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**REDUCTION AND OXIDATION PROPERTIES OF THE MANGROVE
SEDIMENT, PHUKET ISLAND, SOUTHERN THAILAND**

by

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CONTENTS

	Page
Abstract	1
I. Introduction	1
II. Materials and Methods	3
(a) Description of investigated area	3
(b) Measurements	4
(c) Theory of redox measurements	6
(d) Chemical consequence of the changes of Eh in the sediment	7
III. Results	7
IV. Discussion	7
(a) Vertical distribution of redox and pH profiles	7
(b) Horizontal distribution of redox and other influencing factors	10
V. Conclusions	12
Acknowledgements	12
References	13

ABSTRACT

Measurement of redox potential of mangrove sediments was carried out at the Ao Nam-Bor mangrove shore, Phuket Island, Southern Thailand. The surface sediment was found to consist of an oxidized layer which was only a few mm. thick; below this there was a redox discontinuity or transitional layer about 1 cm. thick followed by a reducing sediment.

The relationship between redox potential, microbiological activities, nutrients (NO_3^- , PO_4^{--} , etc.), organic materials, sediment grain size, sediment pH and macrofauna are discussed.

I. INTRODUCTION

There are normally 3 distinctive layers in the upper half meter of sediments from marine and fresh water environments. The upper surface layer is an oxidized layer usually with oxygen, and with a redox potential higher than +100 mV (often > +400 mV). The bottom layer is a reducing layer, very often black, which contains sulfide, and with a redox potential below +100 mV. In between these 2 layers, there is a transitional layer which has a steep redox gradient (Fenchel, 1969, Ruttner, 1971). These three layers are the result of the decomposition of organic com-

pounds in the sediment. These decomposition processes involve the utilization of available free oxygen, but when no free oxygen is available they continue anaerobically resulting in the formation of reduced residual substances (Ruttner, 1971). These processes of utilization and decomposition of substances are carried out by various microbiological activities (Blackburn, *et al.*, 1975, Fenchel, 1969, 1971, Rodina, 1972, Wood, 1967, Ramm and Bella, 1974).

In the deeper layer of the sediment, which is anaerobic, the anaerobic bacteria utilize oxidized compounds in the dead organic matter (SO_4^{--} ,

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NO₃⁻, Fe⁺⁺, etc.) resulting in the formation of H₂S, NH₃, Fe⁺⁺, etc. and energy (Fenchel and Jansson, 1966). These reduced substances will diffuse upwards to the discontinuity layer where oxygen and chemoautotrophic bacteria are present. Some of the chemoautotrophic bacteria will oxidize these compounds and the energy thus obtained will be utilized for reducing external CO₂ and synthesis of organic matter (Fenchel, 1971). In addition when light penetrates into the reducing layer, the photosynthetic bacteria will become very active and this process contributes to the formation of particulate matter (Blackburn, *et al.*, 1975, Fenchel, 1969, 1971). These processes were summarised by Fenchel 1971 as in Fig. 1.

the presence of oxygen; and thirdly by a photoautotrophic bacterial oxidation which oxidizes sulfide in the presence of light under aerobic condition. These pathways of oxidation were summarized by Blackburn *et al.* (1975), as in Fig. 2.

On tidal flats and in an estuarine environment many exchange processes are going on between the tidal waters and the landward mangrove covered fringe areas. These exchanges include both removal and accumulation of large amounts of organic materials from leaves and twigs and roots and other form of organic matter, and exchanges of chemical compounds (Ramm and Bella, 1974).

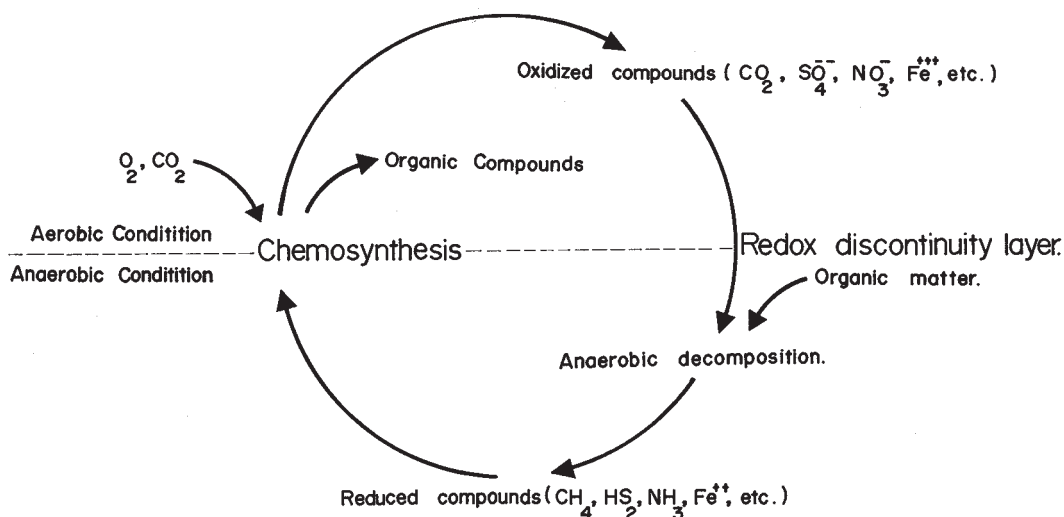


Fig. 1—The cycling of energy in the sediment.

The redox conditions of the reducing sediments are controlled by the sulfide cycles in the marine environment (Berner, 1963 cited by Fenchel, 1971). The sulfate reducing bacteria reduces sulfate to sulfide which may accumulate in the reduced layer, or diffuse upwards to the surface, where it re-oxidized. (Jørgensen and Fenchel, 1974). Blackburn *et al.* (1975) found that sulfide oxidation in sediments was carried out in 3 different ways: firstly by a chemoautotrophic bacterial oxidation of sulfide; secondly by a spontaneous oxidation in

The mangrove area investigated during the present study is situated close to a tidal flat and an estuary, and thus has characteristics of both. The soil itself is incapable of supporting life because it requires microbiological activities to produce metabolites which react with the raw material in the soil and transform them into substances that can be utilized by animals and higher plants (MacNae, 1974). The supply of nutrients and organic materials is influenced by

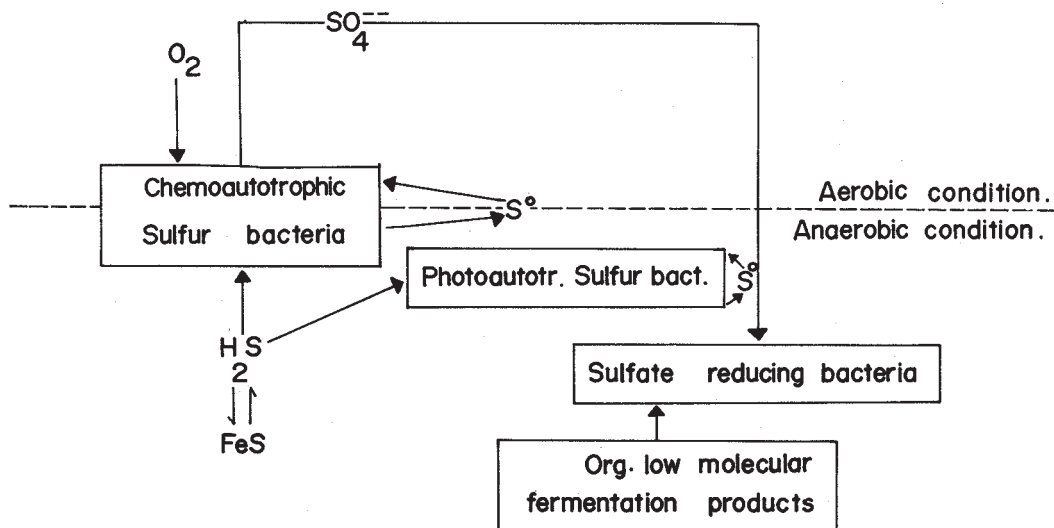


Fig. 2—The cycling of sulfur in the sediment.

the tides. These factors govern the total biological activities of the bacteria, fungi, and the feeding and burrowing activities of crabs, polychaetes and snails which produce the faecal or pseudo-faecal materials resulting in a further increase of soil fertility (Nichols, 1974, MacNae, 1974).

Frith *et al.* (1976) found more than one hundred macrofaunal species in the same mangrove shore at Ao Nam-Bor, and found that different areas of this shore were dominated by different groups of animals. Fenchel (1969, 1971) found that the vertical distribution of the microfauna was correlated with the redox (reduction and oxidation, or Eh) profile in the sediments. Pearson *et al.* (1976) found that the benthic macrofauna biomass was related to the Eh of lake sediments.

The aim of the present study was to investigate the Eh, pH, sediment grain sizes and organic contents in the Ao Nam-Bor mangrove shore sediments, Phuket Island, Southern Thailand, and to attempt to relate these factors to the distribution of macrofauna in different areas of this mangrove shore.

II. MATERIALS AND METHODS

a) DESCRIPTION OF INVESTIGATED AREA

This investigation was carried out at the Ao Nam-Bor mangrove shore from June 1976 to February 1977 during low tide periods. This consists of 3 biotopes, a mangrove forest, a sand flat and a mud flat. There were in total 10 stations in these 3 biotopes; 7 in the mangrove forest, 2 on the sand flat and 1 on the mud flat (see Fig. 3). Three of the mangrove forest stations (stations 1A, 1B and 2) were located in the landward fringe area. Station 1A was relatively undisturbed, but station 1B and 2 were probably somewhat polluted by a recently built chicken farm. In the mangrove forest proper, station 3A (the most landward) was located along the banks of a shallow and narrow channel ($\frac{1}{2}$ m. deep, 1 m. wide). This latter channel joined a larger channel ($1\frac{1}{2}$ m. deep and 3 m. wide) along whose banks stations 3B, 3C and 4 were located. Adjacent to the seaward side of the mangrove forest was a sand flat where two stations (5A and 5B) were located. Station 5A was covered with about 5 cm. thick layer of shell

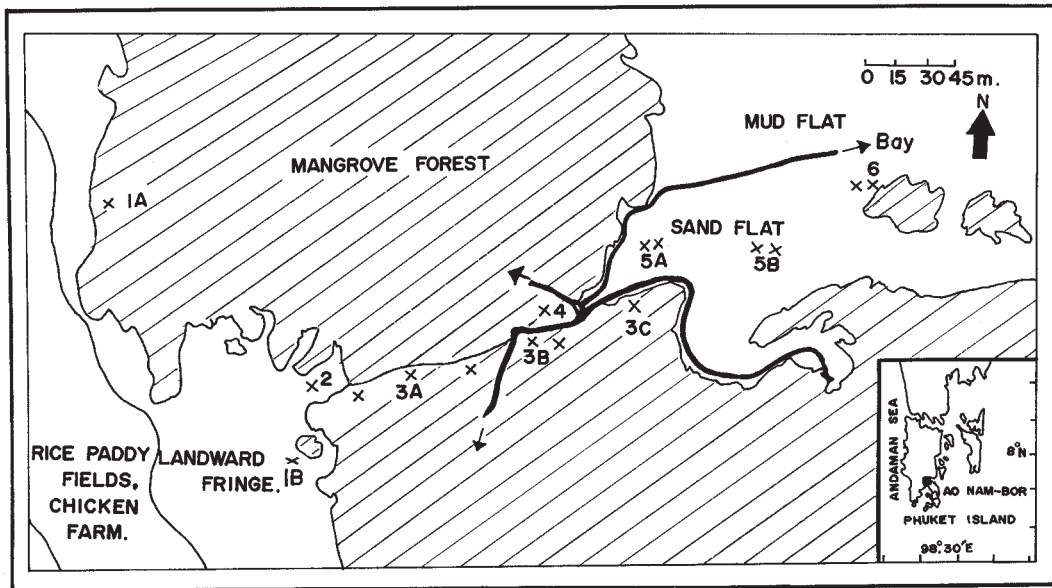


Fig. 3—Map of the investigated Ao Nam-Bor mangrove shore.

- × = sampling station.
- 1A – 6 = number of stations.
- = small-narrow tidal channel.
- = big tidal channel.
- = Ao Nam-Bor mangrove shore (in inset).

fragments but station 5B consisted of more or less fine sand. The mud flat, the most seaward station (station 6), was situated near the bay of Ao Nam-Bor.

The mangrove forest (stations 1–4) investigated covers an area of 4.1 km.² and is situated on the west coast of Southern Thailand (98°25'E, 7° 51'N). The mangrove is partly sheltered by the island, Koh Taphou Yai. The tidal range is 3 m. at spring tide and 1 m. at neap tide. The climate is humid tropical with a wet Southwest Monsoon Period from May to November and a dry Northeast Monsoon Period from December to March. During the study period of 1976–77, 2455 mm. and 230 mm. of rain were recorded during the wet and dry seasons respectively. The mangrove forest consists predominantly of trees, *Rhizophora apiculata*. A few trees of *R. mucronata* Lank and *Sonneratia alba* Smith were, however, also present along the seaward edge of the forest (Christensen

and Wiium-Andersen, 1977). The incoming sea water often carries a heavy load of sediments from 3 offshore tin dredges. Moreover the Phuket River, during the rainy season, deposits a large amount of silt and clay from land tin mines into coastal waters.

b) MEASUREMENTS

Sediment core samples were taken during low tide with Perspex tubes 5.2 cm. in diameter and 50 cm. in length. The tube was pressed about 15 cm. into the sediment, a rubber stopper was placed in the tube. The core samples were then removed and another rubber stopper was placed under the sediment core. The sediment samples were brought to the laboratory. Two hundred ml. sea water was cautiously poured onto the top of the core and left standing at room temperature (25°C) for half hour. The redox potential was measured on the sampling day. Core samples

were taken at all stations (1-6), up to 10 samples being collected per station. It should be noted that in order to obtain a representative redox profile from the surface down to a 10 cm. depth, areas around the burrows of animals were avoided, as these areas may well have been oxidized. At stations 3A, 3B and 3C, samples were taken both at the top, and the edge, of the channel banks.

The redox measurement was carried out with a self made Pt-electrode and a calomel reference

electrode of Radiometer type K 401 with a potential of 244 mV in relation to the standard hydrogen electrode. The self made Pt-electrode was constructed by soldering a piece of Pt wire (about 0.5 mm. in diameter and 2 cm. in length) to a piece of Ag wire of the same diameter, and then the Ag wire was soldered to a long Cu wire (see Fig. 4).

The connected wires were inserted into a 1 ml. graduated pipette, the tip of the Pt wire being about 0.5 cm. off the tip of the pipette. The tip of the pipette was then sealed with epoxy (Araldit)

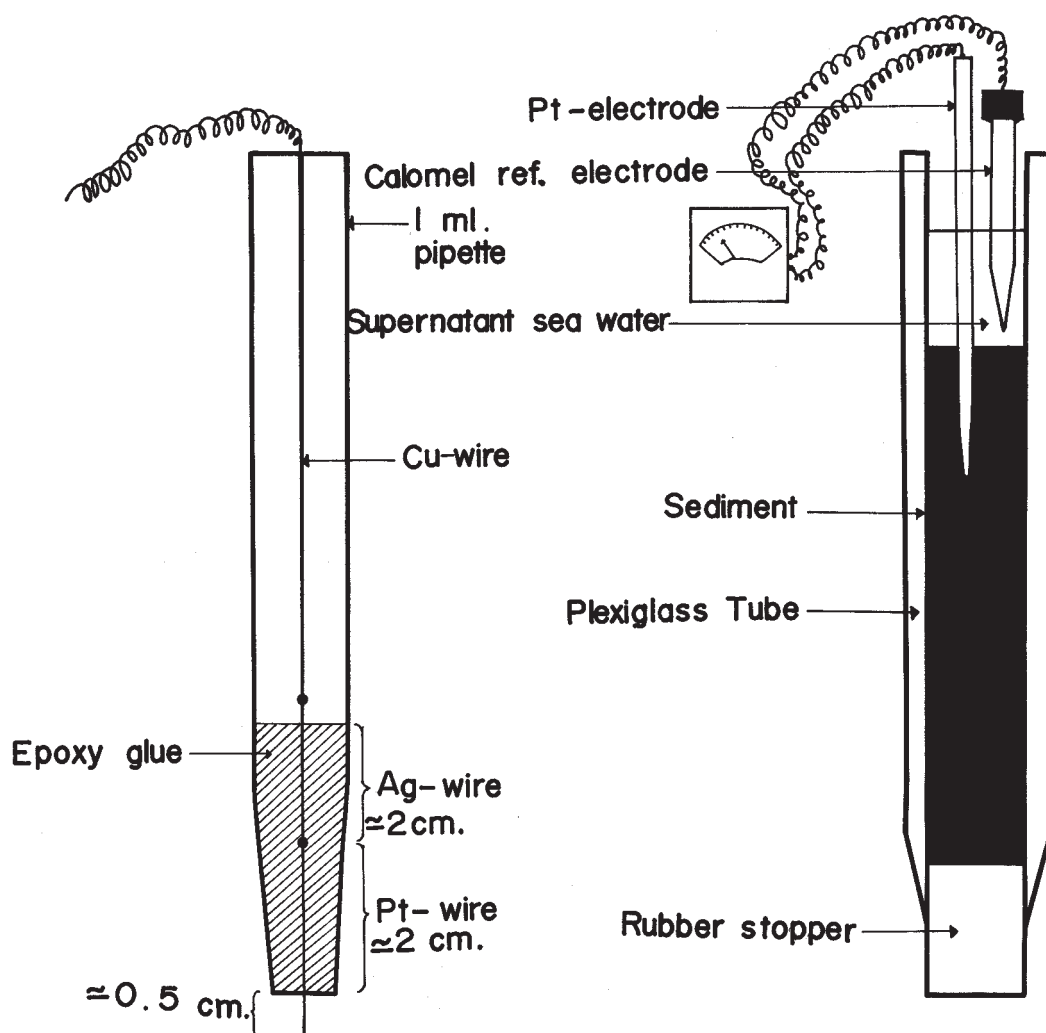


Fig. 4—Self made Pt-electrode assembly and Redox measurement set up.

glue (see Fig. 4) and at each station the Eh values were recorded when drifting was less than 1 mV/min. (Fenchel, 1969). The Pt-electrode was cleaned with scouring powder before every measurement and it was checked at regular intervals with quin-hynone solution to assure normal functioning of the electrode.

Soil samples were taken from each station and were dried at 105°C for 24 hours for analysis of grain size and organic content.

To determine grain size 150 grams of dried sample was sieved through an automatic sieving machine for 5 minutes. Sieve hole diameters are 2.0, 1.0, 0.5, 0.25, 0.125 and 0.063 mm. Each resultant subsample was weighed to 0.1 grams of accuracy, and the weight of these was expressed as a percentage of total dried weight.

To determine organic content 5 grams of dried sample was ashed at 550°C for 2 hours and then reweighed, and the mean values of ignition loss was expressed as a percentage of organic content of total dried weight.

c) THEORY OF REDOX MEASUREMENTS

The redox system is defined as a reduction agent which is capable of liberating an electron, and an oxidation agent which is capable of accepting an electron. In nature, processes often involve more than one electron together with hydrogen ion (H⁺), as :—



It can be written as :—



Thus, every reduction agent has its corresponding oxidation agent counterpart forming a so-called "redox system" (Rodina, 1972, Peterson, 1966).

The redox potential can be measured by placing a Pt-electrode as an electron reservoir in the sample, so that an exchange of electrons between the reservoir (Pt-electrode) and the sample will occur.

The electrode potential can be measured by using an additional reference electrode in the sample. If the reference electrode is a standard hydrogen electrode, the measured potential is called Eh. Considering equation (1) thermodynamically, then the Eh (mV) can be expressed as:—

$$\text{Eh} = \text{E}_o + \frac{\text{RT}}{\text{nF}} \ln \frac{\text{a}_{\text{ox.}} \cdot \text{a}_{\text{H}^+}^m}{\text{a}_{\text{red.}}}$$

where R	=	The gas constant
T	=	The absolute temperature
F	=	The Faraday constant
n	=	Number of electrons involved
m	=	Number of hydrogen ion (H ⁺) involved
a _{ox}	=	Activity of oxidation agent
a _{red.}	=	Activity of reduction agent
a _{H⁺} ^m	=	Activity of H ⁺
E _o	=	Standard potential

The reference hydrogen electrode is, however, not practical to use. Thus, a saturated calomel electrode was used instead with a potential of 244 mV in relation to the standard hydrogen electrode at 25°C. The potential measured by a Pt-electrode and a calomel electrode is therefore converted to Eh value by adding +244 mV, as follow:—

$$\text{Eh (mV)} = \text{Eh} + 244 \quad (2)$$

Inserting the constant values of R, F, $\ln = 2.3026 \log$, $\log \text{a}_{\text{H}^+}^m = \text{pH}$

$$\text{Eh} = \text{E}_o + \frac{0.1983 \text{ T}}{\text{n}} \log \frac{\text{a}_{\text{ox.}}}{\text{a}_{\text{red.}}} - \frac{0.1983 \text{ T}}{\text{n}} m - \text{pH} \quad (3)$$

As shown from equation (3) the Eh value is dependent on the pH value when H₂O is present. This process often occurs in nature such as in mangrove

sediments. The present measurements have not been corrected for pH deviations.

d) CHEMICAL CONSEQUENCE OF THE CHANGES OF EH IN THE SEDIMENT

Mortimer (1941–42 cited by Ruttner, 1971, Fenchel, 1969) presented a table which showed the redox state of certain substances at different mV values as follows:—

Eh (mV)	Substances Occur
< + 60	S^{--}
> + 100	SO_4^{--}
< + 200	Fe^{++}
> + 300	Fe^{+++}
< + 350	NH_4^+
> + 450	NO_2^-, NO_3^-

It is seen that when Eh is lower than +035 mV in the discontinuity layer NH_4^+ dominates over oxidized nitrogen compound and that iron occurs as Fe^{++} below +200 mV as insoluble Fe^{+++} or its complex in more or less oxidized environments. The sulfate-sulfide reaction is important because below +60 mV S^{--} dominates over its oxidized sulfur compounds and combined with Fe^{++} as insoluble FeS which is noticeable as a black layer. When the Eh is more than +100 mV, SO_4^{--} is formed and again utilized in the metabolic processes of bacteria, *Microspira desulfuricans* and other species, and it is often associated with cellulose degradation (Ruttner, 1971, Jørgensen and Fenchel 1974).

III. RESULTS

The results from this investigation are clearly summarised in Figs. 5–14. Below each figure a brief explanation is given. The results are discussed in Section IV (see Discussion).

IV. DISCUSSION

a) VERTICAL DISTRIBUTION OF REDOX AND pH PROFILES

As shown from the results of this investigation, the vertical redox measurements at each station were found to be more or less identical, apart from the differences in the thickness of the oxidizing layer which, particularly at station 5, was up to several cm. thick (see Figs. 5–10). All redox potentials at the sediment surface were higher than +100 mV, thus indicating oxidizing conditions, as was also shown by Ruttner (1971) for fresh water lake sediment. It should be noted that the electrical value of +100 mV represents the change from anaerobic to aerobic conditions. Thus, values above +100 mV indicate aerobic condition and those below is anaerobic condition. Below the sediment layer, there was a sharp and steep fall in the redox potential of the discontinuity or transitional layer at all localities. This drop from +100 mV to –200 or –400 mV was found to vary in accordance with the reducing capacity of the sediment (Figs. 5–10). It is noteworthy that the very high aerobic and anaerobic

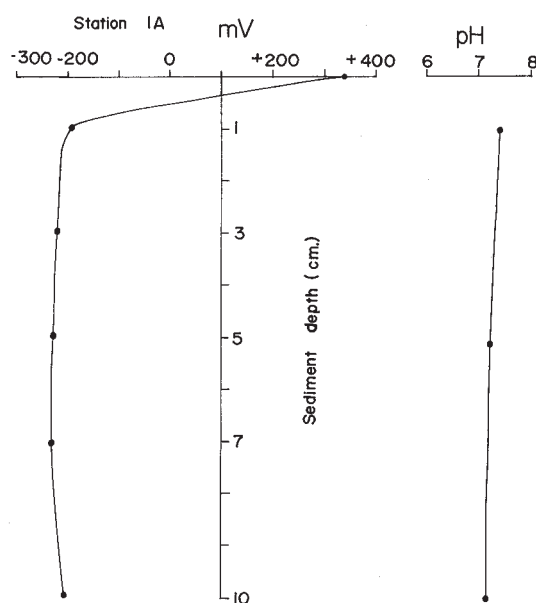


Fig. 5—Vertical redox and pH profiles in the landward mangrove fringe sediment of station 1A. Note that a 1–2 mm. thick surface oxidized layer is followed by a redox discontinuity layer, 1 cm. thick, with an abrupt change in Eh mV. Below this, the reduced sediment and pH values were relatively constant.

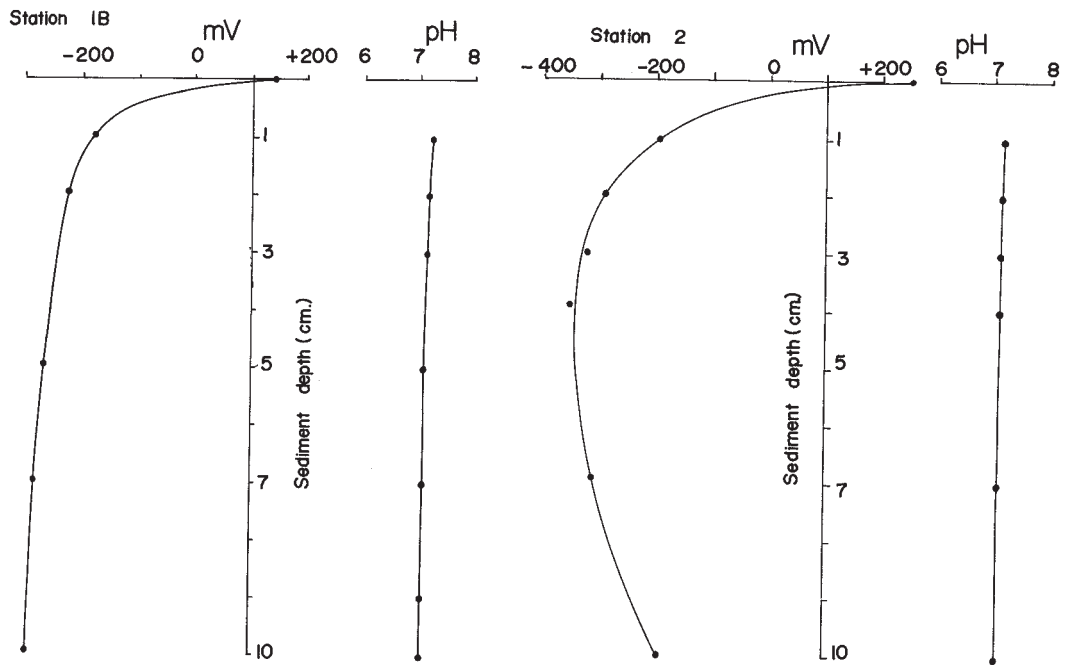


Fig. 6—Vertical redox and pH profiles in the landward mangrove fringe sediments of stations 1B and 2. The 3 redox layers and pH profiles at these two stations were more or less identical to that of station 1A (see Fig. 5).

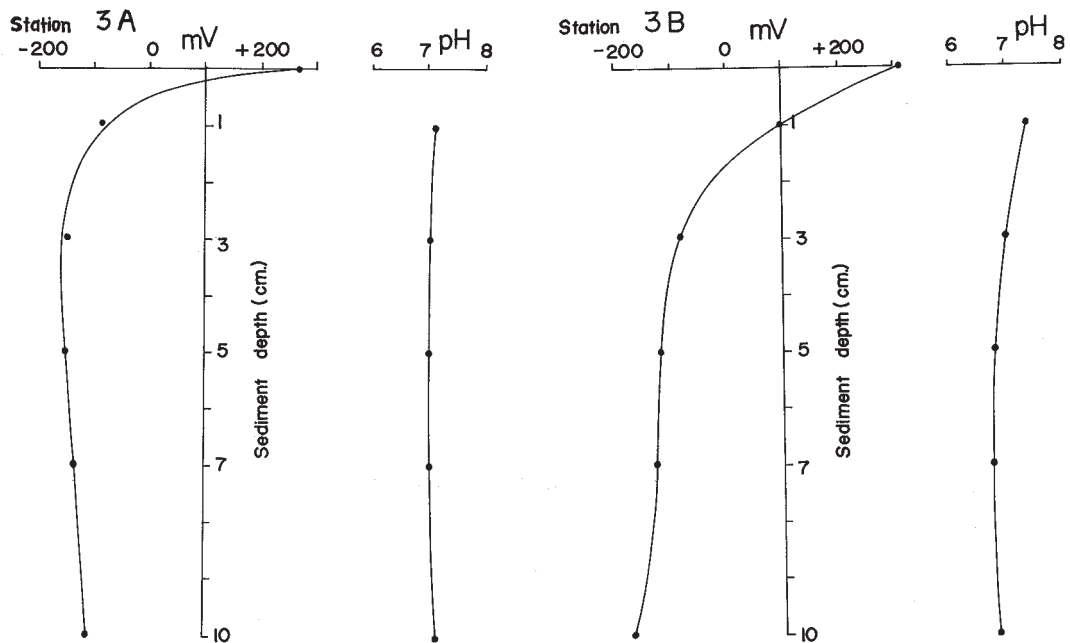


Fig. 7—Vertical redox and pH profiles in the mangrove forest sediments of stations 3A and 3B. The surface oxidized layer was relatively thicker (5–10 mm.) than those of stations 1B and 2, but the discontinuity and reduced layers were similar (see Fig. 6).

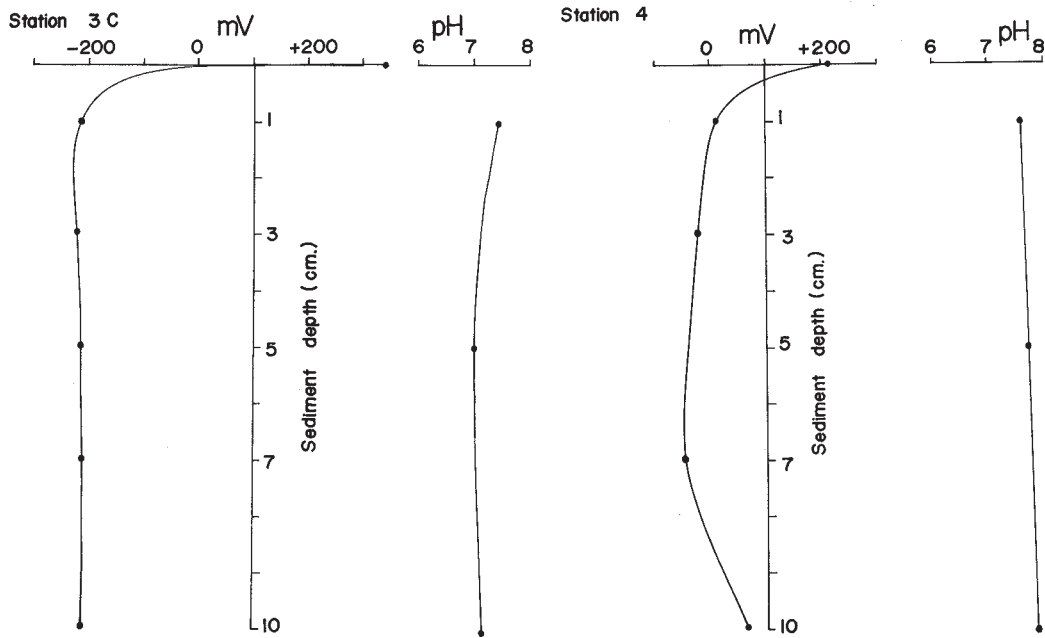


Fig. 8—Vertical redox and pH profiles in the seaward mangrove fringe sediments of stations 3C and 4. The 3 redox layers and pH values at station 3C were more or less identical with those of previous stations (see Figs. 5–7). In addition, the surface oxidized and discontinuity layer at station 4 were also similar to that of previous stations but there were relatively higher Eh values in the reduced sediment. The pH values were relatively high approaching 8 (see Fig. 8).

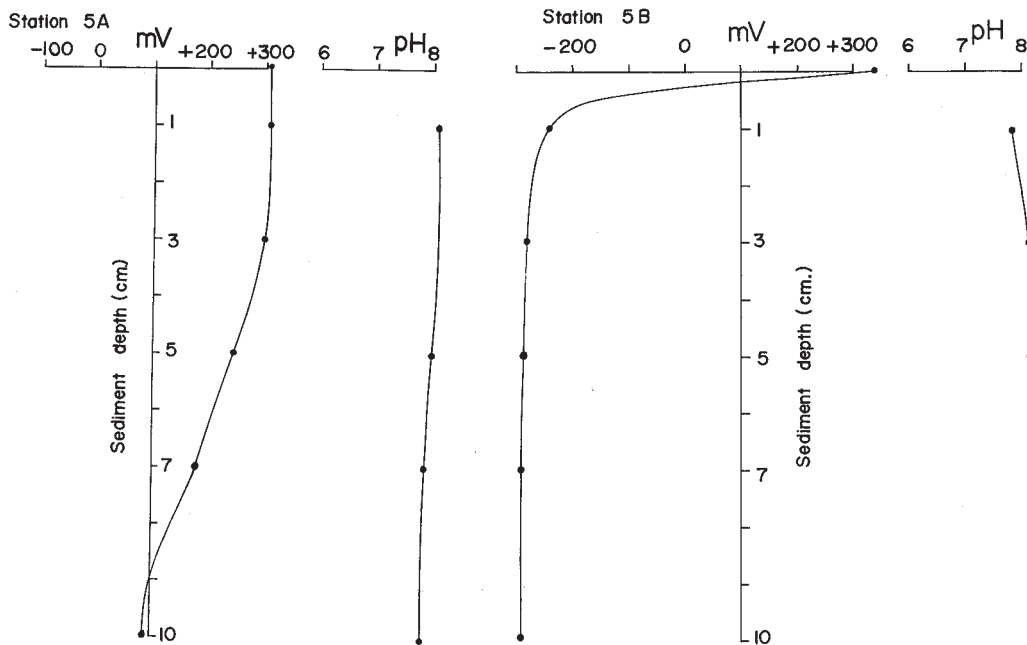


Fig. 9—Vertical redox and pH profiles in the sand flat sediments of stations 5A and 5B. The very thick surface oxidized layer (8.5 cm.) at station 5A resulted in a deeper reduced sediment layer. The 3 redox layers in the sediment at station 5B were identical with those of the previous stations (see Figs. 5–8). The pH values at these two stations were identical, the value being around 8.

microbiological metabolic activities and high decomposition rates of organic material in this discontinuity layer would partially account for the drop in the redox potential (Ruttner, 1971, Fenchel, 1969, 1971).

In the sediments of stations 2 and 4 there was a noticeably high density of burrowing crabs and polychaetes with up to 29 and 25 individuals/ m^2 respectively (Frith *et al.*, 1976). The results for the Eh values of these sediments (station 2 and 4) clearly showed that the high density, and the activities, of these burrowing animals did not apparently influence the general reducing conditions of the sediments (see Figs. 6 and 8). It is noteworthy, however, that the surfaces of the burrows were in fact oxidized, and in all probability the sediment locally about the burrows was to some extent oxidized as was found to be the case by Hylleberg (1975) in lugworm activity experiments. Furthermore in these sediments the redox potential did in fact increase very slightly at a depth of 10 cm. (Figs. 5–10), which may have been due to a decrease in the intensity of anaerobic decomposition at this depth due possibly to a lack of accumulated organic material (Ruttner, 1971).

In general, the vertical pH profiles of the mangrove forest stations (1 to 4) were all similar (see Figs. 5–8), with a slightly higher pH value at the sediment surface than at a lower depth. This slight drop in the pH value was certainly due to microbiological activities which produce H_2S and CO_2 from anaerobic decomposition processes (Ben-Yaakov, 1973). The vertical pH profiles of the sand and mud flat sediments (stations 5 and 6) were similar to each other (see Figs. 9–10), but differed from those of the previous stations (1 to 4). It is noteworthy that the pH of the sand and mud flat sediments (pH = 8) was almost the same as that of sea water (pH = 8.2). This may well have been due to the fact that these 2 stations were covered by sea water by more than 84% of the tides (Frith *et al.*, 1976), and due to the coarser nature of their sediments, water percolation was more efficient.

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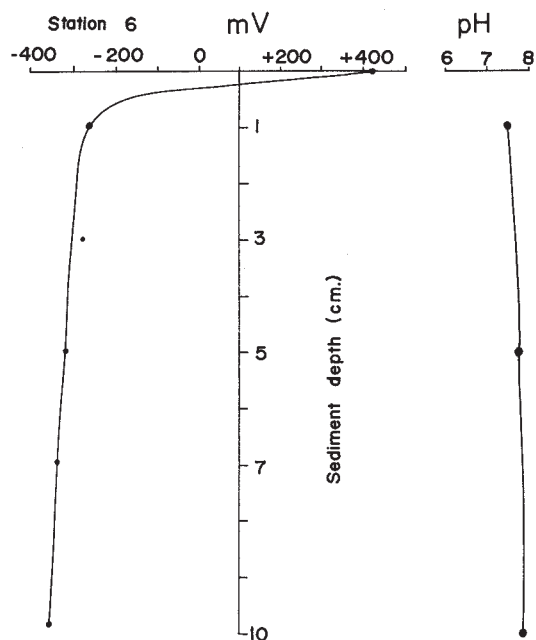


Fig. 10—Vertical redox and pH profiles in the mud flat sediment of station 6 (the most seaward station). The 3 redox layers and pH profiles were identical with that of station 5B (see Fig. 9).

b) HORIZONTAL DISTRIBUTION OF REDOX AND OTHER INFLUENCING FACTORS

The results from this investigation clearly showed that the greater amount of coarser sand in the sediments brought about a thicker oxidized layer, noticeably in station 5A where the Eh value was greater than +100 mV (see Fig. 11). Furthermore in sediments of station 5A with large amounts of shell fragment, the Eh value was even higher. The thickness of the oxidized layer has also been shown by several workers to be influenced by water turbulence, churning over of sediments and water percolation (Fenchel, 1969, Dale, 1974, Graetz, 1973, Wood, 1967).

Conversely the results indicated that sediments with a high mud content (see Fig. 14) had a very low Eh value (see Fig. 12). This correlation is clearly illustrated in Fig. 15. Several reasons have previously been given to explain this latter finding. Firstly, mud particles are very well packed causing very slow water percolation (Fenchel, 1969); secondly, the internal surface of mud particles

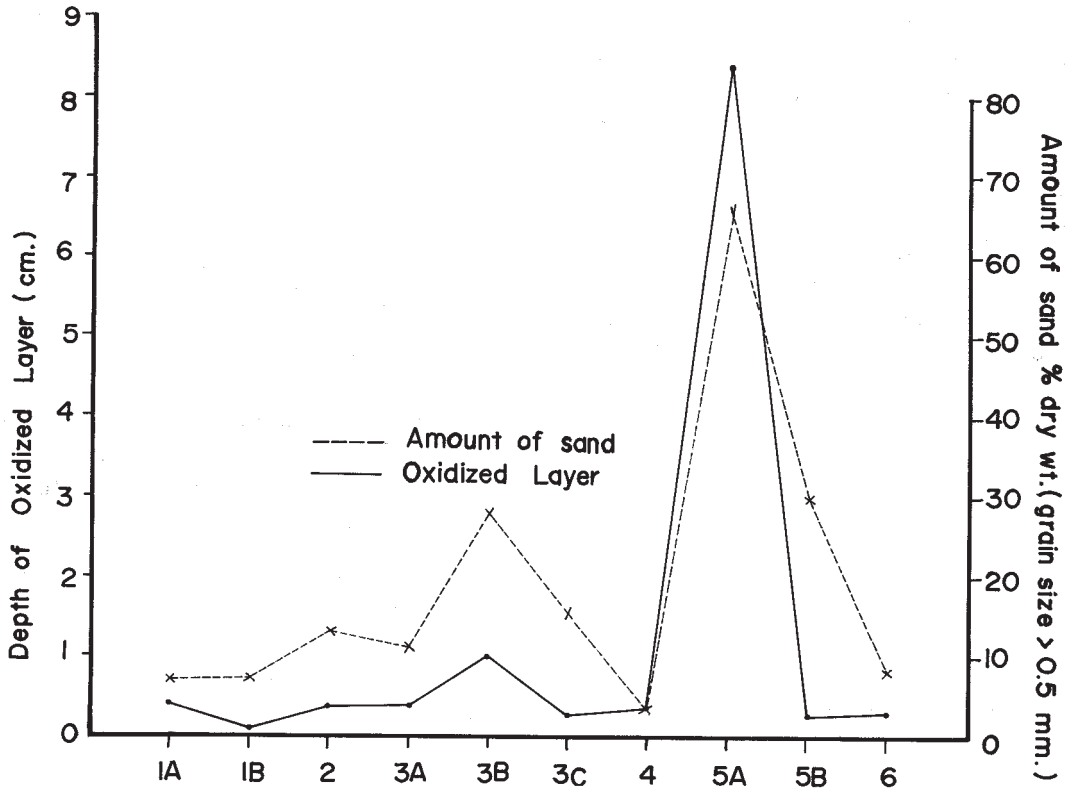


Fig. 11—The relationship between the thickness of oxidized layer (cm.) and the % of coarse sand (dry weight, grain size > 0.5 mm.) of station 1 to 6 (from land to sea).

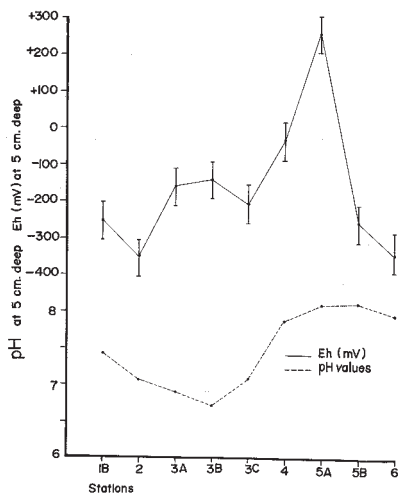


Fig. 12—Horizontal distribution of Eh (mV) and pH values at 5 cm. deep in the sediments of station 1 to 6 (from land to sea).

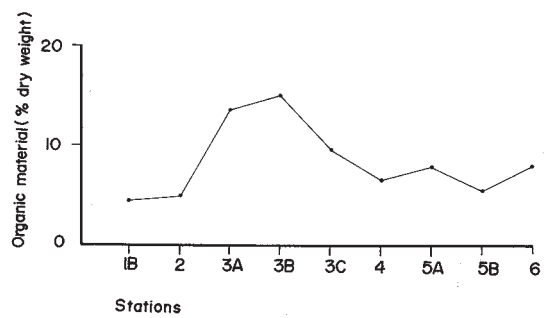


Fig. 13—Horizontal distribution of organic material (% dry weight) present in the 10 cm. thick surface sediments of station 1 to 6 (from land to sea).

is very high because 1 g. of mud has an internal surface not less than 2500 cm.² which thus allows a large bacteria population to attach itself to the free surfaces (Blackburn, *et al.*, 1975, Dale, 1974, Fenchel, 1969); and thirdly the organic materials will adsorb to the high surface area giving rise to a higher activity of microorganisms with a large oxygen consumption (Fenchel, 1969). It can be seen from Fig. 13 that the average content of organic material in the mangrove forest sediment was around 10%. The results from this study did

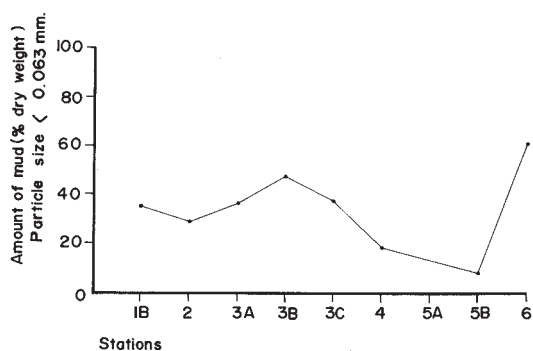


Fig. 14—Horizontal distribution of mud (% dry weight, particle size < 0.063 mm.) present in the 10 cm. thick surface sediments of station 1 to 6 (from land to sea).

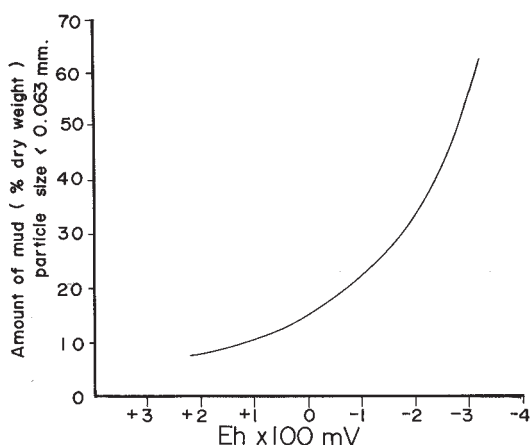


Fig. 15—The correlation between the Eh (mV) and the % of mud content (dry weight).

not show any apparent correlation between the distribution of the macrofaunal species found by Frith *et al.*, (1976) and the sediment redox conditions in the same mangrove shore.

V. CONCLUSIONS

The results of the present investigation clearly showed that:—

(a) in the mangrove soil the depth of the oxidized layer normally was only a few millimetres thick with Eh ranging from +200 to +420 mV, and consisted of oxidized substances which would be partly released into the water and partly used locally.

(b) below the oxidized layer there was a redox discontinuity layer about 1 cm. thick with a sharp decline in the Eh. In this layer, the microorganisms reach their maximum activities in the recycling of organic matter.

(c) in the deeper layer, with a strong reducing sediment and an Eh lower than +100 mV, H₂S was present and formed FeS, a black sediment.

(d) Eh is related to grain size, surplus organic materials, micro and macrobiological activities.

(e) the pH values in the mangrove forest sediments were more or less neutral while those of the sand flat and mud flat were basic and similar to that of sea water pH (8.2).

(f) there was no apparent correlation between the Eh and the distribution of macrofauna.

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