# Early Diagenetic Alteration of Recently Deposited Organic Matter in Coastal Marine Sediments West of Unguja Island, Zanzibar

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Abstract—Variations in the content of organic carbon (OC), nitrogen, CaCO, and diagenetically sensitive elements (Cu, Fe, Mn, Pb, Zn), stable-isotope composition of OC and nitrogen and C/ N ratios were used to assess the diagenetic evolution of organic matter (OM) in coastal sediments west of Unguja Island, Zanzibar. Finer grained sediments had lower contents of CaCo. (averaging 72%) compared to the coarser sediments (averaging 92%), suggesting an input of terrigenous clastic material. Also, finer sediments were characterized by higher contents of OC and nitrogen (>0.7 and 0.1% respectively), an indication that particle size plays a role in the preservation of OM. The stable-isotope signatures of OC and nitrogen for five sites, which had mean values ranging from -18.9 to -19.6% and from 1.21 to 4.78% respectively, indicated that sedimentary OM was mainly of marine origin. Contents of OC and nitrogen at three sites showed general downcore decreases, suggesting progressive degradation of OM over time. The content of CaCO, and C/N ratios at all sites were invariable downcore, implying the lack of preferential removal of nitrogen and/or carbon-bearing compounds during early diagenesis. Of the five elements measured, solid phase Mn had the highest level (>10 µg/g), whereas lowest values were observed for Cu and Pb (< 3 μg/g). In all cases, element enrichment levels did not vary markedly with depth. The results indicate that the degradation of OM in these coastal sediments takes place under oxic conditions and that the oxygenated layer is thick.

### INTRODUCTION

Mineralization of organic matter (OM), which involves five oxidants (O<sub>2</sub>, NO<sub>3</sub>, MnO<sub>2</sub>, FeO(OH), and SO<sub>4</sub>) occurs in sequence (oxidation, iron reduction, manganese reduction, denitrification, sulphate reduction and methanogenesis) and takes place in both oxic and anoxic environments (Froelich *et al.* 1979, de Lange 1986, Shaw *et al.* 1990). Depending on the availability and amounts of labile organic material and oxidants, some steps in this sequence may not occur. For example, in lacustrine environments where sulphate concentration is low its reduction does not occur

and the reactions proceed directly to the methanogenesis. Furthermore, depending on the oxidation potential of an element, various major and trace elements are either released to the sediment pore water, or adsorbed onto the sediments during early diagenetic alteration of OM by micro-organisms. As a result, changes in the levels of major and trace elements in sediments can be related to the effects of diagenetic processes (e.g. Froelich *et al.* 1979, de Lange 1986, Shaw *et al.* 1990, Warning & Brumsack 2000).

Although it has been estimated that about 3-4 billion tonnes of carbon are introduced to the world's oceans each year (JGOFS Canada 1989),

the amounts incorporated into the sediments and those recycled during early diagenetic processes are poorly known. This is surprising since oceans cover about 71% of the earth's surface and are considered to be major sinks of carbon and nitrogen through the burial of OM, the formation of deep bottom water, and primary productivity (Walsh 1989). Owing to shallow depth, high sedimentation rates and higher primary productivity compared to the oceanic realm, continental margins are particularly important (Walsh 1991). These three factors allow the rapid deposition of labile (more susceptible to diagenesis) OM to the sea floor in the continental margins. Therefore, it is hypothesized that continental margins are sites where releases of large quantities of nutrients, carbon dioxide and molecular nitrogen occur during diagenesis.

Although the Zanzibar channel is assumed to receive large quantities of labile OM, which would be highly susceptible to diagenesis owing to relatively shallow depths and a high primary productivity of about 150-250 mgC/m²/day (Bryceson 1977), information on its diagenetic alteration is lacking. Also, basic data such as sedimentation rates and spatial variations in the contents of sedimentary OC and nitrogen in Tanzanian waters are scarce.

Rates of diagenetic alteration of OM depend largely on the availability of labile OM and the degree of resistance to biodegradation. For example, terrestrially derived materials are more resistant to microbial degradation in the marine environment relative to autochthonous marine OM. Therefore, in order to unequivocally interpret the effect of diagenesis on OM, it is necessary to identify the various sources (types) of OM. One way of identifying sources and estimating their relative contribution to the total OM pool is through the use of C/N ratios and stable isotopes of OC and nitrogen. The OC stable isotope compositions of terrestrial material is distinct from that of autochthonous marine material with  $\delta^{13}$ C values for terrestrial material averaging -27% and that of marine phytoplankton for tropical and temperate areas averaging -20% (eg. Rau et al., 1989, Sackett et al., 1965). Similarly, 15N for terrestrial material is considered to be close to the atmospheric value

of 0% whereas that of marine plants averages 6% (Létolle 1980).

The present investigation of the Zanzibar channel west of Unguja Island (Fig. 1) addresses the affect of diagenesis on the OM inferred from associated variations in trace element enrichment. The study specifically documents downcore patterns in Cu, Fe, Mn, Pb, and Zn in shallow coastal sediments, as well as variation in the sources of OC and nitrogen using the contents and isotopic signatures of nitrogen and OC.

# **Study Area**

The study area, located on the west coast of the Unguja Island (Zanzibar), coastal Tanzania, extends from the Tumbatu Island in the north to the Menai Bay in the south (Fig. 1). Water depths are variable with relatively deep waters occurring in the northern part (west of Tumbatu Island) and west of several islets and sand banks fringing the coastline.

## MATERIALS AND METHODS

Eight sediment cores were collected in 1999 in water depths ranging from 10.5 to 45 m, either by divers (water depths < 33 m), or by modified lightweight gravity corer (muddier areas with water depths >33 m). Plastic (PVC) pipes (3.61 cm diameter and 1.2 m length) were used during coring. Cores collected by divers are denoted as HC (hand cores) while those by modified lightweight gravity corer are denoted as PC. Cores recovered from shallower areas (water depths in brackets) are HC 1 (10.5 m), HC 2 (29m), HC 12 (16 m), HC 15 (20 m), HC 16 (30 m) and HC 20 (32 m), while those from deeper areas are PC 5 (36 m) and PC 9 (45 m). Cores were frozen until processing when they were thawed after and subsampled at intervals of 1 cm. The resulting slices were dried at 50°C and then ground to a fine powder in an agate mortar.

The content of CaCO<sub>3</sub> was determined by acid leaching of approximately 2 g of material with hydrochloric acid. The samples were left to stand overnight, washed free of salts four to five times with deionised distilled water, dried in an oven at

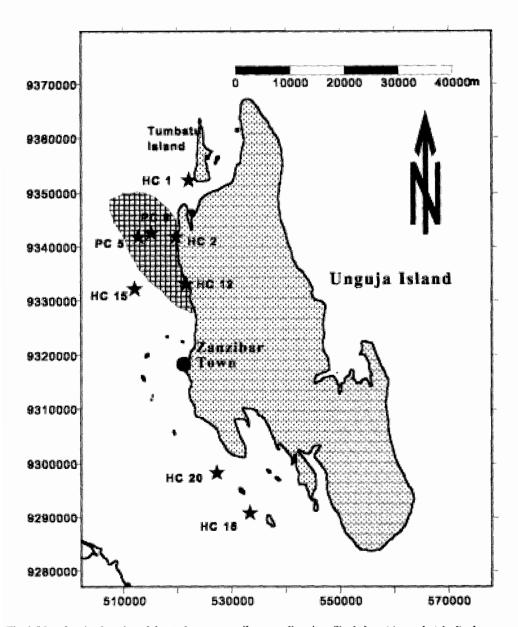


Fig. 1. Map showing location of the study area as well as sampling sites. Shaded part (cross-hatched) where cores HC 2, PC 5 PC 9 and HC 12 are located represent area that is studded by muddler sediments. Sandier sediments characterize the remaining part of the study area

50°C and re-weighed. Reproducibility of the method is within  $\pm 5\%$  (n = 5). CaCO<sub>3</sub> content is reported as dry weight percentage (%dw).

Solid phase Cu, Fe, Mn, Pb and Zn levels were determined by flame atomic absorption spectrophotometry (Model GBC 906 AA with HG 3000 hydride generator at the Southern and Eastern African Mineral Centre (SEAMIC) in Dar es Salaam. Sediment samples (ca. 0.5g) were digested

with aqua regia at  $80^{\circ}\text{C}$  on a hot plate. Contents of OC and total nitrogen were determined using a C-H-N analyser at the Department of Geology and Geochemistry, Stockholm University (reproducibility is within  $\pm 0.1$  and  $\pm 0.01\%$  respectively). Nitrogen and OC contents are reported as dry weight percentages, whereas elemental levels are reported as  $\mu g/g$  of dry bulk sediment.

Stable isotopes of OC and nitrogen were measured using an isotope mass spectrometer at the Department of Geology and Geochemistry, Stockholm University. The measured values are reported in  $\delta$ -notation with negative values indicating depletion and positive values indicating enrichment relative to standard materials (Vienna Pee Dee Belemnite (VPDB) for carbon and atmospheric nitrogen for nitrogen). The  $\delta$ -values are mathematically given by:  $\delta X(\%_o) = (R_{\text{sample}}/R_{\text{std}}-1)x10^3$ , where X is  $^{13}$ C or  $^{15}$ N,  $R_{\text{sample}}$  is the isotopic ratio (e.g.  $^{13}$ C/ $^{12}$ C,  $^{15}$ N/ $^{14}$ N) of the sample and  $R_{\text{std}}$  is the isotopic ratio of the standard.

### RESULTS

Lithologically, two types of sediments have been observed muddy sediments with mud content > 80% dry weight at sites HC 2, PC 5, PC 9, HC 12, and coarse carbonate sand with mud content < 20% dry weight at sites HC 1, HC 15, HC 16, HC 20

(Fig. 1). Fine-grained sediments lack macroscopic shell debris and are confined to a narrow zone north of Zanzibar town (Fig. 1). Coarse carbonate sand is rich in intact and fragmented shells of various organisms, including gastropods and bivalves.

Sediment cores recovered at sandier sites (HC 1, HC 15, HC 16 and HC 20) had sand fractions (>0.063 μm) greater than 70% and were rich in whole/broken shells, whereas cores from sites HC 2, PC 5, PC 9 and HC 12 had < 20% sand fractions (>0.063 μm). The muddier sites (HC 2 and HC 12) had the highest levels of OC and nitrogen while the sandier site (HC 1) had the lowest levels (Fig. 2). The OC content at sites HC 2, PC 9 and HC 12, which averaged 1.1±0.1%, 0.9±0.1% and 1.1±0.2% respectively, showed a general downcore decrease to the base of the cores (Fig. 2). A similar trend of downcore decrease was observable for the nitrogen content at sites HC 2 and PC 9 (Fig. 2). The mean nitrogen content at

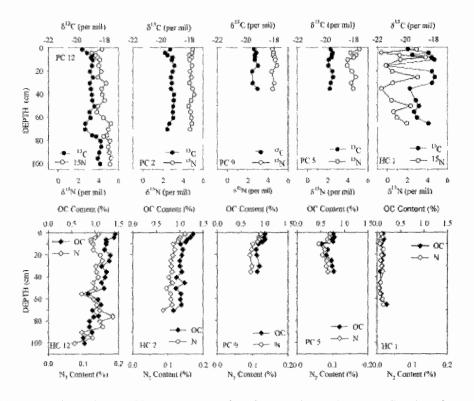


Fig. 2. Downcore variations in the stable isotopes of organic carbon and nitrogen (upper panel) and total contents of organic carbon and nitrogen (lower panel) at sites HC 1, HC 2, PC 5, PC 9 and HC 12 off the west coast of Unguja Island

these two sites (HC 2 and PC 9) was 0.11±0.01%. Site HC 1 showed relatively constant values of OC and nitrogen contents while site PC 5 showed a downcore increase in both OC and nitrogen below 10 cm (Fig. 2). The mean values of OC and nitrogen for site HC 1 were 0.1±0.0% and 0.01±0.00% while for site PC 5 were 0.7±0.1% and 0.08±0.01% respectively. Content of nitrogen at site HC 12, which averaged 0.13±0.02%, showed a similar downcore trend as that of OC except below 75 cm where there was a general downcore decrease (Fig. 2).

The OC stable isotope values ( $\delta^{13}$ C) and nitrogen ( $\delta^{15}$ N) at site HC 1, which averages -  $20.0\pm1.0\%$  and  $1.2\pm1.3\%$  respectively, were highly variable with a lack of any general downcore trends (Fig. 2). The OC isotope values at site HC 12 that averaged -18.9 $\pm0.4\%$  showed a change of >1% between surface and base of the core (Fig. 2). A shift towards higher values (enrichment) of about 1% was particularly noticeable below 70 cm (Fig. 2). Other three sites (HC 2, PC 5 and PC 9 with mean  $\delta^{13}$ C values of-19.3 $\pm0.2\%$ , -19.6 $\pm0.1\%$  and -19.4 $\pm0.1\%$  respectively) showed nearconstant trends in  $\delta^{13}$ C (Fig. 2). A similar downcore

trend was observable at these sites for the nitrogen isotope values (Fig. 2). The  $\delta^{15}$ N values at these three sites (HC 2, PC 5 and PC 9) averaged  $4.8\pm0.2\%$ ,  $4.5\pm0.4\%$  and  $4.6\pm0.2\%$  respectively. The  $\delta^{15}$ N for site HC 12, which averages  $4.5\pm0.5\%$ , showed a general downcore increase changing from approximately 3.8% at the surface to approximately 5.2% at the bottom of the core (Fig. 2).

The C/N ratio values at site HC 12, which averaged 9.8±1.9,showed a trend of downcore decrease in the upper 85 cm followed by more erratic values (Fig. 3). Erratic C/N values are observable also at site HC 1that averaged 10.6±2.3 (Fig. 3). The C/N values showed slight downcore increases to the base of the core at sites HC 2 and PC 9 whereas at site PC 5 they were relatively invariable downcore (Fig. 3). The mean C/N ratio values at these three sites (HC 2, PC 5 and PC 9) were 10.8±0.4, 10.1±0.3 and 10.1±0.4 respectively.

Generally, contents of CaCO<sub>3</sub> did not show any major downcore variability except at site HC 15, which showed a downcore decrease with a sharp change towards lower values at about 35 cm (Fig. 3). Sites with the highest carbonate contents (>

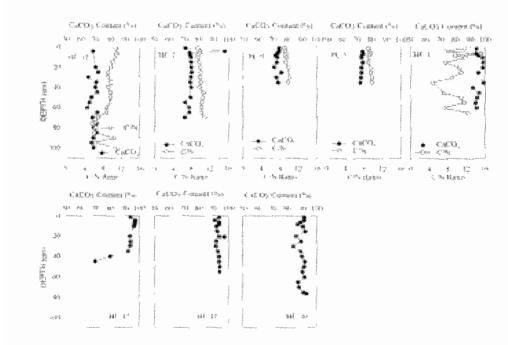


Fig. 3. Variations in the C/N ratios (sites HC 1, HC 2, PC 5, PC 9 and HC 12) and contents of calcium carbonate of coarse-grained (sites HC 1, HC 15, HC 16, and HC 20) and fine-grained sediments (sites HC 2, PC 5, PC 9 and HC 12) off the west coast of Unguja Island

90% CaCO<sub>3</sub>; sites HC 1, HC 15, HC 16, and HC 20) were located in sandier areas, whereas sites with lower CaCO<sub>3</sub> content (<80% CaCO<sub>3</sub>, sites HC 2, PC 5, PC 9 and HC 12) were located in muddier areas (Figs. 1 and 3). Highest carbonate contents (>95% CaCO<sub>3</sub>) were recorded at Site HC 1 and the lowest values (<70% CaCO<sub>3</sub>) at Site HC 12 (Fig. 3).

With the exception of Pb, concentration of solid phase Cu, Fe, Mn, and Zn were highest (Fig. 4) in muddier sites (PC 9 and HC 12) than in sandier sites (HC 1, HC 15, HC16 and HC 20). Inter-site comparison showed that Mn contents were high relative to other elements with sites PC 9, HC 12, HC 15 and HC 20 having the highest concentrations (Fig. 4). Mn contents showed downcore increases at sites HC 15 and HC 20. Furthermore, there was an enrichment of Mn concentration of more than two orders of magnitude below 35 cm that was associated with

a change to lower values of CaCO<sub>3</sub> at site HC 15 (Figs. 3 and 4). The concentration of Mn changed from 10-30  $\mu$ g/g in the 0-35 cm interval in the sediment to 70-80  $\mu$ g/g at the base of the core. At site HC 12, the concentration of Mn showed a downcore decrease from 36  $\mu$ g/g at the surface to 28 $\mu$ g/g at 80 cm (Fig. 4). Site HC 20 showed near constant concentration values downcore, but the trend was erratic below 70 cm (Fig. 4). The other sites (HC 1, PC 9, HC 16 and HC 20) showed nearly constant Mn concentration downcore (Fig. 4).

Solid phase Cu at the six sites (HC 1, HC 12, PC 9, HC 15, HC 16 and HC 20) showed near constant downcore concentration values (Fig. 4). With regard to the downcore trends in the concentration of solid phase Pb, the trend was erratic at sites HC 1, HC 12, HC 16 and HC 20, whereas constant downcore trends were observable at sites PC 9 and HC 15 (Fig. 4). At site HC 15,

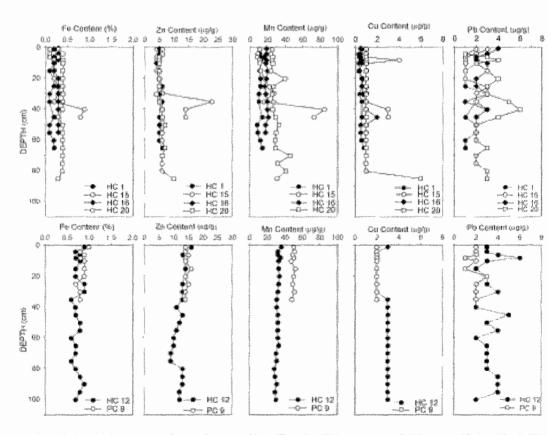


Fig. 4. Variations in the contents of trace elements of iron (Fe), zinc (Zn), manganese (Mn), copper (Cu) and lead (Pb) for sandy sites HC 1, HC 15, HC 16 and HC 20 (upper row) and muddy sites PC 9 and HC 12 (lower row)

the Pb values changed from  $1\mu g/g$  in the 0-35 interval to  $3\mu g/g$  below 35 cm in the sediment (Fig. 4). Highest concentration of Pb was observed at site HC 12 and HC 20 with mean values of  $3.26\pm1.01\mu g/g$  (n = 23) and  $2.95\pm1.19\mu g/g$  (n = 20) respectively.

The Fe contents showed near constant downcore trends at sites HC 1, HC 9, HC 16 and HC 20, and more erratic values at site HC 12 (Fig. 4). Furthermore, the Fe contents increased downcore changing from 0.1% at the surface to 0.8% at the bottom of the core at site HC 15 with a sharp change occurring at about 35 cm. (Fig. 4).

The concentration of Zn at site HC 12 showed a trend of downcore decrease from approximately 15µg/g at the surface to 9µg/g at about 80 cm, thereafter the values increases to about 13µg/g (Fig. 4). At site HC 15, the Zn concentration was nearly constant at 4.5µg/g from the surface to about 35 cm after which the concentration increased to approximately 17µg/g (Fig. 4). The Zn concentration at site HC 1, HC 9, HC 16 and HC 20 showed near constant values downcore (Fig. 4).

## DISCUSSION

## **Sources of Organic Matter**

Stable isotopes of OC and nitrogen as well as C/N ratio have been used separately, or in combination globally, to estimate relative proportions of terrestrial OM preserved in the aquatic environment, either at molecular level, or in bulk OM (e.g. Muzuka, 1999; Fernandes & Sicre, 2000; Oldenburg et al., 2000). The means of  $\delta^{13}$ C and δ15N values for all analysed cores fall within a narrow range of -18.9% to -19.6%, and 4.5% to 4.8% respectively, with the exception of core HC 1. The mean values of the two parameters for all analysed cores, particularly those of 13C, suggest that the organic material preserved in the studied nearshore sediments has a marine origin. A marine origin of the OM preserved in these coastal marine sediments on the west coast of the Unguja Island is further supported by the C/N ratio values. The C/N ratios are commonly used as source indicator because the C/N ratio values for unaltered phytoplanktonic material range from 4 to 10, while that of terrestrial organic material is higher than 12 (Meyers, 1994). This is further supported by the higher CaCO<sub>3</sub> content, which shows lack of dilution by siliciclastic material from land likely due to the absence of major rivers capable of transporting large quantity of terrestrial material.

Marine in situ sources of OM may include invertebrates and autotrophic organisms such as phytoplankton, macroalgae and sea grasses. The stable isotope compositions of invertebrates have a wide range of  $\delta^{13}$ C and  $\delta^{15}$ N (-27 to -16% and -6.6 to 12.3% with a mean of about -22% and 7% respectively) (Bouillon et al., 2002a,b) and reflect trophic levels. In the natural environment, there is enrichment in isotope composition of organic carbon and nitrogen by about 1% and 3% respectively between food source and consumer (e.g., Minagawa & Wada, 1984; Owens, 1987; Vander Zanden & Rasmussen, 2001). Thus, sediments being the source of food for many benthic invertebrates, enrichment in 13C and 15N for invertebrates relative to the sediments is anticipated. Although there is such a possibility for the invertebrates to contribute significantly to the preserved OM in the present study area, the result of nitrogen stable isotopes preclude this possibility.

The stable isotope compositions of nitrogen for marine phytoplankton have been shown to be higher than 6% (see Létolle, 1980 for review). Therefore,  $\delta^{15}$ N values falling in the range of 4.5% to 4.8% would indicate some terrestrial contributions contrary to the 13C data. Such discrepancy can be a result of higher relative proportion of OM derived from macro algae or fractionation owing to higher concentration of nutrients in coastal waters. The nitrogen stable isotope compositions of marine macrophytes, such as algae, range from 4%0 to 10%0 (Stephenson et al., 1984; Ostrom & Macko, 1992). Although Site HC I has isotope values lower than the globally reported δ<sup>15</sup>N values for macrophytes, it is possible that this was caused by nitrogen fixing bacteria. The <sup>15</sup>N result at site HC 1 is in agreement with globally reported isotopic composition of nitrogen for bacteria fixing atmospheric nitrogen, which has been observed to fall within a narrow range of -2 to 2‰ (Létolle, 1980; Gearing, 1988). Accordingly,

both data sets (<sup>13</sup>C and <sup>15</sup>N) reflect a marine origin with a significant contribution from macrophytes such as algae.

# **Preservation of Organic Matter**

As pointed out previously, the muddier sites (HC 2, PC 5, PC 9 and HC 12) had higher contents of OC, nitrogen, Mn. Fe, Zn and Cu relative to sandier sites (HC 1, HC 15, HC 16 and HC 20). This can be attributed to factors such as surface area /volume ratio of sediment grains, pH and Eh of the medium, etc. Generally, the accumulation of metals from the overlying water to the sediments is dependent on a number of environmental factors such as pH, Eh, ionic strength, anthropogenic input, the type and concentration of organic and inorganic ligands (molecules or ions surrounding the central metal ion), and the available surface area for adsorption caused by the variation in grain size distribution (Binning & Baird, 2001). Surface/volume ratio has been suggested to be responsible for preferential preservation of OM and enrichment (adsorption) of metals (Keil & Cowie, 1999; Binning & Baird, 2001). Finer particles have higher surface area/ volume ratios than coarse-grained sediments, and are likely to contain large amounts of OM and trace elements. Thus, the observed difference in the levels of OC and metals between sites with fine particles and those with coarser particles can be attributed to differences in surface/volume ratios and thus, different degree of binding capacity of OM and metals.

Lower contents of OC and nitrogen at site HC I could be related to the presence of coarse sediments and higher rates of oxygen supply resulting from tide fluctuations. This site most likely is affected by fluctuation in tides and thus in the level of oxygen penetration owing to its location in shallower (10.5 m) depth. Presence of a 3 cm long worm between 24 and 27 cm testifies that there is plenty of oxygen and the depth of bioturbation is wide. Several workers have pointed out that oxygen is a major factor controlling preservation of OM (e.g. Jennerjahn & Ittekkot, 1999). Accumulation of solid phase Mn and Fe takes place in oxic environment (Shaw et al., 1990; Calvert et al., 1993; Saulnier & Mucci, 2000), while accumulation of Cu and Zn occur in anoxic conditions (Calvert et al., 1993; Warning & Brumsack, 2000). Thus, low concentration of Cu and Zn at this site and all other remaining suggest that oxygen penetration is high and degradation of OM is through oxidation.

# Diagenetic Evolution

Distribution of diagenetically sensitive elements such as Fe, Mn, Pb, Zn and Cu in sediments may show oxic/anoxic fronts. Since Cu, Zn and Pb are charcophile elements, which are concentrated in sulphide deposits in the Earth's crust, it is expected that sediments deposited in anoxic environments will display higher enrichments of these elements. Therefore, low levels with essentially constant downcore distributions suggest that there is no formation of sulfide minerals and the diagenetic reactions for analysed sediments takes place in the presence of oxygen. High levels of Mn with a general lack of downcore decrease at sites HC 1, PC 9, HC 16 and HC 20 may be an indication that the diagenetic process is taking place in oxic condition in these coastal sediments.

An increase in the concentrations of Pb and Zn below 35 cm at site HC 15 can be attributed to a change from oxic to anoxic conditions. However, an increase in the concentrations of Mn and Fe at this site is contrary to the expected trend. Manganese and iron are enriched in oxic sediments in form of Mn (IV) and Fe (III) oxyhydroxides and are reduced and remobilised and then released as dissolved Mn (II) and Fe (II) into the pore water in anoxic condition. Because of this, solid phase contents of these two elements normally show a downcore decrease as the oxidation changes from oxic to anoxic conditions. Enrichment of these elements, particularly Mn at this site, that are reduced at early stages of suboxic reduction, could be a result of upward diffusion to the oxic-anoxic boundary followed by precipitation and adsorption of these elements to the sediments particles.

The contents of organic carbon and nitrogen observed in this study are generally lower relative to the mean values of 1.5% and 0.15% respectively for coastal areas that have little influence of anthropogenic input (Wollast, 1998). Furthermore, a downcore decrease in the contents of OC at sites HC 2, PC 9, and HC 12, as well as nitrogen at sites

HC 2 and PC 9 may be attributed to either diagenetic alteration of OM or changes in rates of fluxes of OM as a result of variability in primary productivity. Diagenetic alteration of OM is supported by a downcore increase in the C/N ratio values at sites HC 2 and PC 9. Since the level of oxygen seem to influence the rate of OM degradation, lower contents of OC in the coastal sediments west of Unguja Island can primarily be attributed to the diagenetic alteration of OM.

# CONCLUSION

Sedimentary OM off the Zanzibar town is generally of marine origin. This is an indication that there is limited transport of terrestrial based material to the coastal waters. Concentration of heavy metals is low relative to maximum permissible concentrations recommended by the National Institute of Public Health and Environment in the Netherlands (Crommentjuijn et al., 1997). This shows that although the sediments can be a potential sink and source of pollutants to the water column, coastal sediments off the west coast of Unguja Island are pristine with minimum human impact. However, the current population growth rate of the Zanzibar town and dumping practices of untreated municipal waste such as used batteries, scrap metals, etc to the ocean may enhance input of heavy metals. Deliberate actions are required to protect these pristine sediments by treating and reducing amount of municipal wastes introduced in the ocean.

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