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Anthropogenic impacts recorded in the sediments of Lunawa, a small tropical estuary, Sri Lanka

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Abstract The Lunawa Estuary has been selected as a model for studying the long-term diagnosis of tropical estuarine pollution and its impact on ecosystems. Surface and short-core sediments from the Lunawa Estuary were collected, and analyzed for total organic carbon (TOC), nitrogen, sulfur and hydrocarbon contents, hydrogen index and other related sediment properties. Water quality and surface sediment data indicate that the Lunawa Estuary is presently an anoxic water body. The upper part of the sediment cores, characterized by very high TOC values of more than 10%, and absence of bioturbation along with strong laminations indicate anoxic water since 1970 AD, determined by ^{14}C dating. However, before 1970 AD, lower TOC content and presence of bioturbation and homogenous sediments with animal traces suggest the presence of oxic bottom water and thus a much better physicochemical condition. The lower part of the cores may also suggest the influence of gradual global warming. Regular laminations in the upper portions of

the cores probably resulted from monsoon pulses with material preserved under anoxic condition.

Keywords Sri Lanka · Lunawa Estuary · Anoxia · Organic matter · TOC

Introduction

Estuaries are transitional zones between rivers and seas and are important ecosystems where oceans and rivers contribute to a specific biodiversity. They are important water bodies for human food sources and for recreational activities. They are also spawning grounds for

many marine organisms, including commercially important fish (Claridge et al. 1986). Unfortunately, for a long time, humans have considered estuaries as dumping sites partly because of disregard for the water quality of estuaries and partly because of the belief that tidal flushing may dilute and disperse the unwanted substances. However, when the limitations are exceeded,

ecosystems are badly affected. Recently, multiple negative ecological impacts, such as loss of biodiversity, harmful algal blooms and disease and declines in fisheries on these fragile habitats due to anthropogenic activity, have been documented (Paerl 1997; Conley 2000). Anthropogenic pollution has affected coastal areas especially in developing countries, e.g., Patos Estuary, Brazil, (Mirlean et al. 2003), Yalujiang Estuary, North China (Wu et al. 2003), due to the unplanned management of the environment. Estuaries in tropical South Asia especially are greatly affected by anthropogenic and global warming impacts.

The Lunawa Estuary in the southwestern coast of Sri Lanka is one of the most eutrophic estuaries in tropical South Asia, probably due to recent anthropogenic impacts. Commonly, an estuary deposits fine sediments and preserves a high resolution record of recent environmental changes in the sedimentary column. In addition, a small estuary such as the Lunawa Estuary with about 0.5 km² area is more sensitive to anthropogenic impacts. In this study, the authors seek to understand the present and the past eutrophication-pollution history of the biologically dead estuary and its high primary productivity system. The authors reconstructed the environmental changes using short sediment cores deposited approximately during the last 100 years, based on organic matter preservation, sedimentary structural

changes, grain size, saturated hydrocarbons and ¹⁴C dating.

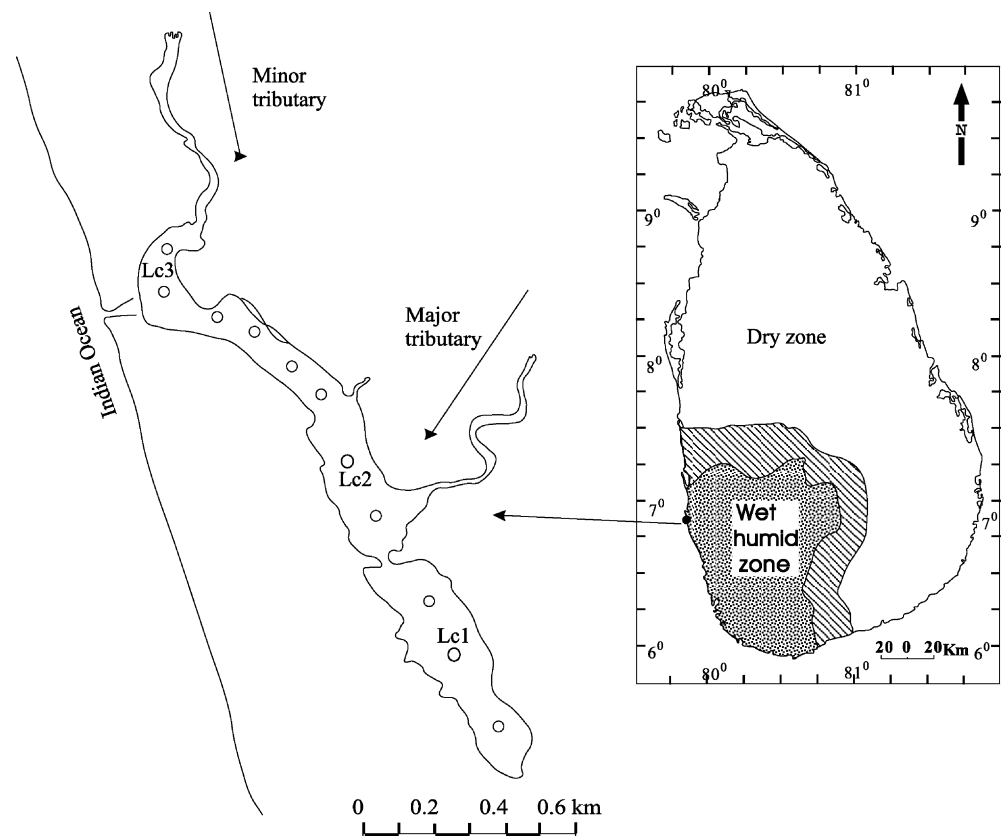
This paper documents the nature of human influence and certain natural changes that caused a gradual deterioration of the Lunawa Estuary and its biodiversity during the last 100 years and hopefully the general lessons learned through this study can be used to minimize similar problems elsewhere.

Study area and sampling

The Lunawa Estuary is on the western coast of Sri Lanka just 10 km south of Colombo. The Lunawa Estuary is fed by two tributary streams, which are almost dry except during rainy seasons. At present, the Estuary mouth to the sea is closed and the estuary stays stagnant. Natural closure of the sea mouth due to the build up of a spit bar by drift currents has completely stopped replenishment of estuary water with a fresh daily supply of saline water circulated by tidal currents. Although it has not been suggested previously, this estuary could have been a former river, which changed its course, abandoning the present estuary as its main channel.

Figure 1 shows stations where surface and core sediment sampling and water quality measurements were

Fig. 1 Sampling stations at the Lunawa Estuary, situated at the wet humid zone of Sri Lanka. Two short cores were collected at stations LC1 and LC2. Water quality was measured and surface sediment samples were collected at all the locations



performed. The main phase of the sampling was performed in March 1997 and an additional phase of sampling was performed in August 1998 to obtain a tentative knowledge about the seasonal variations. During April, Lunawa area had dry weather while in August there were thunderstorms.

Using a Water Checker U-10 (Horiba Ltd.), vertical changes of salinity and dissolved oxygen (DO) were measured at 50-cm intervals from surface to bottom in both seasons at all the stations. Surface sediment samples were collected using a Birge–Ekman type grab sampler. Two shorter core samples (about 50–75 cm) were also collected using a gravity corer. When selecting core sites, the locations with finer grain size and greater depths were given priority. Immediately after sampling, core samples were carried carefully to the laboratory of Peradeniya University without disturbing the top layer and they were cut into two halves across the cylindrical axis of the core and placed in a 1-cm thick profile in plastic transparent cases to make X-ray photographs. The remainder of the samples was also cut into 1-cm portions down the core. Then, the samples from one side was used for grain size analysis and microscopic observations, and the other side was pulverized and homogenized to less than silt size and used for quantitative and qualitative organic matter analysis.

Analytical methods

C, H, N, S elemental analyzer

Total organic carbon (TOC), total nitrogen (TN) and total sulfur (TS) percentages were determined by a combustion method with a FISON (Carlo Erba) 1108 elemental analyzer, at a combustion temperature of about 1,000–1,300°C. Samples were ground to fine powders and dried for several hours at 110°C prior to analysis. Before analysis, 10 mg of samples were placed in a silver film; a few drops of 1M HCl were added to remove inorganic carbon; and then dried at 100°C for 45 min and placed into a tin film cup. BBOT [2,5-bis (5-*tert*-butyl-2-benzoxazolyl) thiophene] was the standard used, and regression analysis was the method employed for quantitative analysis. All the elemental percentages were on a dry weight basis. The inherent error for this analysis was $\pm 3\%$ for TOC and TN while TS had $\pm 4\%$ error range.

X-ray photography

A Super Soft X-ray apparatus (SOFTEX) was used to take X-radiograph photos of vertical cross sections of all the cores to determine the presence of lamination and other structural variations.

Grain size analysis

Using a Laser Diffraction Particle Size Analyzer SEI-SHIN-KIGYO PRO OP2 (range 0.1–192 μm), median diameter of sediments was measured. About 1 g of wet sediments was used for this analysis, after treating with 10% hydrogen peroxide (H_2O_2) for 7 days to remove organic matter.

Extraction of geolipids

Organic matter was extracted from the sediments using the soxhelt extraction technique, refluxing for 24 h using benzene:methanol 9:1 solution. Copper granules were added to remove sulfur. Fractionation of extractable organic matter was carried out using a thin layer chromatography (Silica gel 60 PF₂₅₄ containing gypsum, for preparative layer chromatography and hexane as the mobile phase) and using UV light alkanes were identified from the rest of the geo-lipids. The alkane fraction was separated after washing with benzene–methanol solution (9:1). Extracted alkanes were directly used for gas chromatographic (GC) analysis.

Gas chromatographic analysis

Gas chromatographic analysis was done employing GC-14A (SHIMADZU) equipped with a fused silica capillary column (30 m \times 0.32 mm), and a SPL-14A splitless sample injector with helium as a carrier and hydrogen as makeup gases. The oven temperature was increased from 50°C to 300°C at 8°C min⁻¹. Samples were run for 65 min and a flame ionization detector was used for the detection. The *n*-alkanes were identified and quantified by GC using authentic standards. Peak heights were compared along with standard peak height to quantify the desired *n*-alkanes.

¹⁴C dating

A small plant fragment from the Lunawa Estuary (LC1–20) at 20 cm depth was dated using accelerated mass spectrometry (AMS) in the Beta analytical radiocarbon dating laboratory, USA.

Rock eval pyrolysis

Rock eval pyrolysis was performed for 22 samples from core LC2 using a ROCKEVAL 2/T.O.C instrument. The amount of hydrocarbons (mg HC/g rock) released from kerogen during gradual heating in a helium stream is normalized to TOC to give the hydrogen index (HI).

Results

Water quality and surface sediments

Estuary water was extremely turbid with a slight brown color and a feeble H_2S smell. During the first field session, in early March 1997, the lake water oxygenation was very poor and even surface water (0–10 cm depth) in the southern basin had very low dissolved oxygen content (0.4–1.2 mg/l) (Fig. 2). However, toward the sea mouth which is presently closed, oxygenation of surface water was much better (4–5.5 mg/l). The bottom water had very low dissolved oxygen levels (<0.1 mg/l) in all the sampling stations. The marked anoxic bottom water condition was also observed again in the second field session, on August 1998, in spite of thunderstorms; usually during August this humid area of the country (Figs. 1, 2) receives heavy rain due to the southwestern monsoon. Vertical salinity measurements at all the stations show major change at about 1 m depth from salinity around 10 PSU at the top to around 30 PSU at the bottom, during the 1997 field session; and from around 2 PSU at the top to 30 PSU at the bottom, during the 1998 field session. Vertical changes of temperature during both these periods did not show marked

thermal stratification. Surface sediments were black in color with a strong smell of H_2S . There was no living or non-living epifauna or infauna, or any other indications of animal traces in the lake bottom surface, except at the site (LC2) downstream of the main stream mouth which had some gastropod shells. TOC content in surface sediments varied from 1.4% to 12.4% with an average of 11.0% (Fig. 3). TOC content was relatively lower ($\sim 2.5\%$) at the major stream mouth (LC2) and sea mouth (LC3) where the sediments were somewhat sandy silt. TN content varied from 0.1% to 0.8% (Fig. 3). The surface sediments had high C/N ratios ranging from 14 to 31.5 (Fig. 3). The high values were recorded at the northern basin (~ 20) compared to the southern basin (~ 15). At the southern basin TS content was 5–6% and in the northern basin it was 1.5–4% (Fig. 3).

Sediment core

The X-radiograph from the gravity cores revealed regular millimeter scale laminations (alternative dark and light color) in the upper portion of both the cores and a homogenous sediment layer at the bottom (Fig. 4). These laminated parts were 20-cm thick in the core LC2, but, 12-cm thick in the core LC1. The upper portion of both the cores had a strong smell of H_2S , while neither cores had any fossils nor any signs of bioturbation in the laminated parts. The lower portion had many bivalves and gastropod shells and other

Fig. 2 Vertical changes of salinity, dissolved oxygen and temperature at stations LC1, LC2, and LC3 during March 1997 and during August 1998 of the Lunawa Estuary

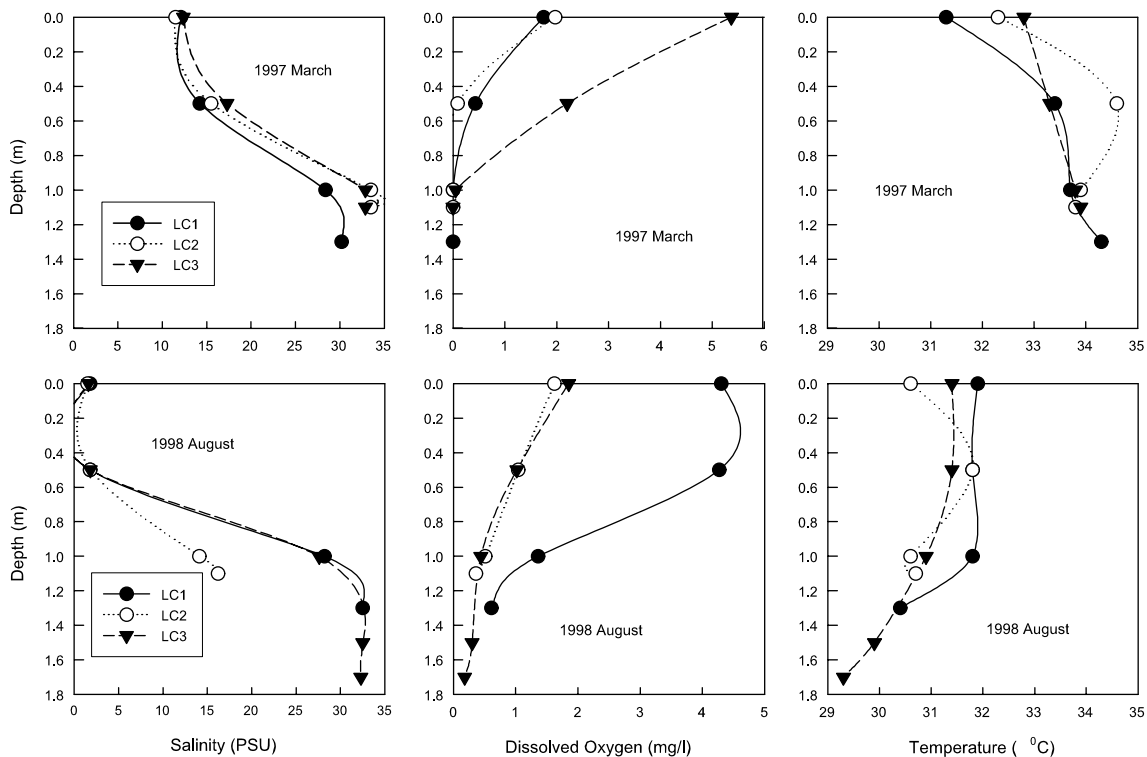
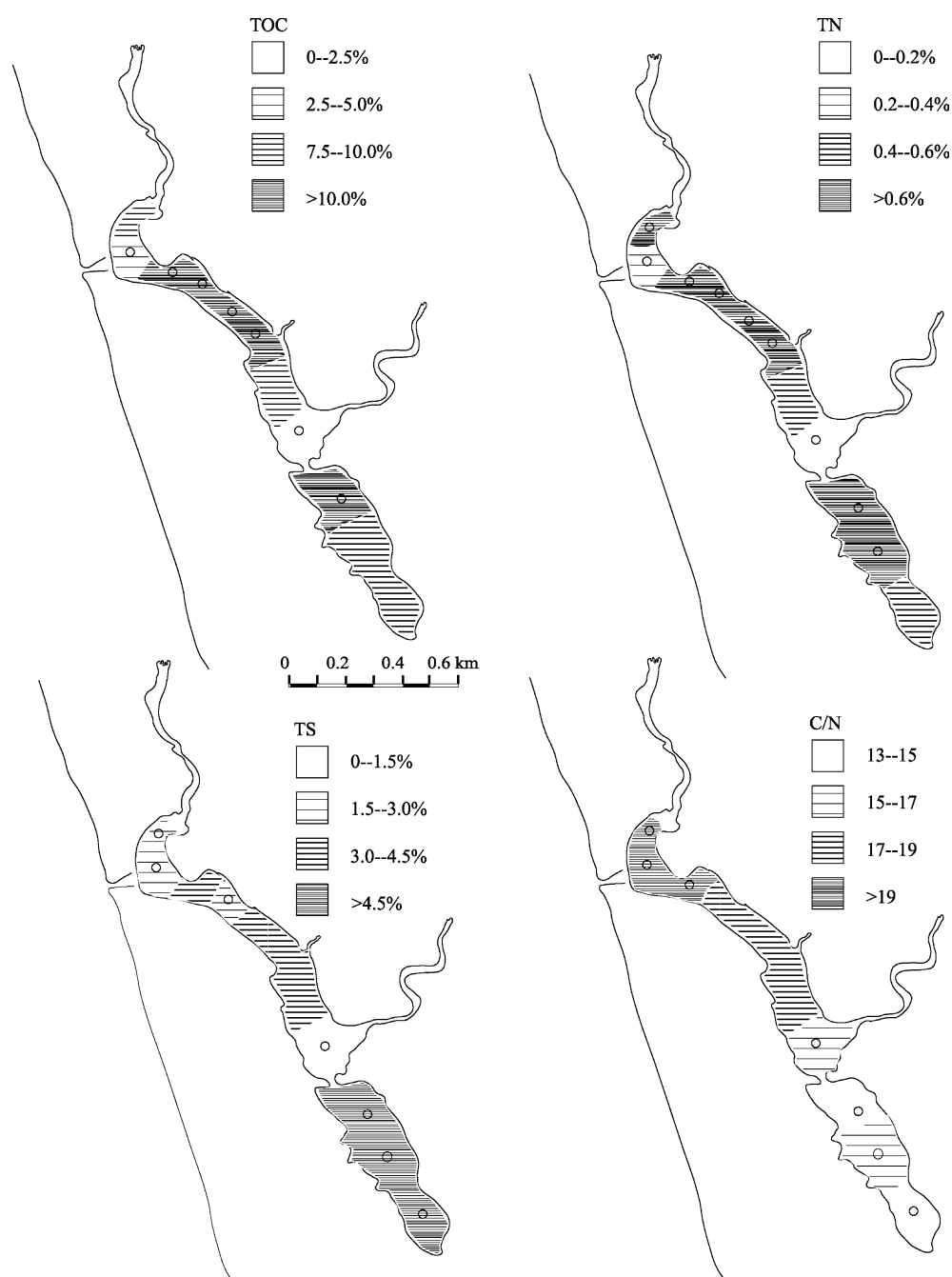


Fig. 3 Surface distribution of total organic carbon (TOC), total nitrogen (TN), C/N ratio and total sulphur of the Luna-wa surface sediments



bioturbation features such as borrowing. Both cores consisted of clay to very fine silt (LC1 range 3.5–6.3 μm ; LC2 range 3.2–4.6 μm ; Fig. 5) and Core LC2 shows a slight increase in grain size toward the surface. Core LC1 shows a fairly consistent sedimentation rate during the lamination zone and the bioturbated zone compared to core LC2, as grain size variation was very small in core LC1 (STDV=0.4) compared to core LC2 (STDV=1.0). A plant fragment from core LC1 (depth 20 cm) was dated by ^{14}C using (AMS) to calculate the

average sedimentation rates and to extrapolate calendar ages to possible historical ages, recorded in the sedimentary cores. The plant material at 20 cm depth (LC1–20) dated $106 \pm 5\%$ compared to the modern standard NBS Oxalic Acid (Beta-129483) was converted to 1950–1960 AD calendar years according to Kigata et al. (1991) by calibration curves of radiocarbon ages. As the LC1 core did not show significant grain size variation (within small 3–4 μm) consistent sedimentation was assumed for the upper part at the

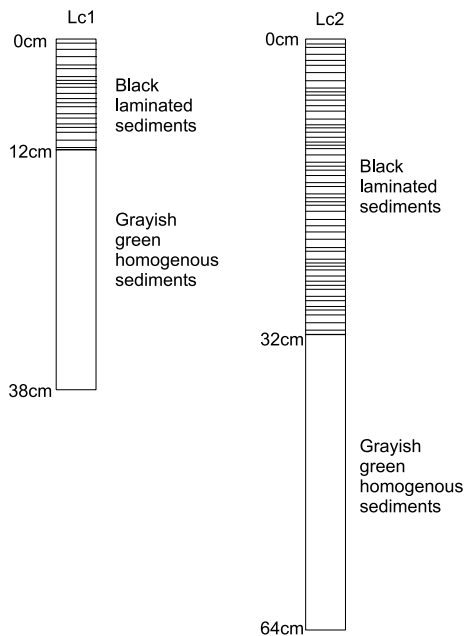


Fig. 4 Lithology and sedimentary structures of LC1 and LC2 cores of the Lunawa Estuary. No fossils or bioturbation were found in the laminated sections

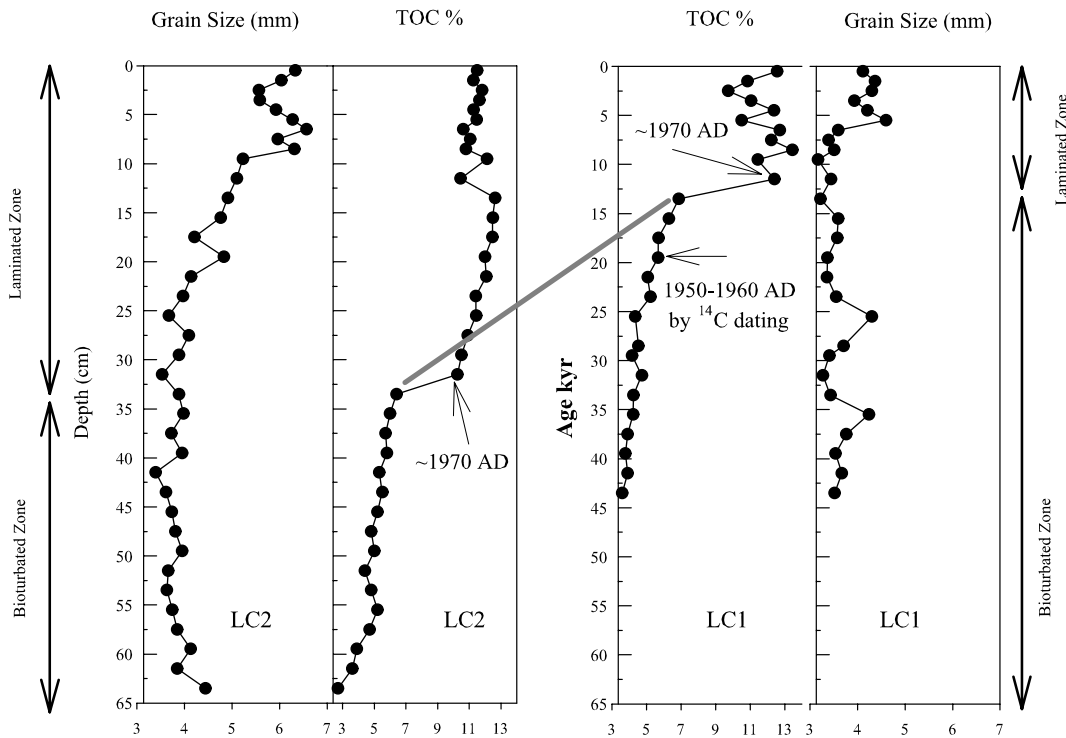
depth of 20 cm (average sedimentation rate is 4.7 mm/year).

The laminated upper zone of core LC2 was characterized by very high TOC (Fig. 6), ranging from 10.3% to 12.7% (mean 11.4%), and high C/N ratios ranged from 18.1 to 23.4 (mean 20.4). TOC in the bioturbated section of core LC2 ranged from 2.7% to 6.4% (mean 4.9%) and C/N ranged from 22.2 to 23.2 (mean 22.4). Organic material preservation was very much higher in the laminated zone than in the bioturbated zone. However, C/N ratio showed a very slight increase to the bottom part of the core LC2 ($\sigma = 1.4$).

The *n*-alkane chromatograms were characterized by unresolved complex mixture (UCM) throughout the core, and the concentrations of *n*-alkanes were clearly enriched within the laminated zone ranging from 67.4 mg/g C to 99.5 mg/gC (mean 78.7 mg/g C) and depleted in the bioturbated zone ranging from 33.3 mg/g C to 58.4 mg/gC (mean 44.3 mg/g C). Carbon preference index (CPI) shows very low values at the laminated zone ranging from 1.2 to 1.5 (mean 1.2), while high values at the bioturbated zone ranged from 2.3 to 2.1 (mean 2.1). Also, the long to short *n*-alkane ratio (H/L) shows similar variations in which low H/L ratios at the laminated zone ranged from 0.7 to 1.1 (mean 0.9) and higher ratios at bioturbated zone ranged from 2.3 to 1.8 (mean 2.0).

Fig. 5 Vertical distribution of grain size and TOC of LC1 and LC2 cores of the Lunawa Estuary. A plant fragment from core LC1 (depth 20 cm) was dated by ¹⁴C using accelerated mass spectrometry (AMS)

Hydrogen Index (HI) calculated from the Rock Eval Pyrolysis shows hydrogen richness in the laminated zone ranging from 215 to 258 (average 238) compared to 146 to 213 in the bioturbated zone (mean 188).



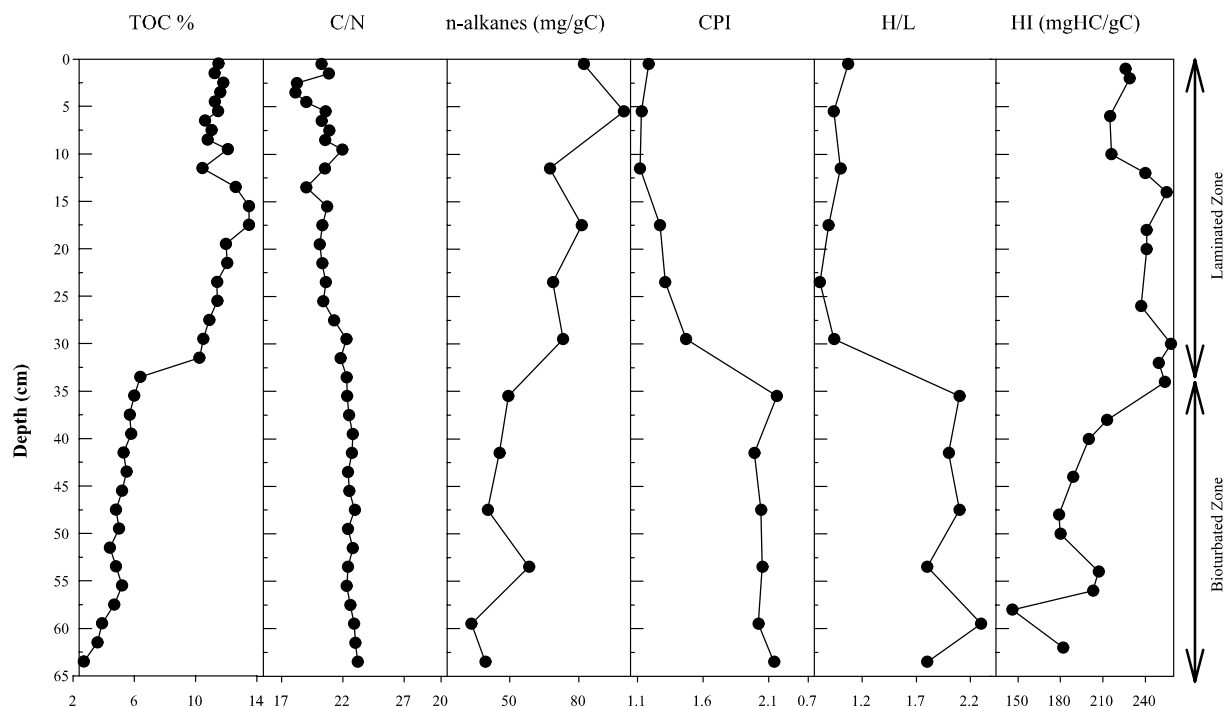


Fig. 6 Vertical changes of TOC, C/N ratio, concentration of n-alkanes, CPI, H/L ratio and HI of core LC2 of the Lunawa Estuary

Discussion

Present condition of the estuary

Major changes of salinity below 1 m depth during both seasons show Lunawa water column has a permanent halocline. As the estuary is presently closed, intense evaporation during the dry season results in sinking of heavier brackish water, forming a strong halocline and making the bottom water sluggish and stagnant. With increasing rainfall, river water supply increases and surface water become less and less saline as observed in the field session in August. Furthermore, low dissolved oxygen and the presence of H_2S in the water column at present show euxinic conditions below the halocline (Fig. 2). Although there is a well-known euxinic deep bottom water that prevails in the Black Sea (Buesseler et al. 1991; Anderson et al. 1994), such a very shallow lake with permanent euxinic bottom conditions as in the Lunawa Estuary is unusual. Even above the halocline, dissolved oxygen is very poor probably because of the oxidation of H_2S seeping from the bottom. As the Lunawa Estuary is very shallow, one can expect quick replenishment of oxygen by wind mixing. However, due to stagnation caused by water stratification, sea mouth closure and surrounding forest cover, wind mixing is minimal. Except for the station in front of the river mouth where several shells were found on the surface

layer, benthic organisms cannot live in the present Lunawa Estuary under such euxinic conditions.

Alwis et al. (1994) showed that the Lunawa Estuary receives many nutrients (NO_3^- 2.6 ppm, and PO_4^{3-} 0.26 ppm) and some organic wastes from industrial and domestic sources. Accordingly, a higher primary productivity by phytoplankton is expected in the water body. However, C/N ratios of more than 15 with an average of 16.7 of the surface sediments suggest a predominance of vascular higher plants, considering C/N ratios around 20–80 for terrestrial higher plants (Meyers and Isiwatari 1993) and 6–9 for aquatic plankton (Hedges et al. 1986). The origin of the vascular plant in the Lunawa sediments could be largely owing to submerged plants, which cover a considerable area of the Lunawa Estuary. Higher TOC contents (>10%) of the Lunawa surface sediments could be mainly from the deposition of these submerged plants preserved under anoxic bottom conditions.

Environmental changes after anthropogenic impact

The history of the depositional environment in both LC1 and LC2 cores can be divided into two major subdivisions (LC2: 0–32 cm and 32–64 cm; LC1: 0–12 cm and 12–38 cm) based on TOC contents and sedimentary structure (e.g., laminations; Fig. 4). The upper zone is characterized by higher TOC (10.3–12.7%) and TN (0.45–0.7%) contents, lower CPI (1–1.4) and H/L ratios (0.8–1) along with the absence of bioturbation while the lower zone is characterized by moderate TOC

(3–6%), TN (0.1–0.3%) contents, along with high CPI (2–2.1) and H/L ratios (1.8–2.1). The absence of extensive burrowing by animals within sediments in the upper part of the core has been a longstanding premise that guides the interpretation of anoxic records (Savrda et al. 1984). Prolonged exposure to anoxia killed most benthic organisms and fish from the Lunawa Estuary.

The upper 32 cm portion in the LC2 core can be correlated to the upper 12 cm in the LC1 core, considering major changes of TOC, lamination, and the related data. In the LC1 core, the depositional age of 20 cm depth is 1950–1960 AD based on ^{14}C dating and the historical reports in Sri Lanka (Alwis et al. 1994). Therefore, the age of the sediments at the 32 cm depth portion in the LC2 core is calculated to be 1967–1977 AD and the age of the bottom (65 cm) of the core is to be 1908–1918 AD, assuming a similar sedimentation rate of 4.7 mm/year. Historical records confirm recreational and fishing activity until the 1970s in the Lunawa Estuary (Johnson and Scrivenor 1981) further confirming the accuracy of the measured ^{14}C dating. Based on these data, environmental history of the Lunawa Estuary can be divided into pre-1970 period, during which the anthropogenic impacts were sub-ordinate, and post-1970 period, during which anthropogenic impacts were dominant.

In the LC2 core, CPI shows a significant upward decrease (~ 1) from 32 cm depth, and similar decreasing trend can also be seen in the vertical change of H/L ratio. CPI and H/L ratios close to 1 can be due to contamination by anthropogenic petroleum wastes (Peters and Moldowan 1993), higher matured organic matter (Bray and Evans 1961) or high planktonic and bacterial productivity. Increase in maturity of organic matter would not be significant in these shallow sedimentary cores that were subjected only to early diagenetic modifications. CPIs in marine bacteria and algae, which contain short chain *n*-alkanes ($< \text{C}_{20}$), range from about 1 to 1.5 (Volkman et al. 1980; Nichols et al. 1988), that is closer to the observed values in the upper portion of the LC2 core. However, a gradual decreasing trend upward in C/N ratio suggests only a small increase in planktonic and bacterial productivity. Therefore, influence of anthropogenic petroleum wastes seems to be significant in the laminated upper portion. Moreover, in the upper part, a significant presence of UCM in the *n*-alkanes, which is one of the markers of biodegraded petroleum (Peters and Moldowan 1993; Demaison and Moore 1980), compared to the homogenous lower part support this interpretation on the anthropogenic impact. Usually highly biodegraded petroleum residues have a CPI or H/L ratio closer to 1.

Even though the influence of petroleum waste is inferred, as discussed above, moderate rather than high values of HI (220–250 mgHC/gC) in the upper part of the core indicates that the major reason for significant increase of TOC from 32 cm upward in the core LC2

cannot be due only to anthropogenic petroleum wastes. As shown in the surface sediment, the primary production of the submerged plants seems to have increased by the higher inflow of nutrients after 1970 AD contributing largely to the organic matter in the pool. Increase of anthropogenic nutrients has increased the productivity of the submerged plants, and deposition of these plants made the bottom water anoxic (Pedersen and Calvert 1990). However, due to increase in nutrient supply, plankton production might also have increased. The anoxic condition was also suggested by the increased HI from 140 to 210 mgHC/gC under 32 cm (1970 AD) in the LC2 to 220–250 mg HC/gC over the 32 cm. HI mgHC/gC is an indicator for oxic/anoxic conditions (Bechtel et al. 2002) as well as for organic type and hydrocarbon generation potential (e.g. Espitalie et al. 1984).

Alwis et al. (1991), suggested, based on documentation, that the Lunawa Estuary fish productivity had severely diminished since 1970 AD because dumping of industrial and domestic wastewater into the estuary had begun due to the establishment of several industries followed by urbanization in the watershed. This coupled with the sea mouth choking due to deposition of sand, changed the estuary environment. Industrial and domestic wastes, most probably rich in nutrients could have caused a sudden increase of primary productivity. In the meantime, the increase of choking completely shut the sea mouth making the estuary stagnant. The environmental crisis in the Lunawa Estuary, resulting from the anthropogenic forcing and accompanied by natural variability, is manifested by dramatic changes of the ecosystems. Before the industrial impact, tidal flushing could have diluted and dispersed organic wastes and the nutrient contents, thus reducing the biological oxygen demand.

The regular millimeter scale laminations at the upper portion of core LC1 and core LC2 probably resulted from monsoon pulses of material preserved under anoxic conditions. These areas have two regular rainy seasons: southwestern monsoon during May to September and northwestern monsoon during December to February. Even though, present analytical resolution is not ideal to understand millimeter scale lamination, careful observation shows darker layers are characterized by finer grains than the whiter layers. Rainy seasons were characterized by coarser grains while the dry season was characterized by finer grain size.

Environment before anthropogenic impact

Both LC1 and LC2 cores, before the 1970 period, were characterized with moderate TOC (3–6%), TN (0.1–0.3%), along with high CPI (2–2.1) and H/L ratios (1.8–2.1). Therefore, anthropogenic influence before 1970 AD was insignificant. A gradual increasing trend of TOC

and TN content from the bottom of the LC2 (since 1860 AD) up to 1970 AD, may imply a gradual increase of primary productivity under natural climatic conditions. This might have occurred due to the increased rainfall bringing more nutrients with global warming after the Little Ice Age.

Conclusions

Anthropogenic forcing and natural variability have caused a gradual deterioration of the Lunawa Estuary since the 1970s depriving the local community of its livelihood. The present study clearly shows the existence of anoxia since 1970 due to multiple effects: the presence of a strong halocline, stagnation, sea mouth closure, high primary productivity coupled by input of waste water with petroleum that had increased nutrient supply, transforming the estuary into a eutrophic water body. However, prior to 1970, the water body was much better with significant biodiversity.

Depositional history of Lunawa Estuary was clearly different from before and after 1970s. Higher TOC (10–12%) and TN (0.45–0.7%) contents, and lower CPI (1–1.2) and H/L ratios (0.8–1) along with the presence of laminations were characteristic features of the sediments deposited after 1970 compared with the pre-1970 period. Both low CPI and H/L ratios of *n*-alkanes of the cores in the post-1970 period show contamination by anthropogenic petroleum wastes and/or increase of planktonic

productivity. However, major TOC increase, was due to an increased primary production of the submerged plant due to greater supply of anthropogenic nutrients, resulting in bottom water anoxia. Before 1970 AD, sediments were characterized by low TOC (3–6%) and TN (0.1–0.3%) contents, along with high CPI (2–2.1) and H/L ratios (1.8–2.1) indicating lesser anthropogenic influence, lower abundance of submerged plant and a moderate planktonic productivity. A gradual increasing trend of TOC and TN contents during this period may imply a gradual rainfall increase probably due to global temperature rise.

The Following remedial measures are necessary to rectify the condition in the Lunawa Estuary although it may take a long period to become a biodiversity-rich, healthy aquatic system: dredging of the estuary and removal of bottom sediments which are possibly contaminated; making arrangements to provide industrial waste treatment facilities; and removal of the sand bar regularly for flushing and breeding of fish and prawn species.

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References

- Alwis PD, Ariyaratna S, Azmy SAM, Dassanayake NH (1994) Environmental pollution and its impact on the fishery management: Lunawa Estuary. Sri Lanka Information 8:1–15
- Anderson RF, Lyons TW, Cowie GL (1994) Sedimentary record of a shoaling of the oxic/anoxic interface in the Black Sea. *Mar Geol* 116(3–4):373–384
- Bechtel A, Gratzner R, Püttmann W, Oszczepalski S (2002) Geochemical characteristics across the oxic/anoxic interface (*Rote Fäule* front) within the Kupferschiefer of the Lubin-Sieroszowice mining district (SW Poland). *Chem Geol* 185(1–2):15
- Bray EE, Evans ED (1961) Distribution of *n*-paraffin as a clue to the recognition of source beds. *Geochim Cosmochim Acta* 22:2–9
- Buesseler KO, Livingston HD, Casso SA (1991) Mixing between oxic and anoxic waters of the Black Sea as traced by Chernobyl cesium isotopes. *Deep Sea Res I* 38 (Suppl):725–745
- Claridge PN, Potter IC, Hardisty MW (1986) Seasonal changes in movements, abundance, size composition and diversity of the fish fauna of the Severn Estuary. *J Mar Biol Ass UK* 66:229–258
- Conley DJ (2000) Biogeochemical nutrient cycles and nutrient management strategies. *Hydrobiologia* 419:87–96
- Demaison GJ, Moore GT (1980) Anoxic environments and oil source bed genesis. *Am. Assoc Pet Geol Bull* 64:1179–1209
- Espitalie J, Senga Makadi K, Trichet J (1984) Role of the mineral matrix during kerogen pyrolysis. *Org Geochem* 6:365–382
- Hedges JI, Clark WA, Quay PD, Richey JE, Devol AH, Santos UdeM (1986) Compositions and fluxes of particulate organic material in the Amazon River. *Limnol Oceanogr* 31:717–738
- Johnson BLC, Scrivenor MLeM (1981) Sri Lanka: land, people and economy. Heinemann Educational Books Ltd., London, pp 145
- Kigata Y, Morishita H, Yonenbe Y, Hattori Y (1991) ¹⁴C concentration in tree trunks. *Seminars in researches using AMS at Nagoya University (IV)*, pp 88–93
- Meyers PA, Ishiwatari R (1993) The Early Diagenesis of organic matter in lacustrine sediments. In: Engel MH, Macko SA (eds) *Organic geochemistry principles and applications*. Plenum, New York, pp 1–17
- Mirlean M, Andrus VE, Baisch P, Griep G, Casartelli MR (2003) Arsenic pollution in Patos Estuary estuarine sediments, Brazil. *Mar Pollut Bull* 46(11):1480–1484
- Nichols PD, Volkman JK, Palmisano AC, Smith GA, White DC (1988) Occurrence of an isoprenoid C₂₅ diunsaturated alkene and high natural lipid content in Antarctic sea-ice diatom communities. *J Phycol* 24:90–96

-
- Paerl HW (1997) Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as new nitrogen and other nutrient sources. *Limnol Oceanogr* 42:1154–1165
- Pedersen TF, Calvert SE (1990) Anoxia vs. productivity: what controls the formation of organic carbon-rich sediments and sedimentary rocks? *Am Assoc Pet Geol Bull* 74:454–466
- Peters KE, Moldowan JM (1993) *The biomarker guide: interpreting molecular fossils in petroleum and ancient sediments*. Prentice-Hall, New Jersey
- Savrda CE, Bottjer DJ, Gorsline DS (1984) Development of a comprehensive oxygen-deficient marine biofacies model: evidence from Santa Monica, San Pedro, and Santa Barbara Basins, California Borderland. *Am Assoc Pet Geol Bull* 68:1179–1192
- Volkman JK, Johns RB, Gillan FT, Perry GJ (1980) Microbial lipids of intertidal sediment, I, Fatty acids and hydrocarbons. *Geochim Cosmochim* 44:1133–1143
- Wu Y, Zhang J, Zhu Z (2003) Polycyclic aromatic hydrocarbons in the sediments of the Yalujiang Estuary, North China. *Mar Pollut Bull* 46(5):619–625