

SULPHATE-INDUCED HIGH ACIDITY IN A PEATLAND - AN EXAMPLE FROM MUTHURAJAWELA

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Abstract: pH and halide contents of water, sulphur content in peat, sulphate sulphur of both were measured in a selected number of localities in the Muthurajawela peatland during a period of five months in the dry season. pH of water ranged from 2.5 to 7.5 and sulphate content varied from 5 to 1150 ppm. The mean value of total sulphur in peat was 8.1%. Sulphate sulphur content varied from 0.01 to 0.54%. The pattern of total sulphur and halide distribution in Muthurajawela peatland revealed that sulphur has accumulated in this marshland from the sea water influx through a man-made canal. The high acidity of peatland is apparently controlled by sulphate in peat. The occurrence of sulphate is determined by flooded conditions, Fe²⁺ ions leached from the hinterland and the carbon content of peat.

Key words: Acidity, Muthurajawela peat, pyrite, sulphate, sulphur.

INTRODUCTION

Sulphur levels in peat are variable and depend on the genesis of the peat. The sulphur in peat is present mainly in three forms *viz.* organic matter, mineral sulphide or mineral sulphate.¹ Two forms of organic sulphur are reported in peat, *viz.* (i) carbon-bonded sulphur e.g. amino acids and heterocyclics and (ii) carbon-oxygen-sulphur bond as in choline sulphate or sulphated polysaccharides. The latter is termed ester-sulphate and frequently accounts for >50% of organic sulphur. The primary inorganic form of sulphur in soils is sulphate. The formation of the different sulphur forms in marine sediments is the result of microbiological and chemical processes.^{2,3} The concentration of detrital organic matter in tropical near-shore waters is low. As a result, a minor amount of syn-sedimentary or 'primary' pyrite is formed. In the tropics, however, large amounts of pyrite can form in tidal muds above mean sea level where mangrove vegetation supplies ample amounts of organic matter.

Dissolved sulphides react rapidly with dissolved ferrous ion or with ferric oxides to form ferrous sulphide. This compound is amorphous according to X-ray diffraction which gives broad lines of Mackinawite tetragonal FeS. In the presence of oxidants such as O₂ or ferric ion, part of the dissolved or solid sulphide can oxidize elemental S. Elemental sulphur reacts with dissolved sulphide to form aqueous polysulphide, which in turn reacts with FeS to form pyrite (FeS₂) either directly or with greigite (cubic Fe₃S₄) as the intermediate. For example, at Everglades, Florida the average pH of water in open marshes is about 7.5.¹ The pH of marine peat in Barrington, Nova Scotia bog ranges from 3.5 to 6.5.¹² The lower limit of pH around 4 is typical of ombrotrophic sphagnum bogs. These waters are probably buffered at this pH by carboxyl groups of organic matter.

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The upper limit of pH is approximately 8.4, typical of shallow eutrophic fens in calcareous terrains.¹¹

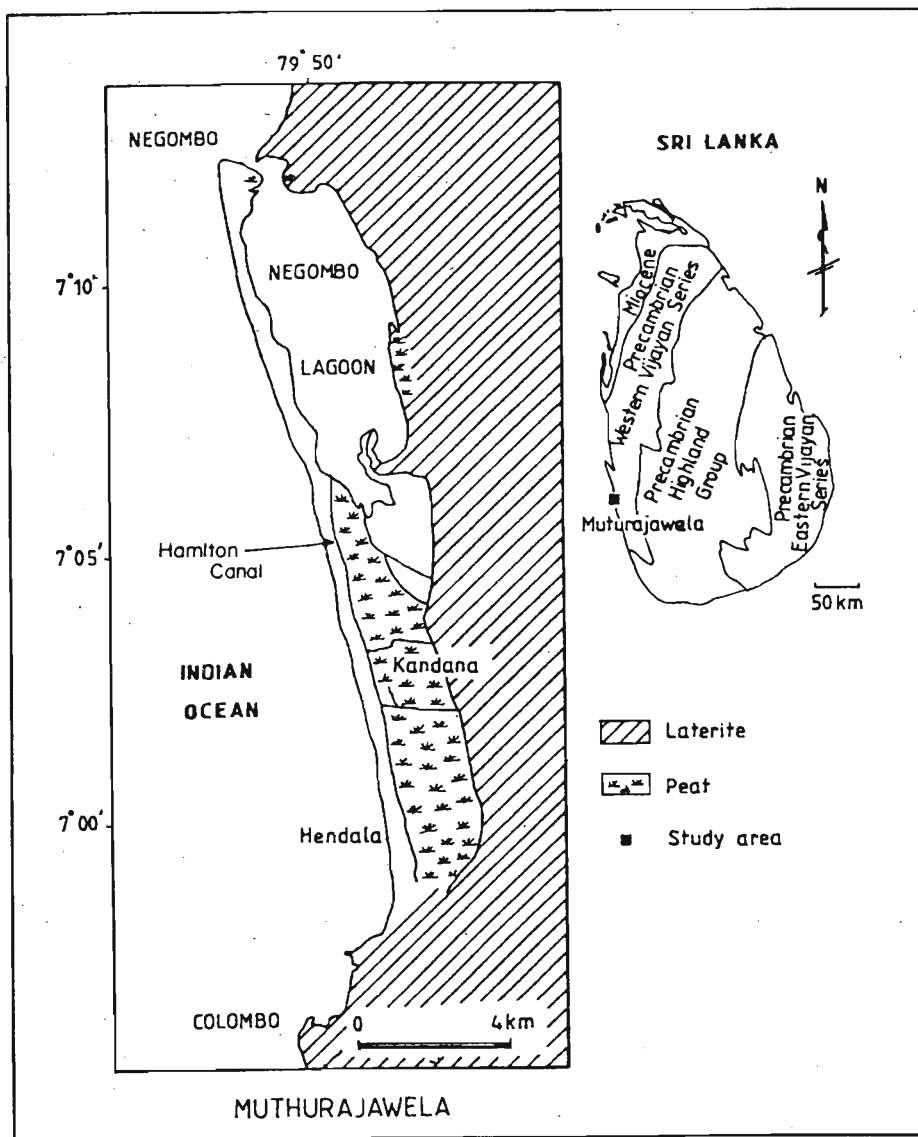


Figure 1: Location of Muthurajawela peat deposit.

In Sri Lanka, a major peat-forming system is present at Muthurajawela tidal marsh covering an area of 20 sq. km along the Western coastal strip of Sri Lanka (Fig. 1). According to carbon dating of Muthurajawela peat, the sediments there have accumulated since 29,000 B.P.⁹ Further peat-forming systems are found

in small fresh water bogs associated with other soils in the Central Highlands of Sri Lanka. Continuous waterlogging and flooding at Muthurajawela provides conditions conducive to peat formation. Marsh vegetation that thrives uninterrupted due to availability of water, generates organic matter. Continuing bulk accumulation of slowly decomposing organic matter of plants follow, and layer upon layer of organic residues are deposited. Accompanying this process is a succession of vegetation, climaxing in forest trees. The peat deposit occurs as a swamp and lies a few centimeters below mean sea level and is constantly supplied with sea water during high tide.⁴ During high tide, a man-made canal (Hamilton canal) constructed for transport purposes some decades ago, brings sea water from the Negombo lagoon to this marshland (Fig. 1). The purpose of the present study was to examine (i) the distribution and origin of sulphur in the Muthurajawela peat and (ii) the sulphate content in water by studying the chemistry of interstitial water.

METHODS AND MATERIALS

About 100 samples of surface peaty sediments were collected from Muthurajawela during the dry season (January to May 1993), when the different tidal zones (subtidal, intertidal and supratidal zones) of the pools of the study area are clearly delineated. The samples were from submerged peat as well as from emerged locations (Fig. 2). Sampling locations were selected considering the drainage pattern, vegetation cover, peat texture and colour. Water samples were collected from the pools and the interstices of peat surface materials. The pH of peat and water samples was measured prior to collection using a soil pH meter.

To determine the sulphate content, peat samples were air-dried and powdered. Five grams of samples were weighed and mixed with 500ppm of phosphorus in 25ml of KH_2PO_4 solution. After shaking for 30 minutes, the solution was filtered through Whatman No. 42 filter paper. To avoid interference, between carbonate and sulphate ions in the analysis, 10% hydrochloric acid was added to the filtrate and the mixture was heated gently until CaCO_3 was removed. 10 ml of filtrate was then pipetted out and distilled water was added to bring the volume to approximately 20ml. 1ml of gelatin- BaCl_2 reagent was added and the content was mixed thoroughly to form a precipitate of BaSO_4 over 30 min. The BaSO_4 content was determined by spectrophotometry as the sulphate content of the extracted solution. The sulphate content of water was also determined by BaSO_4 precipitation.

5 ml of 2:1 HNO_3 - HClO_4 was added to 0.25 g of dried peat samples to measure the total sulphur content. After a few hours, the samples were heated at 225°C and was kept for 2h. Then the temperature was decreased to 100°C and 1:1 HCl added to remove traces of nitrogen. An aliquot of digestion was pipetted out and the converted sulphate was determined by measuring BaSO_4 precipitation as described above. I, F⁻ and Cl⁻ contents of water were measured by ion-selective electrodes (Orion).

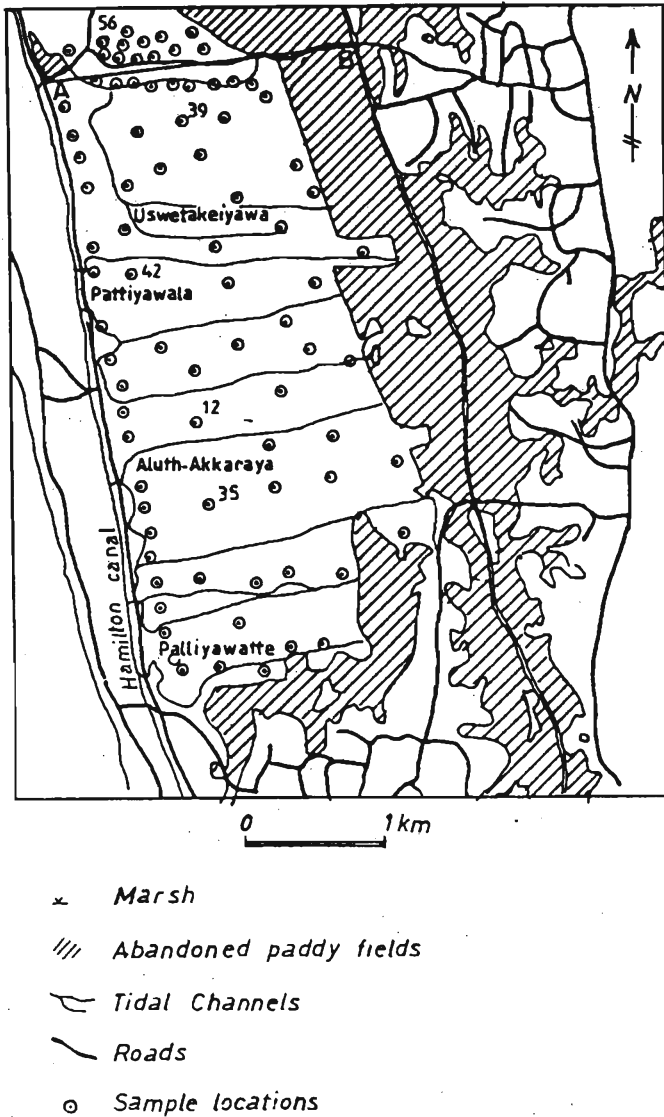


Figure 2: Sampling locations of the study area (A...B represents the sampling profile for halide measurements).

RESULTS

Halide Variation of Muthurajawela Marshland

The Cl⁻ content of water of this peatland was relatively high with a mean of 1343 ppm. The I⁻ and F⁻ contents were comparatively low. The halide contents were higher near the Hamilton canal and decreased towards the hinterland (Figs. 3 & 4).

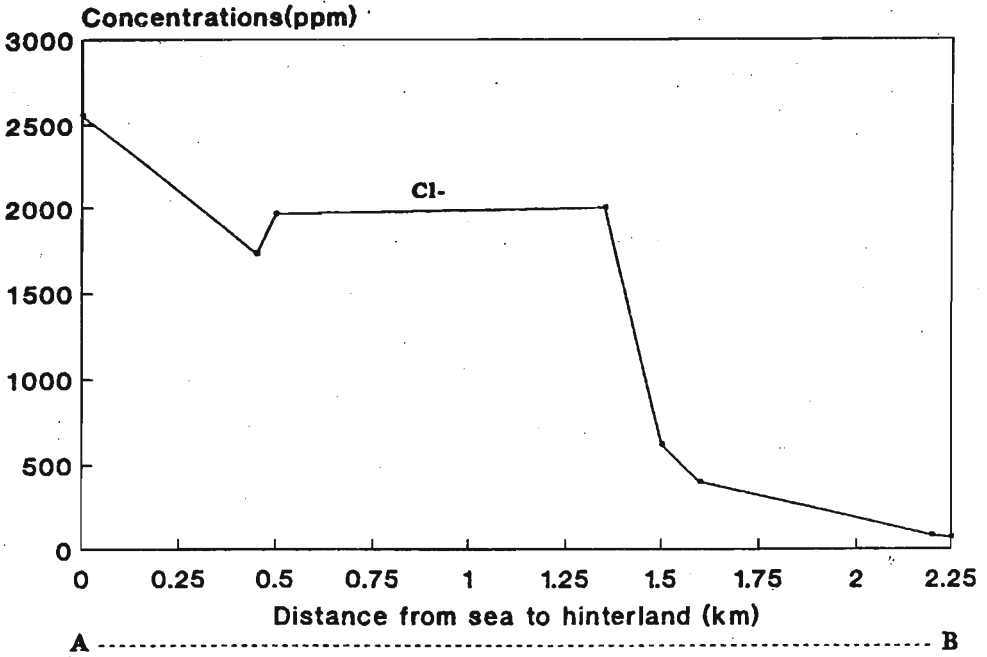


Figure 3: Temporal distribution of concentration of chloride across the peatland (A...B represents the sampling profile).

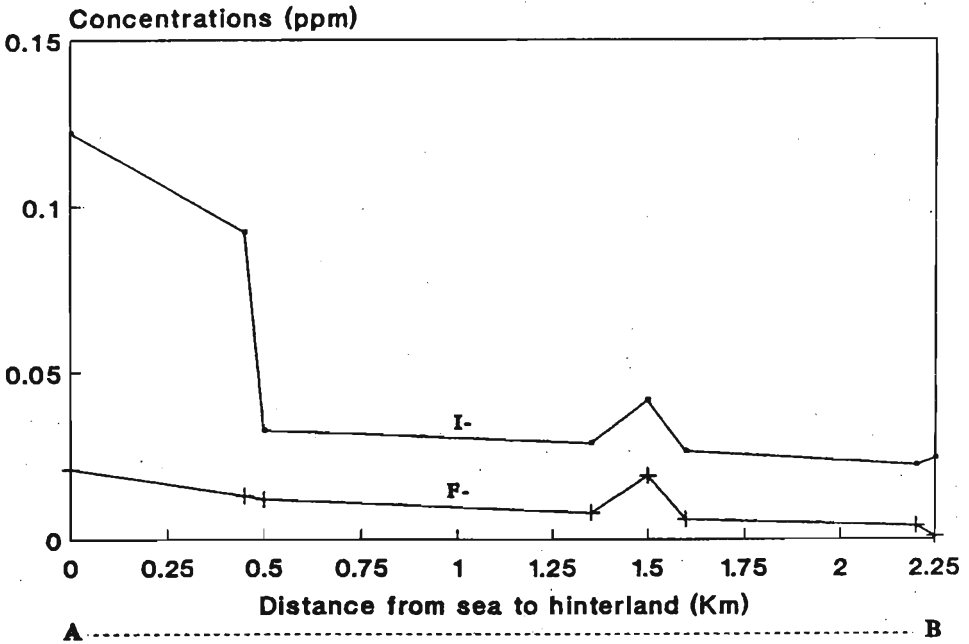


Figure 4: Temporal distribution of the concentration of iodide and fluoride across the peatland (A...B represents the sampling profile).

Total Sulphur and Sulphate sulphur content of peat

In most of the locations total sulphur content gradually increased with depth (Fig.5). The total sulphur content of surface peat in Muthurajawela ranged from 0 to 17% with a mean of 8%. The sulphur distribution on the coastal side of the Muthurajawela peatland is characteristically high. The total 'S' content of peat gradually decreases towards inland (Fig. 6b) except in areas of low elevation such as in the vicinity of small channels and subtidal peats in pools. Comparatively high sulphate concentrations were recorded in the supratidal zone and upper reaches (low flood area) of the subtidal zone. Sulphate content ranged from 0.1% to 0.54% with a mean of 0.41%. Low sulphate contents were measured in the subtidal zone of the marshland (mean of 0.18%). A plot of total S% vs Sulphate S% shows that there was no correlation between them at Muthurajawela (Fig. 7).

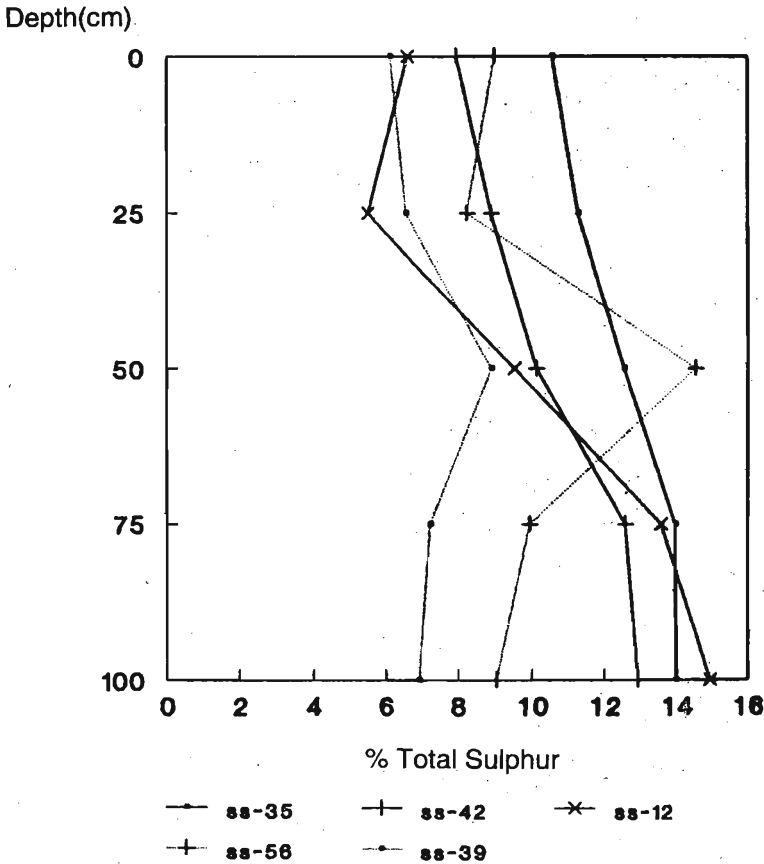


Figure 5: Variation of total sulphur content with depth at selected localities (SS-35,42,12,56,39) of the Muthurajawela Marsh.

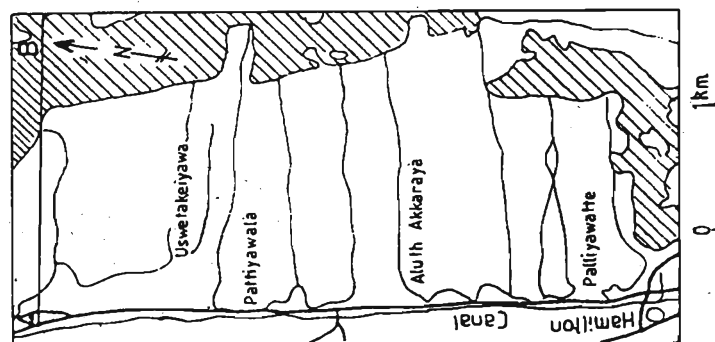
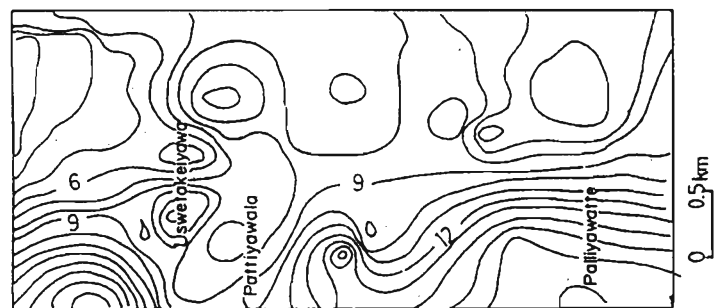
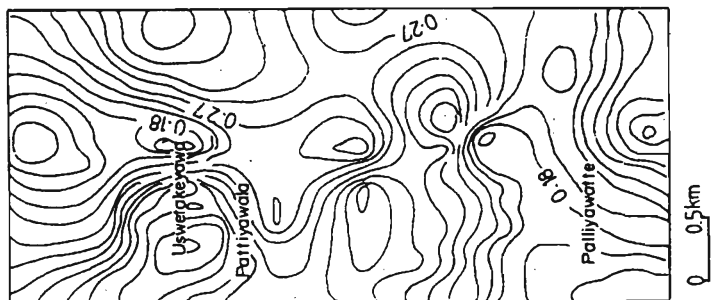


Figure 6(a): Sketch map of Fig. 2.

Figure 6(b): Total surface sulphur distribution map of the study area, Muthurajawela. A contour map was produced by plotting total sulphur content (percentage by weight) in each location. High total sulphur was noted close to the Hamilton canal and parallel to it.

Figure 6(c): Sulphate sulphur distribution map of the study area, Muthurajawela. Contour pattern shows high amounts of sulphate sulphur (% by weight) accumulating in isolated localities.

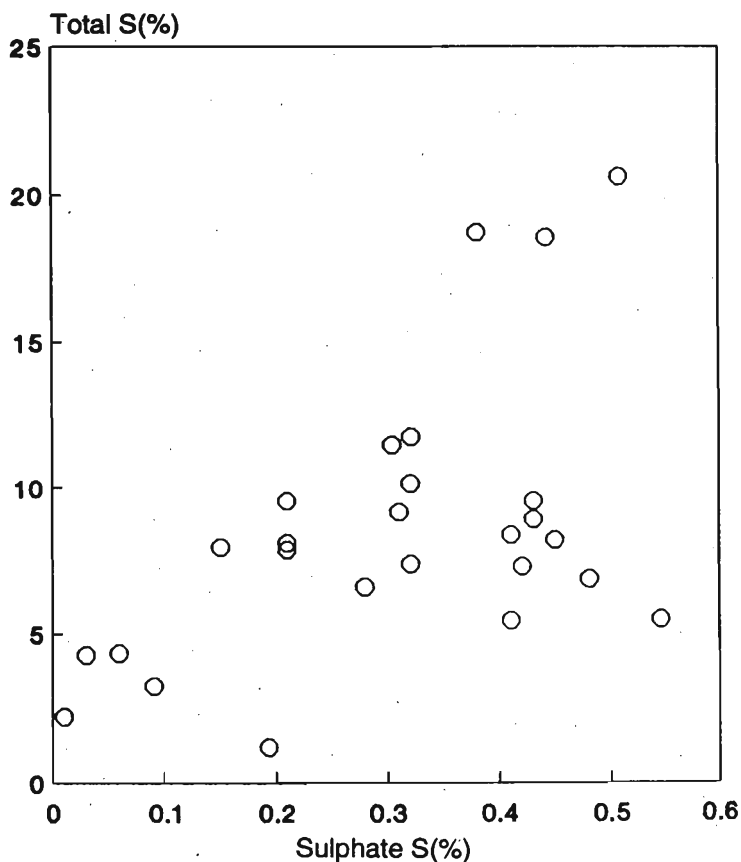


Figure 7: Plot of total sulphur vs sulphate sulphur in peat samples of the study area.

Relationship between sulphate content and pH in the waters of Muthurajawela peatland

Our observations show that there is a close relationship between pH and sulphate contents of the waters of different tidal zones at Muthurajawela (Fig. 8). In the supratidal zone (I in Fig. 8), high sulphate concentrations (mean 780, range 200 - 1050 ppm) were associated with low pH (mean 4.21, range 2.95-5.95). However these parameters showed an inverse relationship in the subtidal zone (II in Fig. 8), where the mean sulphate concentration was 210 ppm (range 20 - 894 ppm) and the mean pH was 5.65 (range 3.20 - 7.85).

DISCUSSION

There appear to be several sources for sulphur accumulation in the marine peat formation, ocean, plants and geological formations of the hinterland. The amount of sulphur found in marine peat is greater than that of fresh water peat. It should be noted that SO_4^{2-} occurs in significant quantities (approximately 0.1%)

in seawater, and therefore is a good source of sulphur for marine peat. In Muthurajawela the major source of sulphur is apparently the influx of sea water during high tide through the Hamilton Canal, since the total sulphur content decreased towards inland. This process is facilitated by the fact that the peatland lies a few cm below mean sea level, on Pleistocene marine sands.⁹ As a result sulphur is continuously added to the surface peat of Muthurajawela.

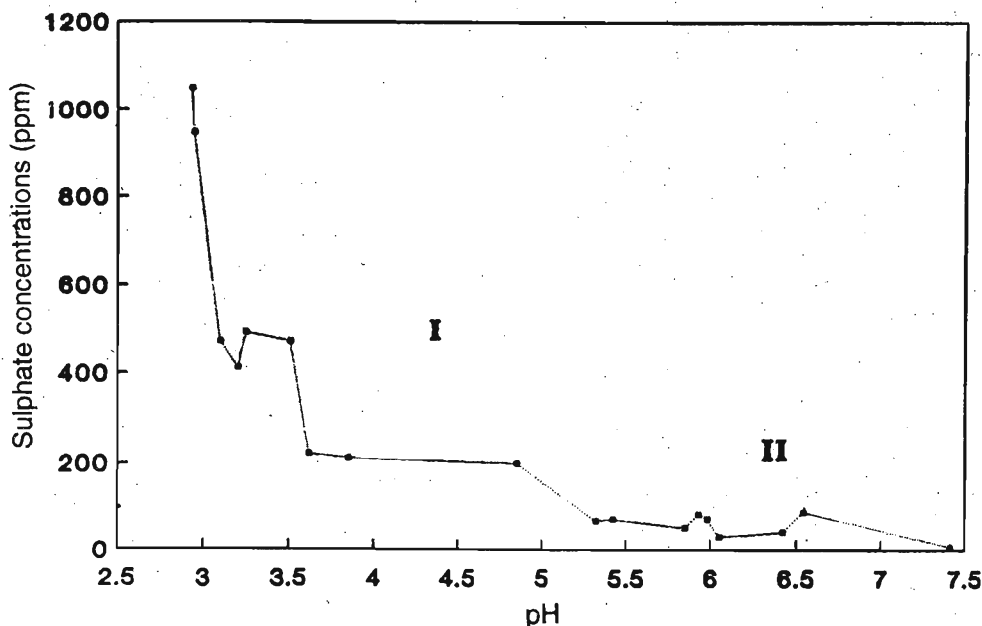
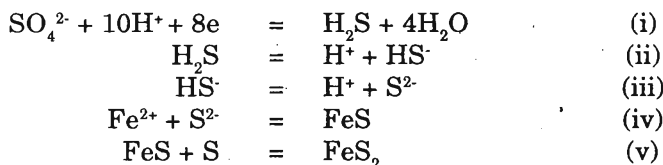


Figure 8: Plot of sulphate concentration vs pH of surface water in supratidal (I) and subtidal (II) zones of the Muthurajawela marshland.

The total sulphur increase with depth is due to the continental build up of pyritic sulphur through the $\text{H}_2\text{S} \longrightarrow \text{S} \longrightarrow \text{FeS}_2$ sequence. Iron is supplied to the peatland sediments from the laterites of the neighbouring hinterlands rich in Fe^{2+} contents. Pyrite formation is envisaged by the following pathways.



It was reported that nearly 100% of iron in Muthurajawela peat is in the form of pyrite.¹⁰ Of the various forms of reduced sulphur, only pyrite was identified by X-ray diffraction.

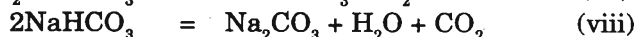
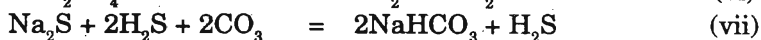
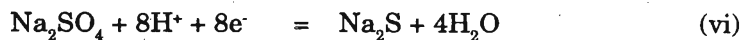
The sulphate concentrations of surface peat depend on environmental changes. Subsequent to rains, high SO_4^{2-} concentrations were recorded in low-lying

peat perhaps due to accumulation of oxidized iron in the surface peat of low-lying area. Further, due to low flooding conditions, high concentrations were recorded in the surface waters of the Muthurajawela peatland. According to our observations, the sulphate distribution in Muthurajawela peatland does not show systematic variation and may depend on organic matter, submerged conditions and the availability of Fe^{2+} (as shown in equation iv and v).

Organic carbon promotes the reduction of dissolved sulphate (SO_4^{2-}) in water to sulphide species.⁶ Under anaerobic conditions *Desulforibrio* and *Desulfotomaculum* bacteria reduce sulphate in peat to sulphide. Strong acidity, nitrate and low temperature retard the sulphate reduction. In acid soils, the concentration of water-soluble sulphate increases, then reaches a peak and eventually decreases⁸ with increasing acidity. The absence of any correlation between total sulphur and sulphate sulphur in Muthurajawela peat could be attributed to the fact that sulphate concentrations depend on a variety of factors including flooded condition, iron content, carbon content, alkalinity and pH etc.

Our observations show an association between pH and sulphate content. But acidity of peat is generally attributed to carbonic, acetic and humic acids. The phenomenon of sulphate-related acidity may be due to O_2 entering the soil and oxidizing the pyrite and sulphur present into sulphuric acid.

Marine peat has a pH near neutrality, whereas freshwater peat has pH values of about 4.⁵ pH values of Muthurajawela marine peat vary between 2 and 7. Low pH values characterized by high sulphate content were recorded mostly in the supratidal zone of the relatively small ponds that run dry during dry periods. The shrinking that results from drying facilitates the O_2 to enter the soil to oxidize the pyrite that is present in abundance in the peat deposit. Thus low pH can be attributed to the presence of pyrite that oxidizes (as a result of water level fluctuations) to sulphate under aerobic conditions created by exposure of the whole region during the dry season. This process is further facilitated by villagers who dig up pyrite-rich peat layers thereby exposing them to oxidation.⁴ The high pH values associated with low sulphate concentrations may be attributed to organic acids present in the peat. However, a neutral pH was recorded in the northern region of the study area where large quantities of gastropod shells have accumulated. With sulphate reduction and Na_2CO_3 formation pH values of peat can drastically increase as interpreted below.



Acknowledgement

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