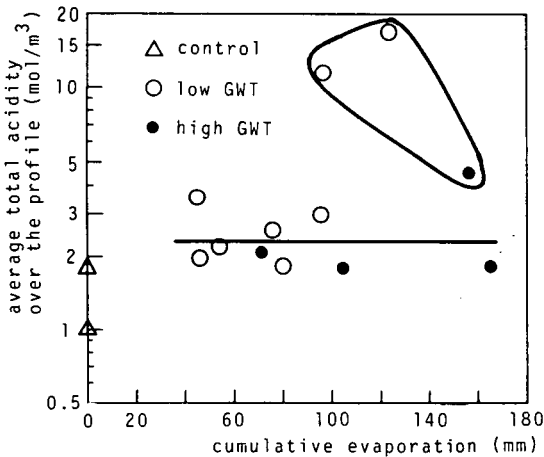
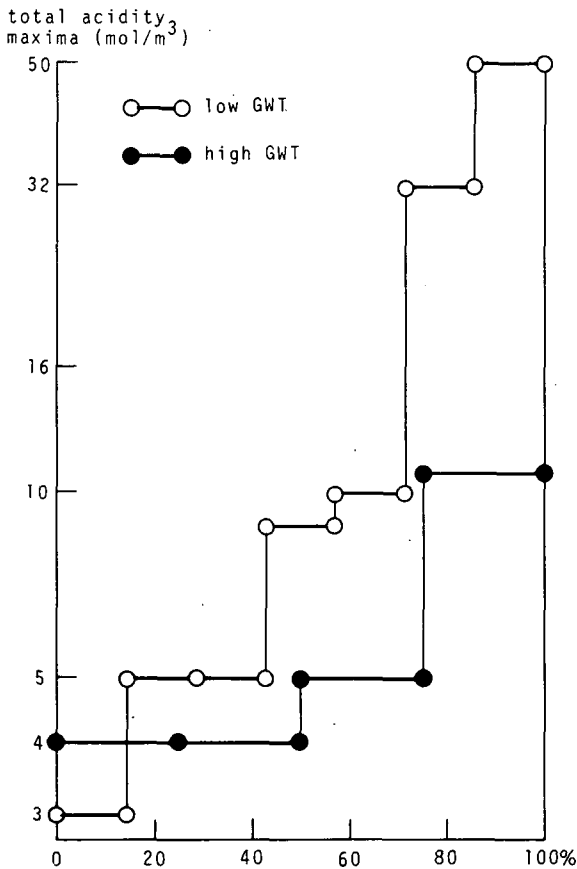Figure 6b Average total acidity of extract over the profile in relation to cumulative evaporation

145

Figure 7 Frequency distribution of total acidity maxima of extracts in the profile

4.4.2 Average pH and total acidity of water extracts in the upper 30 cm

Regardless of groundwater table levels, the average total acidity over the upper 30 cm did not show much variation (Figure 8a, Table 3).

Average pH of surface soil for both groundwater treatments remained 3.5 until the cumulative evaporation exceeded about 100 mm (Figure 8b). After that, the pH tended to fall below 3.5.

5   General results and discussion

Average total soluble acidity over the soil profile did not show much variation with cumulative evaporation or with differences in groundwater levels or other factors related to the evaporation rate.

The position and magnitude of the soluble acidity maximum in the soil profile depends on the groundwater table and the presence of peat. A groundwater table below
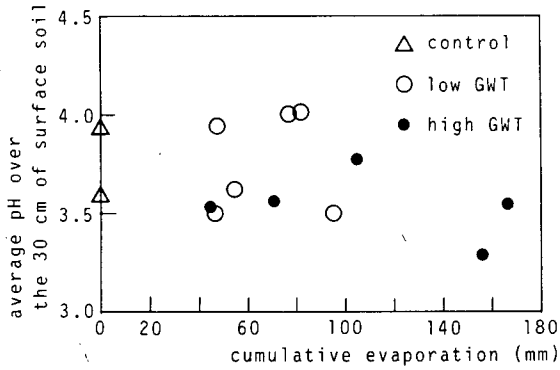
146

Figure 8a Average pH of extracts over the 30 cm of surface soil in relation to cumulative evaporation
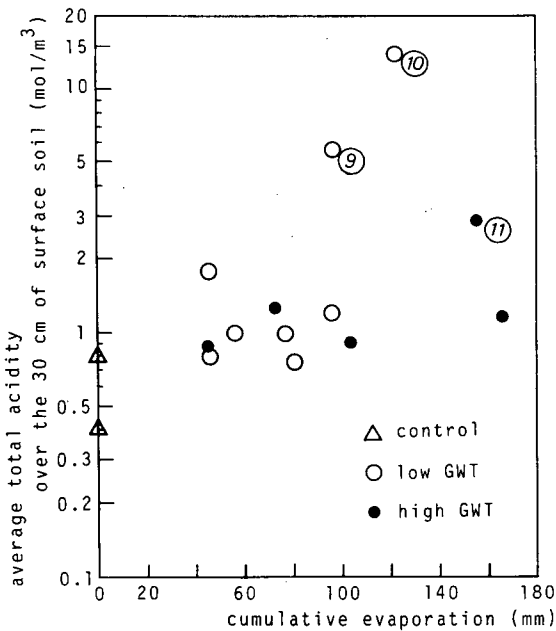

Figure 8b Average total acidity of extracts over the 30 cm of surface soil in relation to cumulative evaporation

the top of the pyritic layer apparently created conditions enhancing the oxidation of pyritic materials, resulting in high acidity maxima.

Hydrogen ions would be expected to move faster in the soil than Al (or Fe) ions because the diffusion coefficient of hydrogen is about three times higher than Al and Fe.

Changes of average pH over the soil profile with cumulative evaporation depended on groundwater depth. In high groundwater table treatment, pH gradually decreased

147

with cumulative evaporation whereas it decreased sharply where groundwater table was low. The pH of the surface soil only started to drop after about 100 mm of evaporation, in both groundwater levels.

The average pH turned out to be a more sensitive indicator for the development of acidity during the 15-week period of evaporation than the average soluble acid concentration.

With longer periods and higher totals of evaporation, as would occur during the dry season in monsoon climates, pH is expected to become less diagnostic; average soluble acid over the profile and in the surface horizon should then become better indicators for the potential growth of crop plants.

Further research is needed to ascertain the critical amount of evaporation causing unacceptable acidification with different groundwater levels and different depths to pyritic material in the field and different agronomic practices.

Disturbance of 10 cm surface soil only lowered the evaporation rate by about 20 percent. Mulching at the start of the dry season would seem to be a promising management practice in acid sulphate soil, even though its effects in this experiment were small. Further work along this line is needed.

The presence of a peaty layer on the surface reduced the evaporation rate and the total soluble acidity in the soil profile. The peaty layer was relatively dense and slightly platy, however. After ploughing it would have been broken up and incorporated in the Ap horizon.

Because of the local variability of acid sulphate soils, only gross differences become apparent by traditional small-sample methods. The variability, as shown by the data in this study, consists of two parts: a limited variation about a mean, and some outliers indicating extremely acid, toxic or potentially toxic conditions. Therefore, sampling methods based on bulking even large numbers of subsamples do not fairly represent conditions in most of the soil mass.

Sampling methods should either be based on extensive replication, or depend on close observation and recording of soil differences over small distances, with interpretation of individual results in relation to the observed characteristics of each sample or profile. In either case, efforts should be made to estimate the frequency distribution of the different values encountered.

The present experiment represents about one month of unchecked evaporation from soils with shallow groundwater during the dry season of a monsoon climate. Therefore, it only shows the beginning of the acidification that bedevils rainfed wetland crop production on acid sulphate soils in such climates.

It is clear, however, that even at relatively low evaporation rates, a groundwater table below the top of the pyritic layer is far more dangerous than a high groundwater table, although this tends to accelerate evaporation and transport of existing acidity to the surface horizon.

Minimizing evaporation during the dry season appears to be the next most important management measure if acidification is to be minimized.

Acknowledgement

the study, Dr. N. van Breemen, Dr. R. Brinkman and Prof. L.J. Pons for their valuable suggestions and comments, Ms. Els Feenstra, Mr. L.Th. Begheijn and the soil laboratory staff for their help in chemical analysis.

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