

A field laboratory method to determine total potential and actual acidity in acid sulphate soils

C.J.M. Konsten and R. Brinkman

Dept. of Soil Science and Geology, Agricultural University, Wageningen, The Netherlands

W. Andriessse

Soil Survey Institute (Stiboka), Wageningen, The Netherlands

1 Summary

A new quantitative method is presented for the determination, in a field laboratory, of total potential and actual acidity of acid sulphate soils. The method is based on the fast titration of the total acidity of the soil sample with sodium hydroxide. For the determination of the 'total actual acidity' a soil sample is suspended in a 1 molar sodium chloride solution and titrated subsequently. The 'total potential acidity' is determined by oxidation, with 30% H_2O_2 , of a soil sample suspended in a 1 molar sodium chloride solution. After the oxidation has been completed, the sample is titrated with NaOH as well. The total acidity thus determined, gives a quantitative measure of the maximal actual or potential acidity which has to be neutralized or leached to permit the soil pH to rise to 5.5 under actual circumstances (actual acidity) or after the reduced soil is completely aerated (= potential acidity).

The method has been tested on some 60 samples of actual, potential and non acid sulphate soils from Vietnam and Indonesia, ranging from clay to peat. The potential acidity determined by way of the proposed method was closely related to the total content of sulphur species. The relation with pyrite was poor because sulphur species other than pyrite were found to be important sources of acidity, especially organic sulphur. pH after oxidation by H_2O_2 turned out to be a very poor parameter for the potential acidity. Total potential acidity varied manifold at a certain pH, especially below pH 2.5.

Guidelines are given for the application of the method in a field laboratory. Two simple volumetric soil sampling devices are proposed which enable a direct determination of actual and potential acidity per hectare of soil over a certain depth.

Résumé

Une nouvelle méthode quantitative de détermination au champ de l'acidité actuelle et potentielle des Sols Sulfaté-Acides a été mise au point.

La méthode est basée sur la titration rapide de l'acidité totale d'échantillons des sols avec l'hydroxyde de sodium. Pour la détermination de l'acidité actuelle, l'échantillon du sol est apporté en suspension dans une solution de chlorure de sodium 1 molar, et titré par la suite. L'acidité potentielle est déterminée par l'oxydation de l'échantillon de sol apporté en suspension dans une solution de chlorure de sodium 1 molar, avec 30% H_2O_2 . Après que l'oxydation est achevée, l'échantillon est titré encore avec NaOH.

L'acidité ainsi déterminée, donne la mesure quantitative de l'acidité maximale actuelle et potentielle qui doit être neutralisée ou lessivée, pour permettre au pH du sol d'augmenter jusqu'à 5,5 dans les conditions actuelles (= acidité actuelle) ou après que le sol a été drainé (= acidité potentielle).

La méthode a été testée sur 61 échantillons des Sols Sulfaté-Acides (actuels et potentiels) et Sols Non Sulfaté-Acides du Delta du Mekong, Vietnam et de la partie orientale de Sumatra, Indonésie, formés sur une gamme large de sédiments, d'argile à tourbe.

L'acidité potentielle déterminée d'après la méthode proposée, a été étroitement liée à la teneur totale de sulfures réduites. Par contre, la relation avec la pyrite n'a pas été significative, car d'autres formes de sulfures réduites que la pyrite, celles organiques particulièrement, ont été aussi d'importantes sources d'acidité. Egaleme nt, le pH après l'oxydation à H_2O_2 n'est qu'un vague paramètre, car l'acidité potentielle totale varie considérablement à certains pH, surtout inférieurs à 2,5.

Il en découle, que quoique de nombreuses méthodes et études préconisent la mesure du pH comme moyen de détermination de l'acidité potentielle, la titration après l'oxydation à H_2O_2 , c'est la meilleure.

Des indications sont données pour l'application de la méthode dans le laboratoire de terrain.

Deux procédés simples d'échantillonnage volumétrique sont proposés, qui permettent la détermination directe de l'acidité actuelle et potentielle par ha de sol sur une certaine profondeur.

2 Introduction

Acid sulphate soils as defined by Pons (1973) are materials and soils in which, as a result of soil formation, sulphuric acid either will be produced, is being produced or has been produced in amounts that have a lasting effect on main soil characteristics. Sulphuric acid is produced by oxidation of unripe soil material containing reduced sulphur species. These soils have conditions unfavourable for plant growth: they often contain free acid, Al^{3+} , Fe^{2+} , Mn^{2+} , H_2S and CO_2 in amounts which are toxic for plants, have low nutrient status and often a high salinity (Coulter 1973; Ponnamperna et al. 1973).

Acid sulphate soils have a worldwide distribution. They occur under widely different climatic conditions, from the tropics to permafrost areas (Kawalec 1973). They are found not only in recent marine deposits, but also in older inland areas (Poelman 1973). Throughout the world their extension is estimated at 12 – 14 million ha (Beek et al. 1980).

Acid sulphate soils have a low potential for agricultural use and their management often requires high technology. Therefore, areas in which these soils occur are still uncultivated or they have been abandoned after agricultural use failed. With increasing population, however, the pressure on these areas is growing, especially in densely populated coastal areas of southeast Asia and western Africa. In fact, these areas have a climate favourable for food production and are suitable for agriculture but for the potential or actual acidity of their soils. Decisions on their development for food production depend, apart from social and economic factors and possibilities of water

control, mainly on the content of potential and actual acid substances of these soils.

Total actual acidity is defined here as the total amount of acidity which exists in a soil at present. Total potential acidity of a soil is the maximal amount of acidity which a partly or totally reduced soil may contain after it has been completely oxidized. Thus the total potential acidity comprises eventually present actual acidity and the amount of acidity which develops upon complete oxidation of the soil.

Identification of developed acid sulphate soils in the field is relatively easy: they have a low pH, usually below 4, they contain water-soluble sulphate and most of them have pale yellow jarosite mottles (compare the 'sulphuric horizon' of USDA, 1975 and FAO/Unesco, 1974). Potential acid sulphate soils, however, are not easily recognized in the field. As is sometimes done in soil survey, actual and potential acidity are determined in a laboratory and related to visual properties of the soil, like soil colour and organic matter content, or to physiography or vegetation (Brinkman and Pons 1973; Thomas and Varley 1982). These relations, however, can only be used within the limits of a certain climatic, sedimentary and vegetational system and their assessment requires intensive integrated surveys of soil, landscape genesis, vegetation, hydrology and land-use history (Pons 1973).

Several field or field laboratory methods for rapid identification of pyrite or potential acidity were developed: measurement of the pH drop after oxidation of a soil sample with H_2O_2 (Van Beers 1962) or after oxidation by air drying (FAO/Unesco 1974; USDA 1975; Van Breemen 1982), the active sulphide test with HCl and lead acetate paper (Neckers and Walker 1952), the sodium azide test developed by Feigl (Van Andel and Postma 1954) which was adapted for the field by Edelman (1973), the semi-quantitative sulphate test with $BaCl_2$ of Poelman (1973).

All these methods have certain disadvantages. They are qualitative methods or at the most, they give an indication of the intensity of acidification (pH). Some of the methods give an indication of the pyrite content only. These are unsuitable for soil materials rich in organic matter, because the latter may contain large amounts of potential acid organic sulphur compounds (Altschuler et al. 1983). The air drying method gives results only after several months. A sound land evaluation, however, requires a quantification of the actual and potential acidity of the soil in order to assess the amount of acid to be neutralized or leached after drainage and oxidation, to make the soil suitable for a given land use. Hence, the aim of the present study was to develop an easy, fast and low-cost quantitative field laboratory method for estimating potential and actual soil acidity.

3 Materials

For the development of the field laboratory method, samples were used of an actual acid sulphate soil with a potential acid peat substratum (the Zuidplaspolder profile) and of a potential acid sulphate soil (the Tholen profile), both located in The Netherlands. In the field, these samples were packed in thick-walled plastic pots, as air-free as possible and they were handled in the laboratory or freeze-dried within 24 hours. The method was tested on 61 freeze-dried samples from the Mekong Delta, Vietnam and from the Berbak area, eastern Sumatra, Indonesia. The latter samples varied from clay to peat, from totally oxidized to reduced materials, from pyrite-rich to non-poten-

tial acid materials without pyrite. A description of the profiles from which the samples were taken, is given in Appendix 1.

4 Methods

Determination of total potential and actual acidity.

Total acidity of the soil was determined by titration up to pH 5.5 with NaOH of a sample suspended in a NaCl solution (1 mol/l), in a soil/solution ratio of 1/5 by volume or 1/2.5 by mass. pH measurements were done with an Orion Digital Ionalyzer, model 801A. Total acidity at pH 5.5 was read from the titration curves. Potential acidity of the samples was determined after they were oxidized, actual acidity was determined of the fresh or freeze-dried samples.

Titration methods

Four titration methods were tested:

1. 'Slow titration' of the soil suspension. Different amounts of NaOH solution were added to 20 ml subsamples of the soil suspension. After various time steps (immediately after titration, after 1 h, 24 h, 48 h and 1 week), the pH of all subsamples was measured and titration curves were drawn;
2. 'Fast titration' of the soil suspension. Subsamples (100 ml) of the soil suspension were rapidly titrated by small additions of NaOH solution. After each addition the suspension was homogenized and the pH measured. Additions were continued until a pH between 6 and 7 was reached;
3. 'Back titration' of the suspension. After fast titration of the soil suspension to pH 6-7 and a 24 h waiting period (during which the pH dropped to 5.5-6), the suspension was back titrated with a HCl solution to pH 5.0-5.5. After another wait of 24 h the pH was measured again;
4. 'Fast titration' of the soil extract. Subsamples (50 or 100 ml) of the soil suspension were extracted twice with a NaCl solution (1 mol/l). The extract was titrated fast.

Oxidation method

After suspending the soil sample in a NaCl solution (1 mol/l), in a soil/solution ratio of 1/5 by volume or 1/2.5 by mass, the suspension was oxidized with 30% H_2O_2 at room temperature or on a moderately warm waterbath. Hydrogen peroxide was added until the mineral soil material became clear grey to clear brown coloured and no foam existed or was formed upon adding further H_2O_2 . A possible surplus of H_2O_2 was evaporated by heating briefly on a boiling waterbath. The suspension was then brought to the original volume by evaporation or by addition of water.

Further chemical analyses

Pyrite was measured as Fe after extraction by HNO_3 . Non-pyrite iron was excluded by a pretreatment with a $\text{HF}/\text{H}_2\text{SO}_4$ mixture. Water-soluble plus exchangeable sulphate and jarosite were determined turbidimetrically as sulphate, after successive extractions by $\text{EDTA} \cdot 3\text{Na}$ (0.1 mol/l) and by HCl (4 mol/l) (Begheijn et al. 1978).

Elemental sulphur was determined turbidimetrically as colloidal sulphur after extraction with acetone and exchange of acetone by water.

Total sulphur was measured after conversion of all sulphur compounds to sulphate by partial fusion in a mixture of sodium carbonate and potassium nitrate at 700°C (Begheijn 1980). Organic S was estimated from the difference between total S and the sum of all other sulphur compounds.

Total dissolved organic carbon (TOC) of the soil suspension extract was measured as CO₂ by IR-spectrometry with a TOC Analyzer, Beckman model 915-B.

NH₄ of the soil suspension extract was determined by spectrometry with Nessler's reagent.

CEC was measured by replacement of adsorbed cations by Li with Li.EDTA and determination of Li by flame photometry; determination of exchangeable Ca and Mg by atomic adsorption spectrometry and of exchangeable Na and K by atomic emission spectrometry (Begheijn 1980). NO₃ in the soil solution was tested qualitatively by the ring test, using concentrated sulphuric acid and ferrous sulphate solutions.

Microscopic examination of pyrite

Fresh and H₂O₂-oxidized samples of the two Dutch profiles were examined for pyrite under a microscope with a combination of transmitted light and incident mercury light (Slager 1967). The microscopic slides were prepared according to Pons (1964).

5 Results

After oxidation, the pH of the soil suspension was measured in the clear liquid above the settled soil mass, as well as in the suspension after homogenization. The pH measured before and after homogenization differed by 0.2 pH unit or less for all samples. Stabilization of pH was faster in the homogenized suspensions. Differences between repeated pH measurements were smaller for the homogenized suspensions (0.3 pH unit). Also, the time required for titration was shorter if the pH was measured in the homogenized suspensions. Therefore, pH was always measured in the homogenized suspensions.

Total acidity was also measured in extracts from soil suspensions. The extractions required much time and work. Besides, total acidity of the extracts was about 15 per cent lower than the total acidity of the suspensions (Konsten 1984a). Therefore, this method was not considered further.

During titration a greenish blue precipitate was often formed. After leaving the suspensions for about two days, the colour slowly changed to orange. Upon addition of a drop of hydrogen peroxide, the colour of the precipitate changed immediately to orange. If a drop hydrogen peroxide was added to the soil suspension before titration, the colour of the precipitate forming in the suspension during titration was orange from the start.

Ten identical peat samples of the Zuidplaspolder subsoil were oxidized by different amounts of hydrogen peroxide. Initially, the pH decreased with increasing amounts of H₂O₂, while total acidity and dissolved organic carbon content of the soil suspension increased. Upon further addition of H₂O₂ the pH increased, while total acidity and dissolved organic carbon in the soil suspension decreased (Figure 1). Ammonium content of the soil suspensions increased upon oxidation. A qualitative test showed that ammonium was not oxidized to nitrate.

During oxidation, volatilization of H_2S , SO_2 and NH_3 was tested qualitatively. Tests for H_2S and NH_3 were negative, the test for SO_2 was positive. Sulphur budgets of some of the Dutch samples showed a decrease in sulphur content by 20 to 40 per cent of total sulphur after oxidation (Konsten 1984a).

Chemical as well as microscopic analyses of samples from The Netherlands showed that not all pyrite was oxidized after treatment with hydrogen peroxide. In particular samples rich in organic matter still contained part of their pyrite after oxidation (Table 1).

Table 1 Pyrite-S content of samples from The Netherlands determined chemically and microscopically before and after oxidation

Horizon and sample number	Pyrite-S content (mass %)		Microscopic pyrite*)	
	before oxid.	after oxid.	before oxid.	after oxid.
<u>Tholen</u>				
A12g	0.24	0.26	+	±
C1g1	0.68	0.13	+	—
C1g2	1.51	0.75	+	+
G1	0.68	n.d.	+	±
<u>Zuidglaspolder</u>				
A12g	0.43	n.d.	+	±
C12g	0.48	n.d.	+	±
CG	1.92	n.d.	++	+
G1	2.92	n.d.	++	+
G2	2.40	n.d.	++	+

n.d.: not determined

*) presence of pyrite framboids:

- ++ very clear
- + clear
- ± little or doubtful
- not present

Figure 2 shows the relation between pH and total acidity after oxidation by H_2O_2 . As expected, an inverse relation was found. The predictive value of the pH after oxidation is low, however, especially below pH 2.5: the lowest and highest acidity at a certain pH may differ by a factor two or three.

Figure 3 represents the relation between the pyrite content of the soil and the amount of acidity which developed upon oxidation of the soil samples (= total potential minus actual acidity). The dashed line shows the theoretical relation between the two. Pyrite content is poorly related to total potential minus actual acidity. Most of the samples show a higher total potential acidity than would be expected from oxidation of pyrite only.

Figure 4 shows the relation between the total S content and total acidity after oxidation. Total sulphur content shows a better relation to total potential acidity than pyrite to total potential minus actual acidity.

After titration the pH continued to decrease slowly for one or two days and then became constant. The relation between total potential acidity measured immediately

after titration (A_0) and measured 48 hours after titration (A_{48}), is extremely close

$$A_{48} = 1.1 * A_0 (r^2 = 0.99, n = 76).$$

For total acidity this relation is

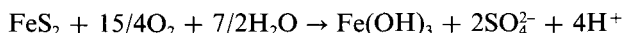
$$A_{48} = 1.8 * A_0 (r^2 = 0.85, n = 58)$$

The back titration always resulted in a lower total acidity than the direct titration methods (Konsten 1984a) and was not further considered.

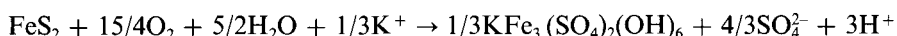
6 Discussion

Total acidity is measured in a 1 molar salt solution in order to eliminate influences of differences in salt concentration on pH and total acidity (McLean 1982). This also enables the use of slightly saline water in remote survey areas where no demineralized water is available. For the method described here, NaCl was chosen instead of the commonly used KCl, because it is cheaper and more easily available.

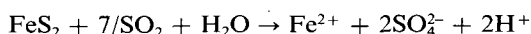
The greenish blue precipitate which was often observed to form in the soil suspension during titration, probably consists of a complex ferrous/ferric hydroxide. Maximal acidity, however, is measured only if, after oxidation, all iron is present in the ferric form. During titration ferric hydroxide will then be formed. This may be illustrated by the oxidation reaction of pyrite. Maximal acidity (4 mol H^+ per mol pyrite) is formed by the reaction



If jarosite is formed, however, the acidity arising from oxidation is only 3 mol H^+ per mol pyrite



Production of acidity is lower still, namely 2 mol H^+ per mol pyrite, if upon oxidation ferrous ions are produced (Van Breemen 1973)



In order to measure the total amount of potential acidity after oxidation it is necessary to turn all iron into the ferric form before titration. This is done by adding a drop of hydrogen peroxide before titration. The precipitate forming then has the orange colour of $Fe(OH)_3$.

Before starting the titration it is very important to oxidize all organic matter as completely as possible. Initially organic acids are produced which raise the total acidity of the soil suspension (Figure 1). Poelman (1968) also warned for this. Upon further oxidation CO_2 and H_2O are formed, thus eliminating again the acidity initially formed by organic matter.

Also upon oxidation organic nitrogen is transformed into ammonium (Figure 1) which neutralizes part of the acidity. This neutralizing effect must be taken into account with samples rich in organic matter. Buffering of acidity by nitrogen amounted to a maximum of 17 mmol/100 g soil for peat samples (Konsten 1984b). The ammonium formed was not oxidized by hydrogen peroxide, probably because of the low pH.

During oxidation part of the potential acidity escaped by evaporation of SO_2 . This was also observed by Van Breemen (1976) in oxidation experiments of pyrite-containing samples from Thailand. Volatilization of sulphur species was also found to occur during natural oxidation of acid sulphate soils (Allbrook 1973; Banwart and Bremner 1975; Thomas and Varley 1982). Comparison of volatilization under oxidation by hydrogen peroxide with evaporation under natural conditions is not yet possible as quantitative data are lacking.

Not all pyrite is oxidized by hydrogen peroxide, as was ascertained chemically, as well as microscopically for the samples from The Netherlands (Table 1). Under field conditions pyrite in mineral soils in Thailand was oxidized almost completely (Van Breemen 1976). Soil material rich in organic matter may, however, still contain pyrite after oxidation in the field, as is the case in the topsoil of the Zuidplaspolder profile. Probably, this stable pyrite is enclosed within the organic matter and thus protected from oxidation. Pyrite crystals enclosed in plant remnants are described by Altschuler et al. (1983).

A fairly good relation exists between pH after oxidation and potential acidity. However, the predictive value of this relation is very small, as is clear from Figure 2. Below pH 2.5, total potential acidity may vary manifold. Predicting potential acidity by measuring the pH after oxidation, as was done in many methods and surveys (Van Beers 1962; Allbrook 1973; Andriesse et al. 1973; Bloomfield 1973; FAO/Unesco 1974; USDA 1975; Van Breemen 1982) therefore is not a sound procedure. Titration after oxidation is a better and safer method to assess potential acidity of acid sulphate soils.

Potential acidity is often assessed by determination of the pyrite content. Chemical analysis of pyrite is complicated and expensive. Besides, as is clear from Figure 3, the relation between pyrite content and total potential minus actual acidity is poor ($r^2 = 0.53$). Not all pyrite is readily oxidized into sulphuric acid. But the main reason for this poor relation is that pyrite is not the only S compound that produces acidity upon oxidation. Other reduced sulphur species may be important as well, especially organic sulphur. Altschuler et al. (1983) report 40 to 60 per cent of total sulphur to be bound in organic form in pyrite peat soils of Florida. From Annex 1 it is clear that samples rich in organic matter may contain considerable amounts of organic sulphur: the subsoil of the Zuidplaspolder profile (2.30% org. S); samples A₂X₃C (2.03%), TL1Cl (2.01%) and TL2B2 (1.92%) from Vietnam. Elementary sulphur is important in the Clg horizon of the Tholen profile (0.54%). As expected, total sulphur content already shows a better relation with potential acidity (compare Figs. 3 and 4).

As can be seen from Figure 4, there is a certain disagreement between total S-content and total potential acidity for many soil samples. This is due to several reasons. First, the buffering capacity of the soil is not accounted for. With the hydrogen peroxide method, the fast working acid neutralizing compounds can act before the acidity is titrated. For example, the calcareous subsoil of the Tholen profile has a pyrite content of 0.7 per cent, while its potential acidity is zero. Second, some of the potentially acid SO_2 is escaping the soil sample during oxidation. Third, acidity in the form of H^+ , Al^{3+} , Fe^{2+} , as well as sulphate from already oxidized horizons may have been transported to other parts of the soil, thus deranging the relation between total sulphur content and potential acidity of different soil horizons.

From Figure 4 it may be concluded that the total potential acidity, as measured

by this titration, gives a good indication of the maximum acidity which may arise upon oxidation of the soil.

Under natural circumstances the acidity after oxidation is less for several reasons:

- Under slow oxidation the slowly working buffer capacity of the soil may have its effect, i.e. the buffering of acidity by the weathering of minerals (Van Breemen 1973);
- End products other than $\text{Fe}(\text{OH})_3$ may be formed, resulting in less acidity being produced (Van Breemen 1973);
- Oxidation of organic matter occurs more slowly, resulting in a more gradual release of acidity by the oxidation of organic sulphur;
- Leaching of soil acidity may occur under field circumstances.

Titration results are influenced by operational time, as was examined by Bruggenwert (1972). During the present study total acidity at pH 5.5 turned out to increase with increasing time between titration and pH measurement. The increase was maximal immediately after titration and lessened with time. After titration, the pH stabilized in all samples in 24 to 48 hours. For all samples, total potential acidity measured after the pH stabilized, was 10% higher than the total potential acidity measured immediately after titration. Finding the same relation for samples from different countries, different parent materials (clay as well as peat), different soil horizons (oxidized, well developed acid sulphate horizons as well as unripe layers), we may conclude this relation to be generally applicable. Therefore, the waiting time of 48 hours may be omitted and total potential acidity may be calculated by multiplying the total potential acidity measured immediately after titration by 1.1 and the total actual acidity measured immediately after titration by 1.8. This also reduces the amount of chemicals needed, the time required for analysis and the chance of mistakes.

7 Conclusions and recommendations

The assessment of potential acidity by existing methods using pH after oxidation or pyrite content has a low predictive value and is not recommended.

The method described here allows a fast and accurate assessment of the maximal potential acidity of acid sulphate soils. Under field circumstances the acidity arising from oxidation of the soil may be lower than the maximal potential acidity, because:

- Part of the acidity may be leached from the soil;
- Part of the acidity may be neutralized by slowly working buffers, for example by weathering of minerals;
- End products other than $\text{Fe}(\text{OH})_3$ may be formed, resulting in a lower acidity of the soil;
- Oxidation of organic matter may occur more slowly, so that acidity formed by oxidation of organic sulphur is released more gradually.

The method therefore gives a safe estimate of potential acidity.

Samples rich in organic matter should be oxidized fully and with care. An amount of 100 ml 30% hydrogen peroxide may be needed to oxidize a 5 ml (10 g) sample of peat. If not fully oxidized, the presence of organic acids in the soil suspension may result in too high a potential acidity measured. A small part of the total acidity may be neutralized by organic nitrogen.

During oxidation with hydrogen peroxide, part of the potential acidity is volatilized

as SO_2 . Evaporation of sulphur species also occurs under natural circumstances.

Larger part of all reduced sulphur is oxidized by hydrogen peroxide, but part of the pyrite may be stable in samples rich in organic matter. The same was found under field conditions.

Potential acidity is maximal 48 hours after titration.

Acknowledgements

Thanks are due to Ir. M.E.F. van Mensvoort (Dept. Soil Science and Geology, Agric. University, Wageningen) and Ir. W.H. Diemont (Neth. Inst. for Nature Management, Arnhem, The Netherlands) for providing soil samples from Vietnam and Indonesia; to Messrs M.A. Bazen and W.C. Markus (Soil Survey Institute, Wageningen) for support during fieldwork; to Ir. C.B.H. Schneider (Netherlands Advisory Service for Soil Technology, Water Management and Fertilizing in Stockfarming) for advice on volumetrical soil sampling techniques; to Messrs. L.Th. Begheijn and M.T.M.H. Lubbers (Dept. Soil Science and Geology, Agric. Univ., Wageningen) for assistance during laboratory work and for analyses of sulphur species and to Ing. A. Jongmans (Dept. Soil Science and Geology, Agric. Univ., Wageningen) for assistance during microscopical analyses.

References

- Allbrook, R.F. 1973. The identification of acid sulphate soils in North West Malaysia. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen. ILRI Publ. 18, Vol. II: 131-140.
- Altschuler, Z.S., M.M. Schnepfe, C.C. Silber & F.O. Simon. 1983. Sulphur diagenesis in Everglades peat and origin of pyrite in coal. *Science* 221 (nr. 4607): 221-227.
- Andel, T.J. van & H. Postma. 1954. Recent studies in the Gulf of Paria. Kon. Ned. Adad. Wetenschappen, Afd. Natuurkunde, 1st series, II, 5. Noord Hollandse Uitg. Maatsch., Amsterdam.
- Andriessse, J.P., N. van Breemen & W.A. Blokhuis. 1973. The influence of mudlobsters (*Thalassina anomala*) on the development of acid sulphate soils in mangrove swamps in Sarawak (east Malaysia). In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen. ILRI Publ. 18, Vol. II: 11-39.
- Banwart, W.L. & J.M. Bremner. 1975. Formation of volatile sulphur compounds by microbial decomposition of sulphur-containing amino acids in soil. *Soil Biol. Biochem.* 7: 359-364.
- Beek, K.J., W.A. Blokhuis, P.M. Driessen, N. van Breemen, R. Brinkman & L.J. Pons. 1980. Problem soils: their reclamation and management. In: Land reclamation and water management. ILRI Publ. 27: 43-72, Wageningen.
- Beers, W.F.J. van. 1962. Acid sulphate soils. ILRI Bull. 3, Wageningen. Begheijn, L.Th. 1980. Methods of chemical analyses for soils and water. Publ. No. 735, Afd. Bodemkunde en Geologie, Landbouw-universiteit, Wageningen.
- Begheijn, L.Th., N. van Breemen & E.J. Velthorst. 1978. Analysis of sulphur compounds in acid sulphate soils and other recent marine soils. *Comm. in Soil Sci. and Plant Anal.* 9: 873-882.
- Bloomfield, C. 1973. Acidification and ochre formation in pyritic soils. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen. ILRI Publ. 18, Vol. II: 40-51.
- Breemen, N. van. 1973. Soil forming processes in acid sulphate soils. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen. ILRI Publ. 18, Vol. I: 66-130.
- Breemen, N. van. 1976. Genesis and solution chemistry of acid sulphate soils in Thailand. *Agric. Res. Rep.* 848, PUDOC, Wageningen, 263 p.

- Breemen, N. van. 1982. Genesis, morphology and classification of acid sulphate soils in coastal plains. In: Acid sulphate weathering. Spec. Publ. No. 10: 95-108, Soil Sci. Soc. Amer., Madison, Wisconsin.
- Brinkman, R. & L.J. Pons. 1973. Recognition and prediction of acid sulphate soil conditions. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen, ILRI Publ. 18, Vol. I: 169-203.
- Bruggenwert, M.G.M.. 1972. Adsorptie van Al-ionen aan het kleimineraal montmorilloniet. Agric. Res. Rep. 768, PUDOC, Wageningen, 120 p.
- Coulter, J.K. 1973. The management of acid sulphate and pseudo-acid sulphate soils for agriculture and other uses. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen, ILRI Publ. 18, Vol. I: 255-274.
- Edelman, Th. 1973. Een methode om in het veld het pyrietgehalte van de grond te schatten. Verslag Regionale Bodemkunde, Vakgroep Bodemkunde en Geologie, Landbouwwuniversiteit, Wageningen.
- FAO/Unesco. 1974. Soil map of the world 1: 5 000 000, Vol. I: Legend. UNESCO, Paris.
- Kawalec, A. 1973. World distribution of acid sulphate soils. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen, ILRI Publ. 18, Vol. I: 292-295.
- Konsten, C.J.M. 1984a. Schatting van actuele en potentiële aciditeit: onderzoek naar een veldmethode voor kartering van gebieden met (potentiële) sulfaat-zure gronden. Interne Mededeling nr. 64, Stichting voor Bodemkartering, Wageningen, 40 pp.
- Konsten, C.J.M. 1984b. Een veldmethode voor de bepaling van het potentiële en actuele zuurgehalte van de grond ten behoeve van bodemkartering en landevaluatie in gebieden met potentiële en actuele sulfaat-zure gronden. Interne Mededeling nr. 67, Stichting voor Bodemkartering, Wageningen. 51 pp.
- McLean, E.O. 1982. Soil pH and lime requirement. In: Page, A.L., R.H. Miller and D.R. Keeney (eds.): Methods of soil analysis, Part 2: Chemical and microbiological properties. Agronomy Monograph No. 9 (2nd ed.), Amer. Soc. Agronomy, Madison, Wisconsin.
- Mensvoort, M.E.F. van, M. Flach & J. Bos. 1983. Report of a mission to Vietnam, March 21 – May 7, 1983. Mission Report No. 8, VH10 Project, Vakgroep Bodemkunde en Geologie, Landbouwwuniversiteit, Wageningen, 37 p.
- Neckers, J.W. & C.R. Walker. 1952. Field test for active sulfides in soil. Soil. Sci. 74: 467-470.
- Poelman, J.N.B. 1968. Verder onderzoek naar het onderkennen en voorkomen van kattezand. Landbouwk. Tijdschr. 80: 95-97.
- Poelman, J.N.B. 1973. Soil material rich in pyrite in non-coastal areas. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen, ILRI Publ. 18, Vol. II, 197-207.
- Ponnamperuma, F.N., Tasnee Attanandana & Gora Beye. 1973. Amelioration of three acid sulphate soils for lowland rice. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen, ILRI Publ. 18, Vol. II: 391-406.
- Pons, L.J. 1964. A quantitative microscopical method of pyrites determination in soils. In: Jongerius, A. (ed.): Soil micromorphology, Elsevier Publ. Co., Amsterdam.
- Pons, L.J. 1973. Outline of genesis, characteristics, classification and improvement of acid sulphate soils. In: Dost, H. (ed.): Acid sulphate soils. Proceedings of the International Symposium, Wageningen, ILRI Publ. 18, Vol. I: 3-27.
- Slager, S. 1967. Achtergronden en methodiek van het in uitvoering zijnde pyrietonderzoek. Dienst Bodemkartering, Afd. Bodemmorfologie, Ministerie van Opbouw, Paramaribo.
- Thomas, P. & J.A. Varley. 1982. Soil survey of tidal sulphidic soils in the tropics: a case study. In: Dost, H. and N. van Breemen (eds.): Proceedings of the Bangkok Symposium on acid sulphate soils. ILRI Publ. 31: 52-72.
- USDA. 1975. Soil Taxonomy: a basic system of soil classification for making and interpreting soil surveys. USDA Agric. Handbook 436, U.S. Government Printing Office, Washington D.C.

Annex 1

Profile descriptions and results of chemical analyses and titration experiments

A1.1 Samples from The Netherlands

Profile descriptions (for full profile descriptions, refer to Konsten 1984a and b)

Th-Slikvaaggrond (Thionic Fluvisol; Typic Sulfaquent) from Tholen

Allg	0- 3 cm	heavy clay, unripe, rich in organic matter, strongly calcareous
A12g	3- 20	heavy clay, unripe, rich in organic matter, non- calcareous; samples from 8-18 cm
Clg	20- 60	heavy clay, unripe, rich in organic matter, non- calcareous; samples 1 from 25-35 cm; samples 2 from 47-57 cm
Gl	60-100	very heavy clay, unripe, rich in organic matter, strongly calcareous; samples from 68-78 cm

ZP-Plaseerdgrond (Mollic Gleysol; Typic Sulfaquent) from the Zuidplaspolder

A11	0- 2 cm	peat, ripe, non-calcareous
A12g	2- 18	peaty clay, ripe, non-calcareous; samples from 5-15 cm
C11	18- 21	peat, almost ripe, non-calcareous
C12g	21- 60	very heavy clay, half-ripe, non- calcareous; samples from 35-45 cm
CG	60- 80/ 90	peaty clay, unripe, non-calcareous; samples from 65-75 cm
G1	80/ 90- 90/100	peat, unripe, non-calcareous; samples from 82-87 cm
G2	90/100-140	peat, unripe, non-calcareous; samples from 110-125 cm

A1.2 Samples from Vietnam

Profile description (for full profile descriptions, refer to Van Mensvoort et al. 1983)

X₄-from Do Hoa State Farm, Duy en Hai District, Hô Chi Minh City Province

A	0- 20 cm	clay, half-ripe, low in organic matter
AC	20- 47	clay, unripe, low in organic matter
C1	47-117	clay, unripe, high in organic matter
C2	117-217	clay, unripe, low in organic matter

X₃₆-from Do Hoa State Farm, Duy en Hai District, Hô Chi Minh City Province, Typic Tropaquent

A	0- 10 cm	heavy clay, ripe, low in organic matter
B21	10- 28	heavy clay, ripe, low in organic matter
B22g	28- 60	heavy clay, ripe, low in organic matter
B23g	60- 91	heavy clay, half-ripe
Cl	91-153	heavy clay, half-ripe, low in organic matter

Results of chemical analyses

Horizon	Sample number	Before oxidation									After oxidation	
		pH NaCl	org.C (mass %)	Sulphur species (mass %, on oven dry basis)								pH NaCl
				pyrite S	elem. S	organ. S	water sol. S	jarosite S	total S	pyrite S	total S	
Tholen												
A12g	Th 1, 2, 3, 4	6.7	—	0.24	—	—	—	—	0.21	0.26	0.17	5.0
Clg1	Th 5, 6, 7, 8	6.7	—	0.68	—	—	—	—	0.80	0.13	0.49	2.6
Clg2	Th 9, 10, 11, 12	6.9	2.06	0.51	0.54	0	0.24	0.04	1.81	0.75	1.25	3.3
G1	Th 13, 14, 15, 16	7.8	—	0.68	—	—	—	—	0.65	—	—	7.8
Zuidplas												
A12g	ZP 1, 2	3.7	—	0.43	—	—	—	—	0.41	—	—	5.1
Cl2g	ZP 3, 4	3.2	—	0.48	—	—	—	—	0.42	—	—	2.8
CG	ZP 5, 6	3.4	—	1.92	—	—	—	—	1.49	—	—	2.3
G1	ZP 7, 8	4.0	20.47	2.92	0.22	0.01	0.62	0.26	4.02	—	—	1.8
G2	ZP 9, 10	5.0	36.31	2.40	0.14	2.30	0.29	0.20	5.33	—	—	1.9

C2	153-280	clay, unripe, low in organic matter
C3	280-330	clay, unripe, low in organic matter

F₂X₄₇-from Farm 85B, Ha Tien Plain, Kiên Giang Province; Typic Sulfic Tropaquept

A1	0- 22 cm	clay, ripe, low in organic matter; pH 3.6
B21	22- 57	clay, ripe, low in organic matter; pH 3.6
B22	57- 85	clay, ripe, low in organic matter; pH 3.6
B23	85-115	clay, half-ripe, low in organic matter
BC	115-150	clay, half-ripe, low in organic matter
C	150-230	clay, unripe, low in organic matter

A₂X₅-from Farm 85B, Ha Tien Plain, Kiên Giang Province; Typic Sulfaquept

B21	7- 25 cm	clay, ripe, low in organic matter
B22	25- 68	clay, ripe, low in organic matter
BC	68- 86	clay, ripe, high in organic matter
C	86-295	clay, half-ripe, peaty

TL1-from Tân Lập Seedfarm, Châu Thành District, Tiền Giang Province

B23	69- 89 cm	clay, ripe, high in organic matter
BC	89-111	clay, half-ripe, high in organic matter
C1	111-178	clay, half-ripe, rich in organic matter

TL2-from Tân Lập Seedfarm, Châu Thành District, Tiền Giang Province

B24	121-136 cm	clay, unripe, low in organic matter
BC	136-146	silty clay, unripe, low in organic matter
C	146-240	silty clay, unripe, low in organic matter

Results of titration experiments

Horizon	Sample number	Tot. act. acid.	Tot. pot. acid.		
		(mmol H ⁺ /100 g soil)			
		quick	quick	24 h after titration	soil extract
A12g	Th4	—	1.61	1.23	—
C1g1	Th5	—	28.3	42.9	22.8
C1g1	Th7	—	33.7	34.2	—
C1g1	Th8	—	17.1	23.7	18.3
C1g2	Th10	—	17.3	31.9	—
C1g2	Th11	—	17.6	28.4	18.2
A12g	ZP1	—	0.59	0.80	—
A12g	ZP2	1.81	2.46	3.37	—
C12g	ZP3	—	18.9	25.7	15.4
C12g	ZP4	3.71	23.4	30.1	22.0
CG	ZP5	—	62.2	78.1	65.0
CG	ZP6	5.36	54.5	73.5	48.3
G1	ZP7	—	156.0	170.8	—
G1	ZP8	4.23	149.8	165.4	—
G2	ZP9	—	233.4	246.0	—
G2	ZP10	2.59	160.6	192.0	—

Results of titrations and of chemical analyses

Sample number horizon	Acidity and pH						Sulphur species (mass %)						CEC and total bases (ionic equivalents- mmol/kg)	
	pH fresh	pH after oxid.	total act.acid.		total pot.acid.		solub. S	jarosite S	pyrite S	elem. S	organ. S	total S		
			(mmol H ⁺ /100g soil)										CEC	total bases
			quick	48h	quick	48h								
X4-A	5.5	5.1	–	–	1	2	–	–	–	–	–	0.03	158	383
Z4-AC	5.3	4.8	–	–	2	3.5	–	–	–	–	–	0.06	183	360
X4-C1	2.9	1.7	14.5	21.3	136.5	151	0.55	0.18	1.24	0.13	1.14	3.24	147	336
X4-C2	2.6	1.3	10.3	20.0	161	180	–	–	0.14	–	–	0.10	125	325
X36-A	5.9	5.9			0	0	–	–	–	–	–	0	162	313
X36-B21	5.8	6.3	0	0	0	0	–	–	–	–	–	0.10	179	261
X36-B22	6.1	6.0	0	0	0	0	–	–	–	–	–	0.04	163	349
X36-B23	6.1	6.0	0	0	0	0	–	–	–	–	–	0.06	148	409
X36-C1	6.4	3.2	0	0	0	7.5	0.07	0.17	0.23	0	0	0.35	120	469
X36-C2	3.6	2.0	4.2	7.9	71.5	80	0.28	0.06	0.77	0.06	0.04	1.15	82.0	684
X36-C3	6.7	2.7	0	0	33	43	0.08	0.08	0.58	0	0.10	0.84	101	645

F2X47-A	3.7	3.4	12.0	18	19	23	1.25	0.18	1.45	0.16	1.13	4.17	158	18.2
F2X47-B21	3.1	2.9	12.5	18	15.5	18	—	—	—	—	—	0.04	154	52.2
F2X47-B22	3.0	2.7	13.5	18.5	16	19.5	—	—	—	—	—	0.20	153	54.2
F2X47-B23	3.2	2.7	12.0	19	17.5	19	0.10	0	0.14	0	0	0.20	175	46.1
F2X47-BC	2.8	1.6	19.0	14.8	103	112	0.35	0.09	0.82	0.10	1.04	2.40	166	42.2
F2X47-C	2.9	2.3	9.5	18	59	75	0.23	0.29	0.80	0.44	0.14	1.93	170	128
A2X5-B21	3.4	2.9	10.5	18.2	22	30	—	—	—	—	—	0.12	96.1	102
A2X5-B22	3.3	2.4	15.0	19.5	40	43	0.20	0.04	0.09	0	0.05	0.38	124	57.7
A2X5-BC	3.0	1.9	17.0	18	82	87	0.26	0.07	0.25	0.06	0.06	0.70	193	31.6
A2X5-C	2.6	1.5	32.0	46	183	220	0.65	0.07	0.96	0.09	2.03	3.80	171	19.1
TL1-B23	3.2	2.1	22	28	73	79	0.27	0.05	0.08	0.06	0.11	0.57	175	64.0
TL1-BC	2.5	1.3	45	56.8	237.5	248	0.80	0.14	0.61	0.14	1.47	3.16	164	29.1
TL1-C1	2.4	1.5	58	80	311	338	1.11	0.11	1.12	0.20	2.01	4.55	40.7	64.7
TL2-B2	3.4	2.9	11.8	—	12	15	0.26	0.11	0.10	0	1.92	2.92	154	158
TL2-BC	2.7	1.8	14.5	24	72	95	0.47	0.17	0.66	0	0	1.20	141	147
TL2-C	2.8	1.8	10	18	118	131	0.37	0.16	1.11	0.10	1.47	3.11	137	203

A1.3 Samples from Indonesia
 (Berbak, east Sumatra)
 Profile descriptions

Sample number	Horizon	Depth	
1-83844	IG	75- 85 cm	peat
83845	IIG	110-120	unripe clay, org. mat.
83846	IIICg	180-200	half-ripe clay, glauconite
2-83847	IG	270-280	peat
83848	IIG	300-310	unripe clay, org. mat.
83849	G	350-360	sediment
3-83850	G	70- 80	peat
83851	G	90-100	unripe clay, org. mat.
83852	G	140-150	sediment
4-83854	G	100-110	unripe clay, org. mat.
83855	G	140-150	sediment
5-83856	G	20- 40	unripe clay, org. mat.
6-83857	G	250-350	unripe clay, org. mat.
83858	G	400-450	sediment
7-83859	IG	310-320	peat
83860	IIG	340-400	—
83861	G	430-460	—
8-83862	G	650-700	peat
10-83864	G	120-140	unripe clay, org. mat.
83865	G	180-200	unripe clay, org. mat.
83866	G	250-280	sediment
11-83867	IG	30-100	half-ripe clay, org. mat.
83868	IIG	150-180	almost-ripe clay, org. mat.
83869	G	210-230	half-ripe clay
83870	G	340-350	sediment
12-83872	IG	80-130	half-ripe clay
83873	IIG	300-350	sediment, shell remains
14-83874	G	45- 60	half-ripe clay, org. mat.
83875	G	100-115	half-ripe clay, org. mat.
83876	G	240-250	sediment
15-83877	G	50- 90	half-ripe clay, org. mat.
83879	G	230-250	half-ripe clay
83880	G	230-250	half-ripe clay, org. mat.
16-83878	G	150-220	—

Annex 2

Manual of the field laboratory method for determination of total potential and actual acidity in acid sulphate soils

A2.1 Determination of total potential acidity

Principle of the method:

Oxidation of all reduced sulphur species in a soil sample, suspended in a sodium chloride solution (1 mol/liter) by hydrogen peroxide and subsequent determination of total acidity by quick titration with sodium hydroxide to pH 5.5.

Reagents:

- H_2O_2 , 30%. (If stabilized hydrogen peroxide is used which contains some phosphoric acid, its acidity should be determined by quick titration with NaOH);
- NaOH solution, 0.50 mol/l;
- NaCl solution, approx. 1 mol/l (i.e. a saturated NaCl solution containing about 6 mol NaCl/l, diluted 6 times).

Equipment:

- Glass beaker (400-1000 ml);
- Stirring bar;
- Waterproof pen;
- (Field) pH meter;
- A buret or two plastic hypodermic syringes without needles (one of 1 ml, one of 5 ml);
- A volumetric sampling cylinder (or a balance).

Sample material:

- Field-moist or dried soil.

Procedure

Put a soil sample of known volume ($V \text{ cm}^3$) or mass ($W \text{ gram}$) into a glass beaker. Add about 5 times V (for volumetric sample) or 2.5 times W (for bulk sample) ml of the sodium chloride solution and homogenize. Mark the height of the suspension surface to the outside of the beaker. Add a small quantity of hydrogen peroxide. Take care with samples rich in organic matter or manganese: they may effervesce strongly. Wait for about one hour, add a new quantity of hydrogen peroxide. Swirl the suspension around from time to time. Repeat additions of hydrogen peroxide until the liquid above the suspension becomes clear and there is no foam anymore at the liquid surface and no foam is formed upon further addition of H_2O_2 . Leave overnight. (The oxidation process may be accelerated by putting the glass beakers on a warm waterbath or exposing them to the sun). Oxidation is complete if the organic matter of the soil material has lost its dark appearance, if the mineral soil has got a clear gray to clear light brown colour and if the liquid above the settled suspension has become clear and transparent: then there is no foam any more at the surface of the solution and the

Results of titrations and of chemical analyses

Sample number horizon	pH fresh	pH after oxid.	Acidity and pH				Sulphur species (mass %)				CEC and total bases (ionic equivalents- mmol/kg)	
			total act.acid.		total pot.acid.		before oxidation		after oxidation			
			(mmol H ⁺ /100g soil)				pyrite S	total S	pyrite S	total S	CEC	total bases
			quick	48h	quick	48h						
83844	2.9	5.4	30	83	2.0	0	0.23	0.38	—	49.1	—	—
845	3.8	4.3	3.8	6.9	4.7	7.1	0.22	0.24	—	1.14	167	111
846	4.2	2.5	2.8	6.3	47.9	53.3	0.83	0.86	—	28.2	212	161
847	3.6	6.3	23	74	0	0	0.24	0.44	—	54.8	—	—
848	4.5	2.1	2.1	4.8	75.0	86.7	1.06	1.03	—	3.78	189	171
849	6.0	3.2	0	0	41.9	47.9	0.72	0.81	—	1.89	210	192
850	3.6	4.2	53	117	31.0	27.0	0.24	0.27	0.05	41.1	—	—
851	4.6	2.7	2.3	6.3	44.1	51.1	0.72	0.63	—	6.66	237	163
852	5.5	2.8	0	0	50.0	56.7	1.11	1.10	—	2.77	220	200
854	4.8	3.1	1.6	4.7	42.7	52.2	0.86	0.87	0.04	2.64	208	188
855	6.9	4.9	0	0	3.0	8.5	0.91	1.00	0.03	2.29	221	276
856	7.6	2.6	0	0	50.6	61.5	1.28	1.29	—	1.96	121	785
857	3.5	1.7	12.6	20	193	226	2.53	4.17	0.13	6.74	207	56.2
858	6.2	1.9	0	0	136	146	2.30	2.56	—	1.83	199	198
859	3.0	3.4	19	71	149	146	0.15	0.61	—	33.3	—	—
860	3.6	2.1	13.9	32.4	136	151	0.70	0.96	0.01	20.6	300	17.0

861	4.5	1.5	2.9	7.8	196	216	2.60	3.24	—	6.00	239	149
862	2.8	4.6	45	81	34.8	44.8	0.24	0.59	—	83.3	—	—
864	3.7	1.7	10.0	15.4	155	165	2.71	2.62	—	10.1	231	52.6
865	3.7	2.2	10.4	15.7	70.7	76.7	0.92	0.96	—	2.95	178	41.9
866	3.9	2.0	4.1	9.0	102	114	1.86	1.77	—	0.25	249	121
867	3.1	2.9	12.8	20.0	57.1	65.5	0.71	1.16	0.02	5.12	132	185
868	6.7	1.9	0	0	90.7	119	1.28	1.90	—	3.26	150	477
869	7.2	1.6	0	0	144	178	3.05	5.05	0.16	5.81	145	386
870	7.4	1.7	0	0	152	168	2.85	3.30	—	3.20	154	448
872	3.6	3.6	7.0	10.6	10.4	13.0	0.10	0.50	—	1.23	161	83.6
873	7.8	3.4	0	0	14.7	21.5	0.91	0.93	—	8.69	215	508
874	5.5	2.2	0	0	55.6	62.9	0.39	0.42	—	5.24	158	265
875	4.5	1.8	4.7	10.5	98.0	137	1.93	3.36	0.07	7.26	164	281
876	7.2	2.3	0	0	69.3	76.8	1.54	2.00	—	0.83	168	284
877	4.9	2.0	2.0	7.4	71.9	99.8	0.92	1.44	—	14.4	125	631
878	6.1	3.0	0	0	65.9	76.4	1.21	1.33	—	3.55	197	410
879	5.5	1.5	0	0	355	387	3.61	5.62	0.27	11.4	195	595
880	5.1	3.9	2.4	3.9	26.7	34.0	0.62	1.15	0.06	21.3	83.9	1157

colour of the supernatant may be anything from colourless to tea brown. Adjust the volume of the suspension to the marked level or, in case the volume is larger, and if possible, evaporate excess water. Add a few drops of hydrogen peroxide to the suspension and homogenize. Measure and note the pH of the suspension. If the pH is below 5.5, titrate the suspension as follows: add exact and known quantities (1.0, 5.0 or 10.0 ml) of the NaOH solution. Homogenize well after each addition and insert the pH electrode into the suspension. After the pH stabilizes, note the pH as well as the quantity of NaOH added. Addition of NaOH solution is to be continued until a pH over 5.5 is reached. Draw a titration curve by plotting the cumulative volume of added NaOH against the pH. Read the amount of NaOH at pH 5.5 from the graph (= B ml). Total potential acidity of the soil is calculated from the following equations:

Total potential acidity (on a volume basis)

$$= 1.1 \times 0.5 B \times \frac{1000}{V} \text{ mol/m}^3 \text{ soil}$$

$$= 550 \frac{B}{V} \text{ mol/m}^3 \text{ soil}$$

or

Total potential acidity (on a mass basis)

$$= 1.1 \times 0.5 B \times \frac{100}{W} \text{ mmol/100 g soil}$$

$$= 55 \frac{B}{W} \text{ mmol/m}^3 \text{ soil}$$

The latter equation gives acidity for the soil as analyzed, field-moist or freeze-dried.

In order to determine the total potential acidity on an absolute dry mass basis, the moisture content of the soil sample has to be corrected for. To determine the absolute dry mass, take a small quantity of the soil sample and dry it for 24 h at 105°C. After cooling (preferably in an exsiccator), weigh again and calculate the correction factor C and total potential acidity as follows:

$$\text{correction factor } C = \frac{\text{moist mass}}{\text{dry mass}}$$

total potential acidity (on an absolute dry mass basis)

$$= 55 \frac{B}{W} \times C \text{ mmol/100 g soil}$$

If after oxidation the pH of the soil suspension equals or exceeds 5.5, the total potential acidity of the soil is zero at pH 5.5.

Remarks

1. Soil samples rich in organic matter may effervesce strongly and give rise to formation of foam. In such cases use high beakers and add hydrogen peroxide in small

- quantities (5 ml each time), especially in the beginning. Add further amounts of H_2O_2 only after effervescence ceases;
2. For the determination of potential acidity it is crucial that the soil sample is oxidized completely, especially if it is rich in organic matter. After complete oxidation, nothing will be left of the soil organic matter, except for some fresh roots, wood remnants, etc. The supernatant solution may have a dark brown colour after oxidation, but it should be clear and transparent after the suspension has settled;
 3. The total amount of hydrogen peroxide needed for the oxidation depends on the organic matter content of the soil: for the oxidation of a 10 g soil sample, about 20 ml of hydrogen peroxide will be required for soil material poor in organic matter, and up to about 80 ml of H_2O_2 for peat samples;
 4. Also, some of the samples poor in organic matter may show a strong effervescence after H_2O_2 addition and this may continue indefinitely even after all sulphur species and organic matter has been oxidized and the colour of the soil has become bright. This effervescence is due to the presence of manganese oxides. MnO_2 acts as a catalyst in the decomposition of H_2O_2 . As soon as the mineral soil becomes bright coloured, the liquid of the soil suspension becomes clear or, after the H_2O_2 has ceased to work and no foam is seen at the surface of the suspension, oxidation is complete.

A2.2 Determination of total actual acidity

Principle of method:

Determination of the total actual acidity of the soil by quick titration of a soil sample, suspended in a sodium chloride solution (1 mol/liter) with sodium hydroxide to pH 5.5.

Reagents:

- – NaOH solution, 0.50 mol/l;
- NaCl solution, approx. 1 mol/l (i.e. a saturated NaCl solution, containing about 6 mol NaCl/l, diluted 6 times).

Equipment:

- A glass beaker (400 – 1000 ml);
- Stirring bar;
- (Field) pH meter;
- A buret or two plastic hypodermic syringes without needles (one of 1 ml, one of 5 ml);
- A volumetric sampling cylinder (or a balance).

Sample materials:

Field-moist soil, packed air-free and analysed, or at least vacuum-dried or freeze-dried, as soon as possible after sampling to prevent oxidation.

Procedure

Put a soil sample of known volume ($V \text{ cm}^3$) or mass ($W \text{ gram}$) into a glass beaker. Add about 5 times V or 2.5 times $W \text{ ml}$ NaCl solution and homogenize. Stir the suspension a few times. Leave overnight.

Measure the pH after stirring the suspension. If the pH is below 5.5 the suspension is titrated as follows. Add a known quantity (1, 5 or 10 ml) of the NaOH solution and homogenize. Insert the electrode and wait until the pH stabilizes. Note the pH, as well as the amount of NaOH solution added. Addition of NaOH is to be continued until a pH over 5.5 is reached. Draw a titration curve by plotting the cumulative volume of NaOH solution added, against the pH. Read the amount of NaOH at pH 5.5 from the graph ($= B \text{ ml}$). Total actual acidity of the soil is calculated from the equations:

Total actual acidity (on a volume basis)

$$= 905 \times \frac{B}{V} \text{ mol/m}^3 \text{ soil}$$

Total actual acidity (on a absolute dry mass basis)

$$= 91 \times \frac{B}{W} \times C \text{ mmol/100 g soil}$$

in which C is the correction factor for the moisture content of the soil:

$$\text{correction factor } C = \frac{\text{moist mass}}{\text{dry mass}}$$

and which is obtained by the procedure as described in Section A2.1.

A2.3 Volumetric soil sampling

For the determination of the acidity of the soil it saves time and effort if volumetric soil samples are taken, instead of bulk samples. From the acidity of field-moist samples on a volumetric basis, the amount of acid per hectare per unit of depth can be calculated directly. Also, with volumetric sampling there is no need for a balance or for determination of the soil moisture content.

Volumetric sampling can easily be conducted with a tube sampler made out of hard PVC pipe. Because of the weak consistency of most (potential) acid sulphate materials, this PVC pipe is suited for the purpose. The sampler can be produced easily and cheaply (fig. 5). A 5-cm piece of pipe (internal diameter about 6 cm), is the sampling tube. A 2-cm piece of the same pipe allows excess sample to move beyond the end of the sampling tube, during insertion into the soil. These two pieces are held in a close-fitting tube of the same material with an internal ring or constriction. Such a holder may be available ready-made in the form of a connecting piece for PVC tubes. If not, it can be constructed by glueing two rings of the appropriate sizes together.

The sampling procedure is as follows: the sampling cylinder is placed on a soil surface that is cut smooth and flat with a spade. The side from which the longer tube sticks out, rests on the soil. A piece of wood is placed on the cylinder and by hammering on it the cylinder is driven into the soil until only the narrower end of the connection

pipe sticks out. Then the whole apparatus is dug out carefully. The soil sticking out from the cylinder is cut off level. The soil sampling tube (the longer one) filled with soil is removed from the connector by twisting it. On the other side of the cylinder the soil is cut of level and the sample is ready. The volume of the sample can be calculated from:

$$\begin{aligned}\text{Volume } V &= R^2 \times H \\ &= 3.14 R^2 \times H (\text{cm}^3)\end{aligned}$$

in which H = height of the sampling cylinder (in cm); R = $1/2$ internal diameter of the cylinder (in cm).

Another cheap sampling device can be easily made from a large transparant plastic syringe. The tapered end of the syringe is cut off. On the outside measuring marks are made to mark, for instance, a volume of 10 or 20 ml. (Figure 6).

The soil is cut to a smooth and level surface. The sampler is pushed into the soil with the open end downward until over the measuring mark. The sampler is then dug out carefully and the soil sticking out is cut of level. With the aid of the plunger the soil sampler is transferred into a plastic bag or directly into a beaker. The volume of the sample can again be calculated from:

$$\text{Volume } V = 3.14 R^2 \times H (\text{cm}^3).$$

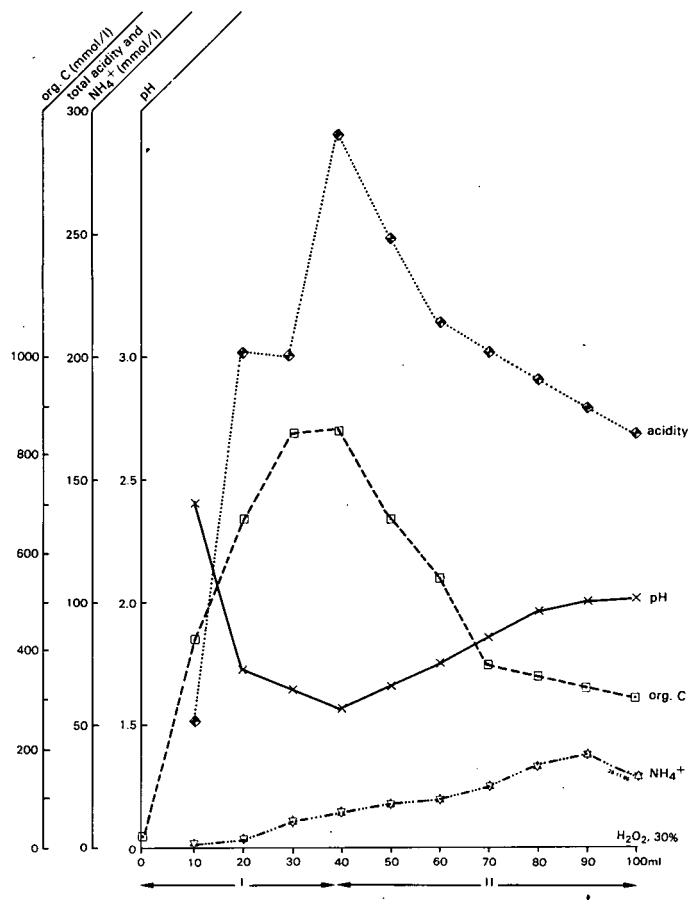


Figure 1 Total acidity, pH, organic carbon and ammonium in the clear supernatant of a suspended peat sample (ZP-G2, refer to text), after oxidation with increasing amounts of hydrogen peroxide

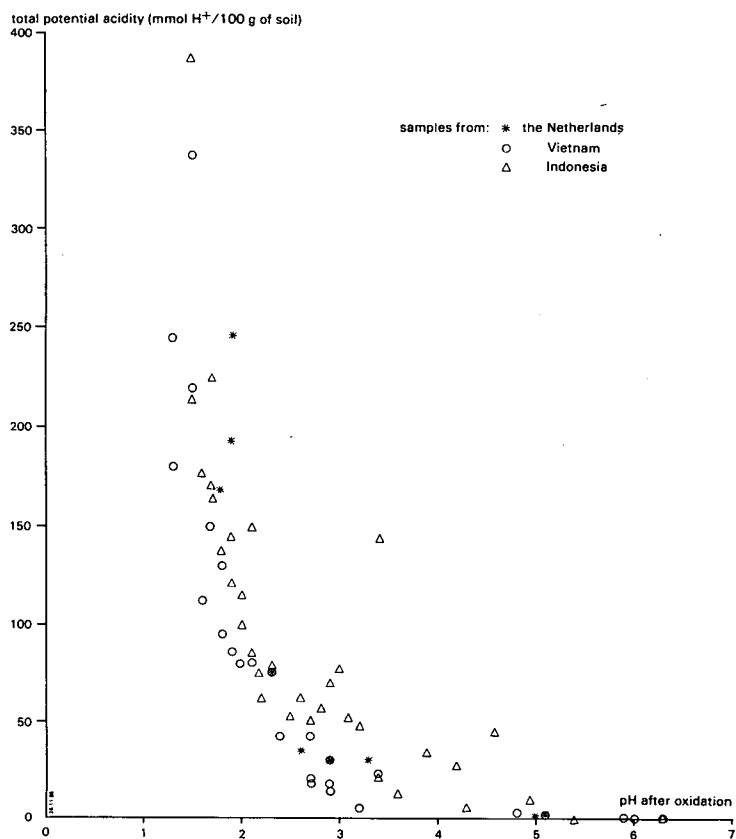


Figure 2 Relation between pH and total acidity of various samples, after oxidation by hydrogen peroxide

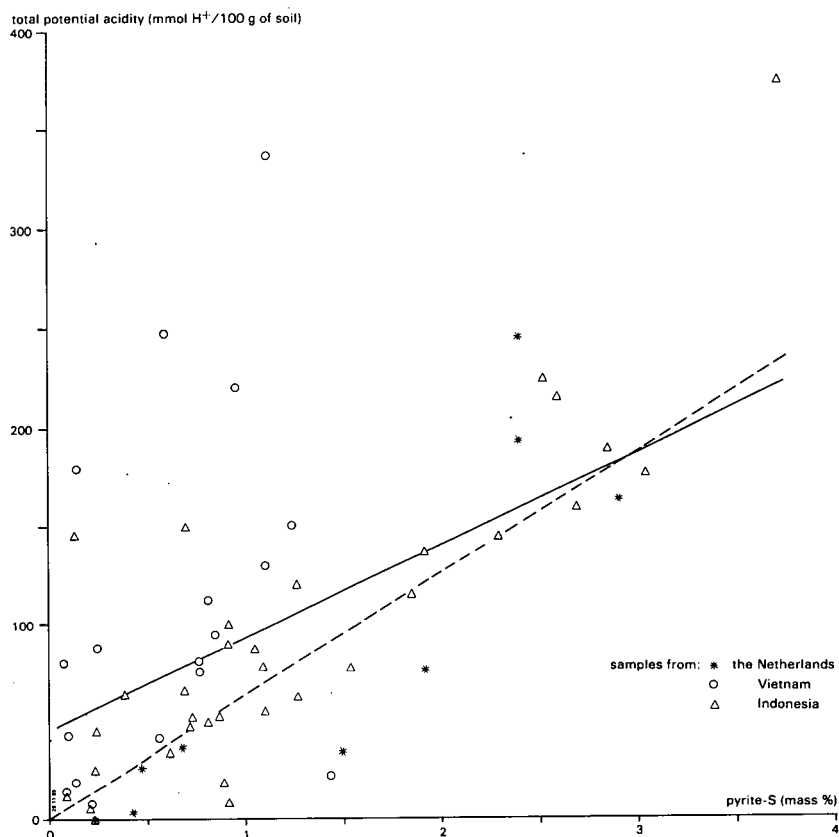


Figure 3 Relation between pyrite-S content and total potential acidity of various samples. Dashed line: theoretical relation according to reaction $\text{FeS}_2 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 4\text{H}^+ + 2\text{SO}_4^{2-}$ ($y = 62.4x$). Solid line: regression line ($y = 47.7x + 43.9$); $n = 34$; $r^2 = 0.20$)

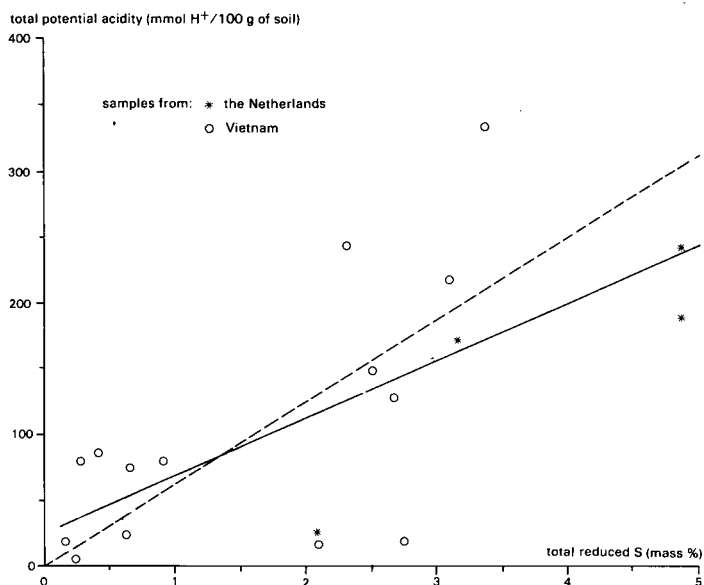


Figure 4a Relation between total reduced S content and total potential acidity of various samples. Dashed line: theoretical relation assuming complete oxidation and formation of maximal acidity. Solid line: regression line ($y = 43.9x + 25.4$; $n = 23$; $r^2 = 0.47$)

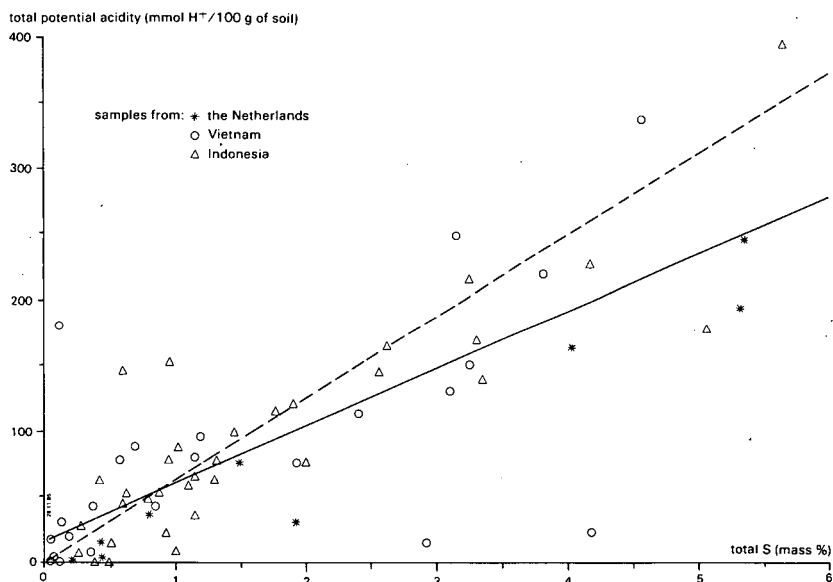


Figure 4b Relation between total S content and total potential acidity of various samples. Dashed line: theoretical relation as in Figure 4a. Solid line: regression line ($y = 43.9x + 16.4$; $n = 70$; $r^2 = 0.64$)

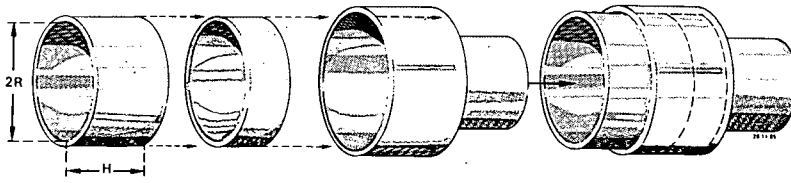


Figure 5 Volumetric soil sampler, made from pieces of PVC tube. ($R = \frac{1}{2}$ internal diameter; H = height of tube)

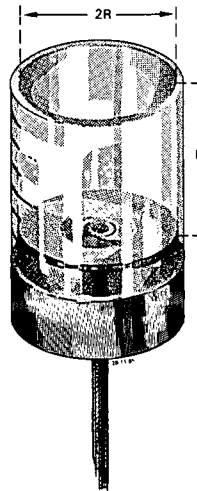


Figure 6 Volumetric soil sampler, made from a plastic syringe. $R = \frac{1}{2}$ internal diameter; H = distance between open end of tube and measuring mark