

FACTORS INFLUENCING THE FORMATION
OF POTENTIAL ACIDITY IN TIDAL
SWAMPS

L.J. Pons and N. van Breemen
Department of Soil Science and Geology,
Agricultural University
Wageningen, The Netherlands

1 Summary

An explanation is offered for the geographic distribution of potentially acid sulfate soil materials in relation to climatic zones and the physiography of coastal plains. For this purpose potential acidity is defined as an excess of pyrite over acid neutralizing components. The essential ingredients and environmental conditions for the formation, accumulation or sedimentation of pyrite and acid neutralizing components are listed and interpreted in terms of actual and past physiographic settings, illustrated by well-known situations. Potential acidity is built up predominantly in kaolinite-rich, non-calcareous sediments in tidal flats below mean high water level, with a dense mangrove vegetation, amply flushed by saline or brackish tides at a sedimentation rate allowing for the mangroves to persist well below mean high water level for at least several decades.

These conditions are favoured by a subsidence of the land relative to the sea level or by low sedimentation rates and by a tropical humid climate. A relative rise of the land or an increase in sedimentation rate lead to rapid siltation of tidal creeks and quick lateral accretion of closed shorelines at levels well above mean sea level minimizes the influence of tidal flushing and mangrove vegetation, and thereby will depress the rate of pyrite accumulation and of decarbonisation and consequently of the potential acidity in tidal deposits.

Of the estimated 500 million hectares fine textured soils developed in marine and fluviatile sediments (FAO/UNESCO, Soil Map of the World 1971-1979: Fluvisols and Gleysols), about 12.5 million hectares are highly pyritic and will acidify upon aeration, or have already done so (Table 1). Still larger areas of pyritic sediments are continuously water-saturated and covered by peat or non-pyritic sediments. Moreover pre-Holocene pyritic coastal sediments, often in combination with peat, commonly give rise to serious acidity problems, especially as a result of open-cast mines in tertiary lignite deposits and coal of carboniferous age.

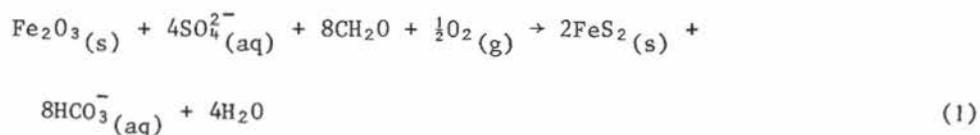
Table 1. Regional distribution of acid sulphate soils (based on data from FAO/UNESCO Soil Map of the World; length of growing periods according to FAO Agro-Ecological Zones Project, Rome)

Region	Area (10 ⁶ ha)	Area (million ha) per length of growing period			
		< 90 days	90-180	180-300	> 300 days
Africa	3.7	0.4	0.7	1.5	1.1
Near and Middle East	-	-	-	-	-
Asia and Far East	6.7	-	0.2	5.1	1.4
Latin America	2.1	-	0.1	0.8	1.2
Australia	-	-	-	-	-
N. America	0.1	-	-	-	-
Europe	-	-	-	-	-
World total	12.6				

Potential soil acidity due to excess pyrite over neutralizing substances is formed mainly in tidal swamps and marshes, but sometimes also in sea bottom sediments. Up to now little is known about the reasons why pyritic contents are dangerously high in some areas and much lower in apparently similar adjacent areas. The aim of this article is to explain, sometimes rather speculatively, the distribution of potentially acid sulfate soils in relation to climatic zones and the physiography of the coastal plains. Such knowledge should help to solve problems in identification, cartography and reclamation of these soils. This article is similar in scope as the paper by Pons, Van Breemen and Driessen (in press).

Acid sulfate soils are formed by oxidation of sulfidic muds when the quantity of sulfuric acid, formed by oxidation of reduced S-compounds exceeds the acid-neutralizing capacity of adsorbed bases and easily weatherable minerals to the extent that the pH drops below 4.

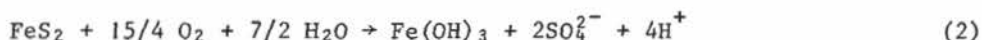
Pyrite (cubic FeS_2) is quantitatively the most important sulfur mineral in such sediments. Accumulation of sedimentary pyrite requires (a) reduction of sulfate to sulfide, (b) partial oxidation of sulfide to polysulfides or to elementary S and (c) either formation of FeS (from Fe-oxides or Fe-silicates) followed by combination of FeS and S to FeS_2 , or direct precipitation of FeS_2 from Fe^{++} and polysulfides. Regardless of the actual pathway, the following overall reaction describes complete pyritization of ferric oxide:



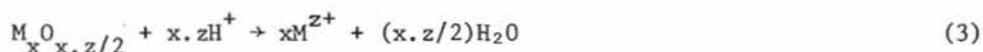
The essential ingredients for the accumulation of pyrite are:

- 1) sulfate, continuously supplied over an appreciable period (e.g. with sea water);
- 2) iron-containing minerals present in the sediments;
- 3) metabolizable organic matter (CH_2O);
- 4) sulfate-reducing bacteria, which are practically always present;
- 5) an anaerobic environment;
- 6) limited aeration for oxidation of all sulfide to disulfide.

Potential acidity can develop only if at least a part of the alkalinity in the form of bicarbonate (HCO_3^-), formed during sulfate reduction, is removed from the system. This requires leaching of the interstitial solution. Leaching is favoured strongly by tidal action and may further accelerate pyrite formation by breaking up diffusion-controlled rate-limiting processes and by supplying dissolved oxygen as well as sulfate from sea water. Removal of HCO_3^- also tends to depress the pH, giving slightly acid conditions which favour pyrite formation kinetically. The pyrite content is a measure for the potential acidity, according to the reaction



If any bases present are represented by their oxide components, the neutralizing capacity follows from the equation



The acid neutralizing capacity of soil material depends on the amount of exchangeable bases and the contents of easily weatherable silicates and of carbonates. If fine-textured marine clays contain appreciable amounts of smectitic clay and are saturated with bases, their exchange complex may inactivate acidity released by up to 0.5% pyrite-S and prevent a drop in pH below 4.0. An example of neutralization by silicates is the replacement of Mg from smectites by Fe(III) from oxidizing pyrite, sometimes up to the equivalent of 1% pyrite-S (Van Breemen 1980). Three per cent CaCO_3 balances the acidity produced by 1% pyrite.

4 Distribution of potential acidity

Potential acidity can be formed most readily in:

- poorly drained inland valleys, subject to influx of sulfate-rich water;
- bottoms of saline and brackish lagoons, seas and lakes; and
- saline and brackish tidal flats and tidal swamps.

Inland valleys, with potential acidity are relatively rare with the supply of sulfates as the limiting factor. Examples include the pyritic papyrus peats of Oeganda (Chenery 1954), pyritic sandy gley soils in valleys in the Eastern Netherlands (Poelman 1973) and the sulfidic peat soils of Minnesota.

Bottoms of saline and brackish lagoons, seas and lakes, may be high in sulfides. Contents of primary (syndimentary) organic matter usually limit sulfate reduction and the quantities of sulfides formed under these conditions (Berner 1971). Subaquatic sediments with potential acidity are generally limited to boreal and temperate climatic zones because there, contrary to tropical zones, decay of organic matter is slow and contents of primary organic matter in sediments are relatively

high (Pons 1965). Subaquatic sediments often contain relatively high amounts of iron monosulfides next to pyrite, resulting in black colours. This may be due to insufficient aeration of the bottom sediments for complete pyritization of sulfide. Examples are the bottom sediments of the Black Sea (Berner 1971) and of the former Littorina Sea (now the Baltic Sea) which contain more than 2% reduced sulfur and little or no carbonates (Wiklander et al. 1950). Isostatic rise of the land after the last glaciation resulted into drainage of considerable areas of Littorina sediments and caused the formation of acid sulfate soils along the Baltic coasts of Sweden and Finland. In the Netherlands, the bottom sediments of the former Zuyder Sea also contain more than 1% reduced sulfur (Ente 1964) but their relatively high carbonate contents prevent acidification upon reclamation.

Pyrite formation in tidal flats and marshes. Saline and brackish tidal flats and tidal swamps are quantitatively most important as a source of potential acid sulfate soils. The bare tidal flats and the lower parts of the swamps are regularly inundated with sulfate-rich water and permanently reduced. The highest parts near and above mean high tide, however, show predominantly aeration and little or no sulfate reduction.

In sediments of bare tidal flats and creek bottoms the content of primary organic matter may limit pyrite formation. They are generally low in organic matter (0.5-2%) in the tropics, but may be organic-rich in temperate regions, especially at high clay content. This explains the relatively high primary pyrite contents in temperate areas relative to those in the tropics (Pons 1965). On tidal marshes and swamps, however, a telmatophytic vegetation may add large quantities of organic matter to the primary organic matter. Telmatophytes which develop roots in reduced muds, include mangroves (Rhizophoraceae) in the tropics and reeds (Phragmites) and rushes (Scirpus) in temperate tidal marshes. Water temperature, salinity and duration of the inundations influence type and distribution of the vegetation, and thus control the supply of secondary organic matter to the mud. Figure 1 shows how the vegetation is adapted to the range of conditions in tidal marshes in different climates.

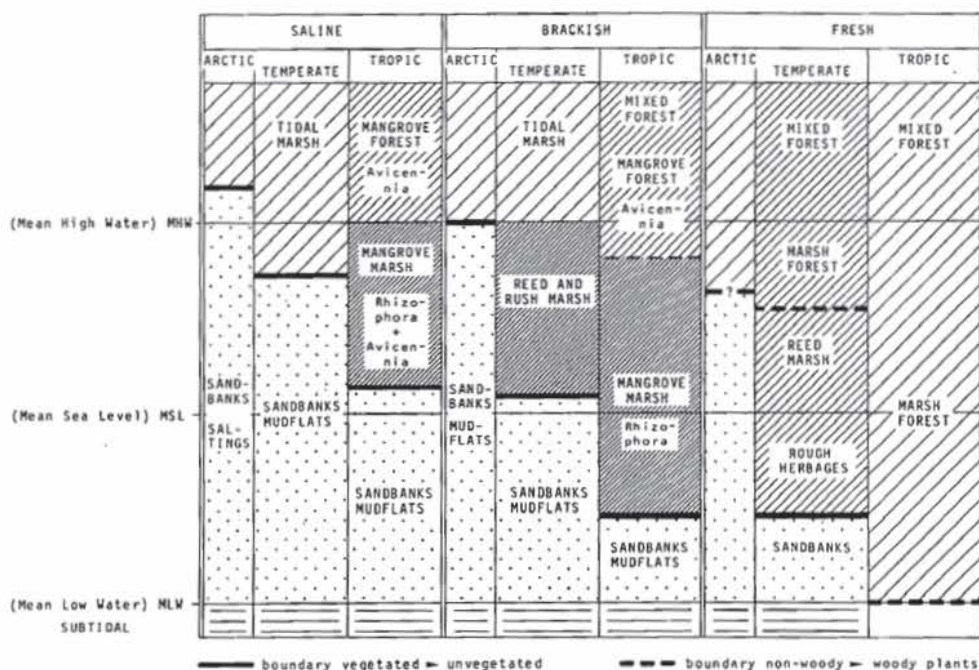


Figure 1. Vegetations of tidal marshes of arctic, temperate and tropic zones in relation to salinity and levels of tides

Adaption of the vegetation to lower topographic levels with longer inundations (and thus more reduced conditions) is greater in the tropics than in temperate and arctic zones and also greater in brackish than in saline conditions. In arid and semi-arid tropical coastal areas the growth of mangrove vegetations is hampered completely, perhaps due to very high salinities (Marius 1972).

Figure 1 illustrates that abundant supply of organic matter, favorable for pyrite accumulation can be expected in the 'low' brackish zone between mean sea level (MSL) and mean high water (MHW) in temperate areas with reeds (*Phragmites*) and rushes (*Scirpus*) and in the 'low' saline and brackish zone between mean low water (MLW) and mean high water (MHW) in tropical areas with *Rhizophora* and other mangrove trees.

5 Neutralizing compounds in tidal environments

Broadly speaking, the contents of neutralizing compounds of tidal

sediments at the time of deposition, viz. exchangeable bases, easily weatherable silicate minerals and carbonates, vary with climates. In the humid tropics, and especially in the smaller estuaries, kaolinite is often the dominant clay mineral in tidal sediments. These sediments are not only low in exchangeable bases but are also ineffective in neutralizing acid by weathering (Vieillefon 1973). Rivers from arid and semi-arid catchment areas supply mainly smectites to their estuaries, and, even though clay contents are often lower than in the humid tropics (Allen 1964), may neutralize an important fraction of the acidity formed upon oxidation. Those of the temperate areas have a mixed clay mineralogy with an appreciable exchangeable base content. Clayey sediments of large rivers of the humid tropics, including the Amazon and the Mekong, have moderate amounts of adsorbed bases and have a fair neutralizing capacity upon weathering.

Most volcanic catchment areas provide sediments rich in weatherable minerals. E.g. in tidal flats of the volcanic island of Java, in contrast to those of Sumatra and Kalimantan, the presence of such minerals lowers or prevents potential acidity (Driessen 1974).

Carbonates are practically absent in most coastal sediments in the humid tropics. Most rivers transport acidic water and non-calcareous sediments because their catchment areas include old, strongly weathered soils. Moreover coastal sea water in the tropics is often deluted with acid river water so any carbonate present runs the risk to be dissolved (Brinkman and Pons 1968). By contrast marine sediments in arid and semi-arid and in temperate zones frequently contain much more primary carbonates.

Summarizing (see also Table 2): the very fine textured clays of the large humid tropical estuaries show a moderately high neutralizing capacity. Sediments of arid, semi-arid and temperate areas and of volcanic regions have generally lower clay contents, but both because of a richer mineralogy and higher carbonate content, these sediments are highest in acid neutralizing capacity. Only the small estuaries in the humid tropics are generally very low in neutralizing materials and hence are often strongly acid or potentially acid.

Table 2. Occurrence of neutralizing ingredients in tidal deposits in environments favourable for pyrite accumulation (xxx abundant, xx fair, x rare, - none)

	Humid tropics			Humid temperate zone		Arid and semi-arid zone	
	Regions with recent volcanism	Small estuaries	Large estuaries	Clayey deposits	Sandy deposits	Clayey deposits	Sandy deposits
Exchangeable bases	xxx	x	xx	xxx	x/xx	xxx	xx
Weatherable silicate minerals	xxx	x	x	xx	xx	xxx	xxx
Primary carbonates	-	-	x/-	x/-	xxx/-	xxx/-	xxx/-

6 Dynamics of tidal environments and the formation of potential acidity

The time required for the formation of appreciable amounts of potential acidity (i.e. of pyrite) is probably in the order of decades to centuries. So, the tidal marsh vegetation has to persist at a given location for at least such a period of time in order to build up sufficient quantities of pyrite. This implies that sedimentation must be slow (Moormann and Pons 1974). Tidal environments with low sedimentation rates often have many well-developed creeks. Estuarine areas generally show numerous creeks in contrast to rapidly accreting coastal systems as in Malaysia (Diemont and Van Wijngaarden 1974) and along the Guyana coast (Brinkman and Pons 1968).

According to Diemont and Van Wijngaarden (1974) reduced substrata of large coastal swamps behind a closed accreting shore line in Malaysia have less than 0.5% pyrite-sulfur, are low in organic matter and show a field pH between 8 and 8.4, reflecting high concentrations of HCO_3^- ($10\text{--}26 \text{ mol/m}^3$) in the soil solution. Those of the estuarine swamps, dissected by tidal creeks, have 1-2.5% pyrite sulfur, are high in undecomposed organic matter and show field pH's between 6.2 and 6.8 in the upper meter, with interstitial water low in dissolved HCO_3^- .

(2-10 mol/m³). Black FeS was locally found in sediments of the accreting coast, but not in estuarine sediments. During spring tides the concentrations of dissolved sulfide in the estuarine sediments dropped to undetectable levels whereas they remained almost constant along the accreting coast. These observations can be explained by much more effective tidal flushing in tidal marshes with a well-developed creek system. Tidal flushing would favour temporary limited aeration, necessary for the complete pyritization of ferric iron and leaching of interstitial water and evacuation of HCO₃⁻ so that a relatively low pH (6.5-7) is maintained.

In tidal environments, dissolution of CaCO₃ (secondary decalcification) may be much stronger than under terrestrial conditions (Van der Sluys 1970, Salomons 1974). This accelerated dissolution is also a result of tidal flushing combined with dissolution of CaCO₃ by CO₂ produced during the decomposition of plant remains. Oxidation of some pyrite during low tides would also remove CaCO₃ (Kooistra 1978).

Summarizing one may conclude that in saline and brackish marshes, dissected by creeks, leaching by tidal action may contribute to potential acidity, both by favouring pyrite formation and by removal of carbonates.

If sedimentation is outweighed by accumulation of organic debris, pyritic peats may develop. Pyritic mangrove peats are known from the Niger delta (ILACO), from Senegal (Vieillefon 1973), in Kenya (unpublished observations by Van Wijngaarden and Pons), and in Malaysia and Indonesia (Driessen 1974). Thin layers of pyritic reed and rush peats are very common e.g. in The Netherlands. In these peats, iron may become the limiting factor for pyrite formation. The same may be true for mangrove marshes composed dominantly of quartz sands (Vieillefon 1973).

During the last 3000 years many deltas, estuaries and coasts in Europe have witnessed a strongly accelerated sedimentation due to deforestation and land reclamation, especially since Roman times.

Elsewhere, including in the humid tropics, this process is now becoming increasingly important. For this reason recent sediments often have a lower potential acidity than sub recent sediments. Moormann and Pons (1974) described the Mekong delta as an example.

Summarizing one may say, that from the point of dynamic development of

tidal environments many factors cooperate to result in high potential acidity in the humid tropics: dense vegetation, low sedimentation rates, and low primary and secondary carbonate contents in recent times increased soil erosion and concomitant accelerated sedimentation in tidal flats has somewhat decreased the rate of formation of potential acidity in many tropical areas.

7 The influence of relative sea level changes
 on tidal environments in relation with
 potential acidity

Both the formation of coastal land forms and the development of potential acidity in their sediments is strongly influenced by relative sea level changes. After the last glaciation the sea level rose by about 3-4 m per 1000 years (Blackwelder et al. 1979) and levelled off until a maximum was reached some 5,500 years BP and, apart from a slight drop some 5000 years ago (Fairbridge 1961) probably remained stable ever since. Slight differences in local tectonisms, however, resulted in different patterns of changes in the relative sea level as illustrated by Figure 2.

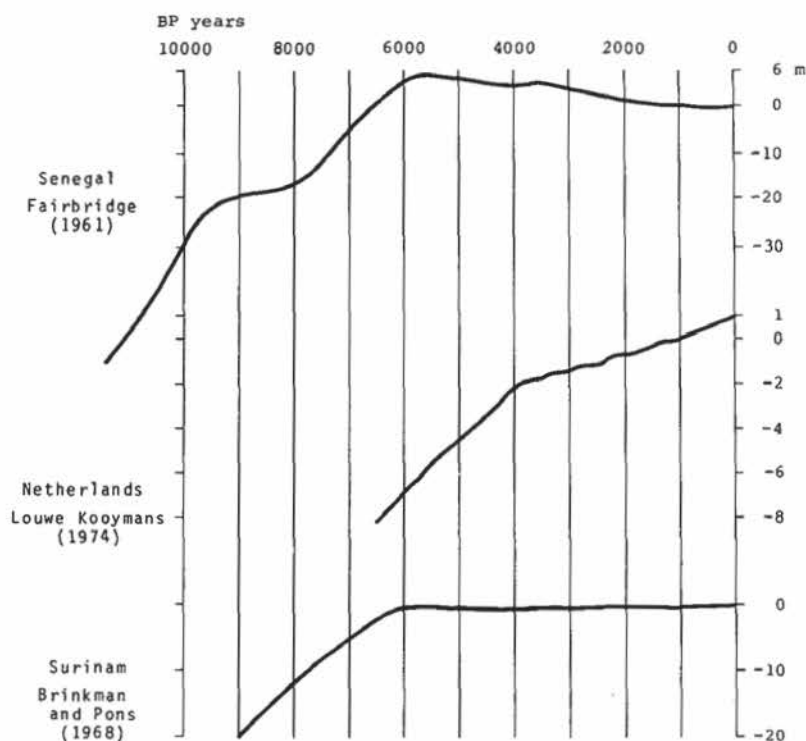


Figure 2. Changes in relative sea levels for the coastal plains of a stable coast, of The Netherlands and of Surinam

Fairbridge's curve applies to stable coasts, e.g. Senegal, Kenya, Australia, etc. The curve of Louwe Kooymans (1974) is not only characteristic for The Netherlands, where land subsidence caused continued rise in sea level after 5,500 years BP, but also for many other subsiding areas as the Orinoco delta, the Mississippi delta, etc. Along the Surinam coast the sea level remained constant during the last 5,500 years (Brinkman and Pons 1968). This pattern is also characteristic for many deltas e.g. the Bangkok plain and the Mekong delta.

Figure 3 illustrates how sea level changes and sediment supply may affect the formation of potential acidity in coastal areas. When the rise of sea level is high relative to the supply of sediment, transgression will take place.

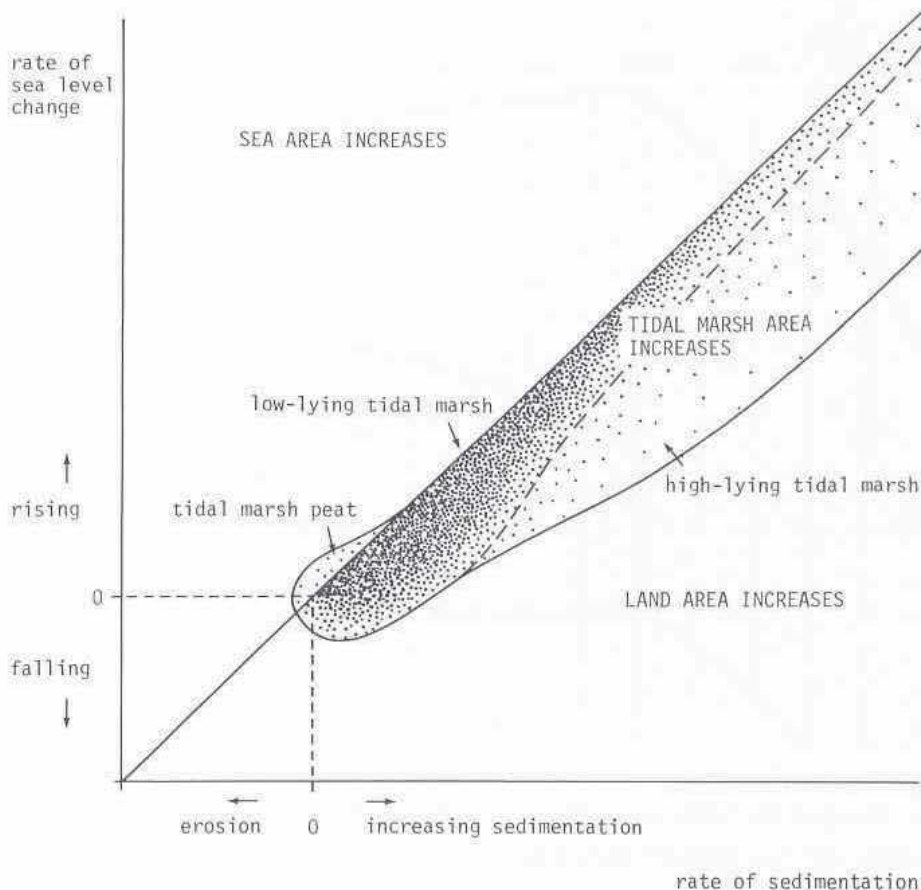


Figure 3. Effect of changes in sea level and sediment supply on the accumulation of potential acidity in tidal swamps. Level of potential acidity is represented by relative density of dot distribution

When sediment supply and relative sea level rise are more or less balanced a broad zone of stationary relatively low lying mangroves will occur (Brinkman and Pons 1968). Under these conditions vertical sedimentation predominates and potential acidity will be built up over considerable depths. If the sediment supply is relatively high the land area will grow by lateral accretion of the coast. Broad areas of relatively high-elevated tidal marshes are formed. The belt with mangroves and other salt and brackish marsh vegetations will shift rapidly seaward with the growing coast and only little potential acidity is formed (Moormann and Pons 1974).

After the last glaciation, in many areas with considerable supply of

sediments the rise in sea level during the early Holocene was approximately balanced by the sediment supply. This resulted in a vertical build-up of sediments under stationary tidal marsh conditions. The silting-up of creeks was also retarded and tidal flushing of the relative low mangrove and salt marshes was maintained during long periods giving rise to thick sediments with high potential acidity. After the stabilisation of the sea level during the late Holocene the still considerable supply of sediments caused lateral coastal accretion in these areas. A zone with high-lying mangroves rapidly shifted seaward with the growing coast. Only limited time was available for the formation of potential acidity. In addition, less favourable chemical conditions in these relatively high lying sediments for both pyrite formation as well as for decarbonation, contributed to their generally low level of potential acidity.

Erosion caused by deforestation in watersheds during the last parts of the Late Holocene has further accelerated the already high rates of coastal accretion in many of these regions.

In areas of low sediment supply, where transgressions took place in early Holocene times, sea level stabilisation in late Holocene times brought about stationary coasts with low lying mangroves. In such areas potential acidity is formed at present. Examples are the estuary of the Siné-Saloum (Marius 1972), the estuary of the Casamance river where recent sedimentation is so slow that locally pyrite peats are formed (Vieillefon 1973), and the estuary of the Saigon river (Moormann and Pons 1974).

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