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RESEARCH ARTICLE

Geochemical contamination in the Densu Estuary, Gulf of Guinea, Ghana

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Abstract

Chemical contaminants are released from mining, domestic and industrial effluents into an aquatic environment. Sediments (n = 10) were collected with an Eckman grab at ten stations in the Densu Estuary for ecological risk assessment. The spatial distribution of organic characteristics and ecological risk of metals—zinc, lead, copper, mercury, iron, and manganese in sediment—were analyzed using standard methods. The organic parameters occurred in the ranges, as follows: % C, 0.76 to 2.05, % TN, 0.06 to 0.015; % TP, 0.44 to 1.38; and C/N, 12.31 to 34.81. The ranges of metal concentrations (mg/kg) were as follows: Fe, 201.10 to 720.90; Mn, 40.10 to 152.70; Zn, 7.3 to 158.3; Pb, 1.9 to 84.7; Cu 3.4 to 23.0; and Hg, 0.01 to 0.05. The mean concentration of metals in the sediment were Fe > Mn > Pb > Zn > Cu > Hg. The highest mean concentration of Fe suggested redox conditions in the Densu Estuary. There is a low contamination factor (CF) for five metals (Zn, Hg, Fe, Cu, and Mn) (CF < 1) to high contamination of Pb ($3 < CF \leq 6$). The average Pb concentration was above local and geological backgrounds, suggesting an anthropogenic source of pollution from industrial and domestic effluents and agrochemicals. The sediment was extremely enriched by Pb (EF > 50) with a positive index of geoaccumulation ($0 < Igeo \leq 2$) than other metals. There is considerable to a very high degree of contamination (DC) ($3 \leq DC \geq 6$) of metals in the sediment of Densu Estuary. The potential ecological risk index (≤ 40 PERI < 80) suggested a very low to moderate ecological risk of metal pollution. The study provides baseline knowledge on geochemical contamination in tropical estuarine systems for the development of effective chemical control strategies towards sustainable management of coastal waters.

Keywords Metal pollution · Potential ecological risk index · Densu Estuary · Gulf of Guinea

Introduction

Uncontrolled population growth, rapid urban development, and rapid industrialization along the coastal areas in Ghana have led to coastal pollution because of anthropogenic inputs such as sewage effluents, municipal waste discharges, and runoff from agricultural and mining activities into the aquatic environment (Armah et al. 1997; Fianko et al. 2007; Monney et al. 2013; Mahu et al. 2015). Estuaries act as major carriers and sources of materials including sediment, metals, and organic pollutants and as areas of accumulation and transport from fluvial sources to the deep sea (Förstner and Wittmann 1981; Hatje et al. 2001; Biney and Asmah 2010). Sediments are good environmental indicators because they act as sinks and sources for various contaminants in the aquatic ecosystem (Salomons et al. 1987; Salati and Moore 2010; Kumar et al. 2011; Botwe et al. 2017; Islama et al. 2018). Sediments also act as permanent records of anthropogenic pollutants inputs and also play an important role in the assessment of ecological risk (Balls et al. 1997; Soares et al. 1999; Grosheva et al. 2000; Mahu et al. 2015).

Heavy metal pollution in aquatic ecosystems is a global environmental problem (Brannon et al. 1980; Demirak et al. 2006; Yan et al. 2016). Heavy metals are among the most persistent pollutants in water, sediments, and biota (Pate et al. 1985; Mucha et al. 2003; Santos et al. 2005; Zhang et al. 2009). Metals such as copper (Cu), iron (Fe), zinc

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(Zn), and manganese (Mn) are essential micronutrients needed for the functioning of the biological systems (Sekabira et al. 2010; Nogueirol and Alleoni 2013; Naggar et al. 2018); however, at certain thresholds and in certain redox and organic chemical interactive forms such as methyl mercury, they become toxic (Soares et al. 1999) and can cause ecological damage (Biney et al. 1994; Ruilian et al. 2008; Salati and Moore 2010). Other elements such as lead (Pb) and mercury (Hg) are toxic, thus necessitating regular monitoring of sensitive aquatic environments for these elements (Peerzada et al. 1990). Studies on metal pollution in sediments from tropical coastal systems are still scarce (Biney et al. 1994; Nyarko and Evans 1998; Biney and Asmah 2010; Mahu et al. 2015; Klubi et al. 2018).

The Densu Estuary lies between latitudes 5° 30′ N and 5° 31′ N and longitudes 0° 18′ W and 0° 20′ W in the Gulf of Guinea, Ghana. The Estuary takes its source from the Densu River and drains into the Gulf of Guinea in the Atlantic Ocean (Hagan et al. 2011; Attua et al. 2014). The Densu River has a total length of 116 km and a total catchment area of 2564 km^2 (Debrah 1999). The basin is endowed with tributaries and sources from the Atiwa Mountains, where there are mining and agricultural activities (WRI 2003; Fianko et al. 2009; Attua et al. 2014). The Densu Estuary is located in an industrial area and receives organic and inorganic contaminants and discharges from different anthropogenic sources (Debrah 1999; Osei et al. 2010; Denutsui et al. 2011). There are intensive industrial, agricultural, and mining activities surrounding the catchments of the Estuary with associated wetlands and mangrove systems serving as sink and source of contaminants (Osei et al. 2010; Denutsui et al. 2011; Addo 2017). The Densu Estuary is an important socio-economic coastal resource because of its fishery and wetland resources (Addo 2017). Chemical contaminations might affect ecosystem function, biota, and human health via transfer in the food web (Nyarko and Evans 1998; Nyarko et al. 2014; Addo 2017; Naggar et al. 2018).

The study was carried out to (i) evaluate the spatial distribution of sediment organic characteristics (organic carbon, total nitrogen, total phosphate, and organic matter); (ii) assess the concentrations of metals (lead, zinc, copper, mercury, iron, manganese, cadmium, and arsenic), degree of contamination and their potential ecological risk; and (iii) identify sources of chemical contaminants in the sediment of the Densu Estuary. The preliminary chemical data provide useful information for policymakers to develop chemical pollution control strategies towards a sustainable healthy estuarine environment.

Sampling and analytical methods

Sampling

The Densu Estuary stretches from Gbegbeyise to Tsokome near Botianor and has its outlets towards the west (Hagan et al. 2011; Attua et al. 2014). Sampling was carried out from land to sea. The land is characterized by intensive human activities such as waste disposal, farming, fishing, and many more, while less impacted areas were towards the sea. The sediments were sampled from ten randomly selected stations (S1 to S10) to assess environmental quality along the stretch of Densu Estuary, which drains into the Gulf of Guinea, Ghana (Table 1; Fig. 1). The surface sediment samples were obtained using an Ekman grab sampler, approximately 0.04 m^2 in the area (Hakanson 1986; Blomqvist 1990). The sediment is characterized by brownish, fine gray to dark muddy color. The surface layer (10–15 cm) was retained for the analyses because this layer controls much of the exchange of metals between sediments and waters and constitutes a reservoir of metals to which benthic organisms are exposed (Nasr et al. 2014). The sediment samples were stored wet in clean zip-lock bags, sealed, kept in ice (− 4 °C), and then transported to the laboratory for analysis. The sediment was sampled in the rainy season, 2017. The coordinates for each station were recorded using a handheld Global Position System (Garmin eTrex 10 Model) (www.garmin.com).

Analytical methods

Sediment grain size and organics in sediment analyses

The particle size of the bulk sediment from each station was determined by a hydrometer method (Gee and Bauder 1986). The percentages of sand, silt, and clay were classified using nomenclature based on sand-slit-clay ratios from the model given by Shepard's classification scheme (Shepard 1957; Poppe et al. 2003). Sediment organic characteristics including organic carbon, total nitrogen, total phosphate, and carbon-to-nitrogen ratio were determined using standard methods (Jackson 1958; Sommers and Nelson 1972; Tiessen and Moir 1993). The samples were pretreated with 10% HCl to remove the inorganic carbonates. Sediment samples were then oven-dried at 60 °C for 24 h to get rid of moisture (Bianchi et al. 2008). The sediment fraction, 5 to 2 mm, was used for organic compound determination. Organic carbon was determined using the rapid-dichromate oxidation technique (Walkley-Black method) with a correction factor of 1.3 (Walkely 1934; Nelson and Sommers 1996). Organic carbon and total nitrogen were measured using an automatic CHN elemental analyzer (Vario El II) and Kjeldahl total digestion technique (Smart et al. 1981), respectively. The results were expressed in percentage of organic carbon and total nitrogen in dry sediment. Total phosphorus was determined by the ascorbic persulfate method and absorbances read in a UV/VIS spectrophotometer at 880 nm (Langner and Hendrix 1982; Johnes and Heathwait 1992; Ma et al. 2017).

The quantity of sediment organic matter (SOM) was estimated by determining sediment organic carbon and using a

Table 1 Description of ten sampling stations at the Densu Estuary, Ghana

Stations	Description of sampling stations	Coordinates (latitude, N, longitude, W)
S1	The estuary is separated by sand bar landwards. Agro-industrial activities, refuse dump, livestock rearing, fishing boat landing sites, and landfill sites at Bortianor zone.	5° 30′ 23.1″, 0° 20′ 03.0″
S2	Landward, refuse dump, cattle rearing, and fishing boat landing sites at Tsokomey zone.	5° 30′ 24.8″, 0° 19′ 54.4″
S3	Water transportation from Densu Beach Resort by boats to Bojo Beach and vice versa. A high-energy environment characterized by river inflow into the estuary at two boundaries, the Bortianor-Tsokomey zone.	5° 30′ 28.6″, 0° 19′ 43.4″
S4	Densu River mixes with seawater and fish farming in the mixing zone.	5° 30′ 31.8″, 0° 19′ 33.7″
S5	Wetlands zone characterized by fishing activities (mainly tilapia, *Oreochromis niloticus*) and Bojo Beach tourist attraction site at Faanaa village.	5° 30′ 33.5″, 0° 19′ 22.1″
S6	Wetlands zone, fishing activities, oyster farming, and massive deposit of oyster shells at Faanaa village.	5° 30′ 35.1″, 0° 19′ 15.5″
S7	Seaward, mixing of fresh and seawater, ducks on the water, shorebirds, mangrove, oyster farming, cage crab culture, fishing activities at Panbros village.	5° 30′ 35.9″, 0° 19′ 10.7″
S8	Seaward with tidal current influence, wetland, shorebirds, mangrove-detritus enrichment at Panbros village.	5° 30′ 37.7″, 0° 19′ 00.8″
S9	Seaward, tidal influence, the Atlantic Ocean, Gulf of Guinea flows into the Densu estuary.	5° 30′ 41.8″, 0° 18′ 48.9″
S10	Densu beachfront, near-shore ocean water	5° 30′ 23.8″, 0° 19′ 42.9″

factor, which assumes that 58% of the SOM was formed by carbon (Jackson 1964; Bianchi et al. 2008). The percentage of organic carbon multiplied by 1.724 gives the percentage of sediment organic matter determined using the Walkley-Black (WB) chromic acid wet oxidation method (Jackson 1964). Organic matter was also determined via combustion (loss on ignition (LOI)) (Ball 1964; Ben-Dor and Banin 1989; Bianchi et al. 2008). The loss on ignition assumes mass loss is due to loss of organic matter (Miyazawa et al. 2000).

The trophic state was computed from water and sediment chemical properties (Hakanson et al. 2003; da Silveira et al. 2013). The sedimentology sensitivity factor relates to the trophic status of an ecosystem (Hakanson et al. 2003; da Silveira et al. 2013). The sedimentology sensitivity factor (SSF) was computed by the modification of three different organic properties of the sediment. The SSF was estimated as follows (Hakanson et al. 2003; da Silveira et al. 2013):

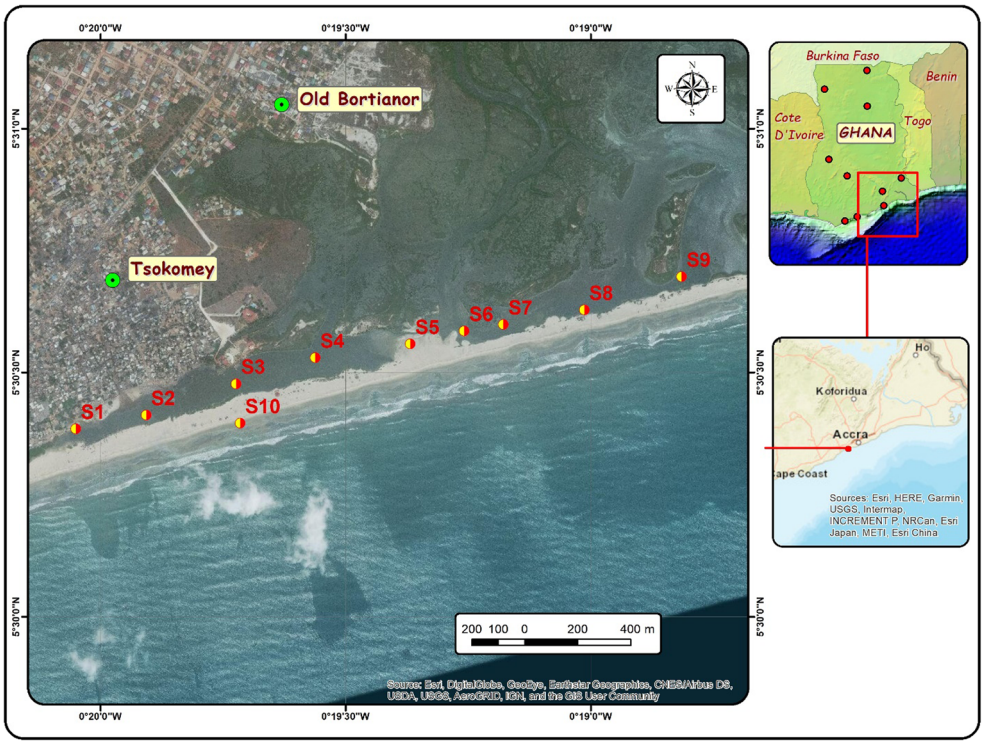

Fig. 1 Map of sampling stations at the Densu Estuary, Ghana

Sedimentology sensitivity factor 1 (SSF_1)

$$= \mathrm{TN}/\mathrm{SOM} \times 100 \quad (1)$$

Sedimentology sensitivity factor 2 (SSF_2)

$$= \mathrm{TN}/\mathrm{LOI} \times 100 \quad (2)$$

Sedimentology sensitivity factor 3 (SSF_3)

$$= \mathrm{TN}/\mathrm{OC} \times 100 \quad (3)$$

where SOM is the sediment organic matter; TN is the total nitrogen; LOI is the loss on ignition; and organic carbon (OC) is the organic carbon. The trophic sediment state is classified based on the following schemes (Hakanson et al. 2003; da Silveira et al. 2013); ultra oligotrophic, < 3.3; oligotrophic, 3.3–4.5; mesotrophic, 4.5–5.5; eutrophic, 5.5–6.5; and hypertrophic, > 6.5.

Metals in sediment analysis

The wet sediment samples were dried at 60 °C to a constant weight (Ismail 1993). The dried sediments were grounded into powder using a mortar and pestle. The homogenized sediment was sieved through 200 and 63 μm mesh-size sieves to obtain the fine-grained size for analysis of metal availability using Kjeldahl total digestion (Hseu 2004). Fine-grained sediment tends to have relatively high metal contents because of the high specific surface area and humic substance of smaller particles (Parsons et al. 2007; Ho et al. 2012; Nowrouzi and Pourkhabbaz 2014). The largest amount of anthropogenic sources of toxic elements in sediment is derived from fine particle sizes (Islam and Tanaka 2004; Dimitrakakis et al. 2014). The sediment particle size of less than 200 μm is recommended for total digestion (Dimitrakakis et al. 2014).

About 0.5 g of fine fraction (63 μm fraction) was weighed and placed in a 100-ml polytetrafluoroethylene beaker for acid digestion using the Kjeldahl total digestion method (Edgell 1989; Watson 1994; Sastre et al. 2002; Hseu 2004; Tuzen et al. 2011). Acid-dissolved solutions were analyzed for the concentration of metals, Zn, Pb, Cu, Hg, Mn, Fe, cadmium (Cd), and arsenic (As). The metal analysis was determined using Perkin Elmer Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) (Model PinAAcle 900T, PerkinElmer, Germany) (Waltham, MA, USA) at the Ecological Laboratory, Institute of Environment and Sanitation Studies, University of Ghana. For quality assurance, the glass beakers, glassware, and digestion vessel were soaked in 15% HNO_3 (*v*/*v*) for 24 h and subsequently rinsed with deionized water before usage. Blank samples (10 mL 65,145% HNO_3), elemental standard solutions (2, 5, and 10 ppm), and standard reference material were used for the calibrations. There is a specific absorbance with wavelengths, acceptable limits, and detection limits for each metal measured in GFAA. The detection limits are enhanced by the use of replicate injections. All detection limits are based on 98 to 100% confident level of 3 standard deviations. Only two elements (Cd and As) were below the detection limits. Certified standard reference material (no. ISE 999) was used for quality control checks. The recovery ranged from 95.3 to 99.9%, depending on the metal being measured. The average of three replicates obtained for each metal in parts per million (ppm) and final results converted to milligrams per kilogram of dry weight.

Enrichment factor

Enrichment factor (EF) is an ecological tool used to evaluate the enrichment of metals in the sediment (Benhaddya and Hadjel 2013; Barbieri 2016). The enrichment factor is a normalization method proposed to assess the concentration of the metals (Simex and Helz 1981; Özkan 2012). It is calculated as a ratio of the element to the normalized element by the same ratio found in the background references (Taylor 1964; Simex and Helz 1981). The recommended normalized elements include Al and Fe (Ackerman 1980; Rubio et al. 2000). The enrichment factor is calculated using the formula (Ergin et al. 1991):

$$\mathrm{EF} = \frac{(\mathrm{X}/\mathrm{Fe})_{\mathrm{sediment}}}{(\mathrm{X}/\mathrm{Fe})_{\mathrm{Background\ reference}}}$$

where X/Fe is the ratio of the concentrations of metal X (element) to Fe (normalized metal or element).

In this study, Fe was chosen as the normalized element because Fe has relatively high natural concentrations and therefore is not expected to be substantially enriched from anthropogenic sources in estuarine sediment (Niencheski et al. 1994; Bhutiani et al. 2017). Iron is often used as a conservative tracer to differentiate natural from anthropogenic sources of pollution (Schiff and Weisberg 1999; Baptista Neto et al. 2000; Ghrefat et al. 2011). An enrichment value factor of $< 1 \leq 2$ is often associated with either no enrichment or depletion relative to the average earth's crust and/or shale average values (Pekey 2006). In this study, the earth's crust abundance (Taylor 1972) and the shale average values (Turekian and Wedepohl 1961), as well as local background, were employed on the same data as a background reference to test the suitability in geochemical index computation. The background values are natural contents of a substance in the sediment completely dependent on the compositional and mineralogical characteristics of the parent geological material (Nowrouzi and Pourkhabbaz 2014; Barbieri 2016). The enrichment factor is categorized (Özkan 2012; Costa et al. 2015; Zalewska et al. 2015) as follows: EF < 2 = no enrichment; $2 \leq$ EF < 3 = minor enrichment; $3 \leq$ EF < 5 = moderate enrichment; $5 \leq$ EF < 10 = moderately severe enrichment; $10 \leq$ EF < 25 = severe enrichment; $25 \leq$ EF < 50 = very severe enrichment; and EF > 50 = extremely severe enrichment.

Geoaccumulation index

The geoaccumulation index (*Igeo*) is used to assess metal enrichment above background concentrations (Müller 1968; Abrahim and Parker 2008; Gong et al. 2008). It is a single metal approach used to quantify metal pollution in sediments when the concentration of toxic heavy metal is 1.5 or more times greater than their lithogenic background values (Gaur et al. 2005; Zalewska et al. 2015). The *Igeo* is calculated using the following equation (Müller 1968; Boszke et al. 2004; Zalewska et al. 2015):

$$Igeo = log_2\,[Cn/1.5Bn]$$

where *Cn* is the measured concentration of the element *n* and *Bn* is the geochemical background value element *n* in average shale and or average crust abundance (Turekian and Wedepohl 1961; Taylor 1972; Wedepohl 1995). The constant factor 1.5 is used to minimize any possible background variation which may be attributed to lithologic variations in the sediment (Loska et al. 2004). The geoaccumulation index consists of seven grades ranging from unpolluted to extremely polluted (Gonzáles-Macías et al. 2006; Aiman et al. 2016). The geoaccumulation index is classified as (García et al. 2008; Özkan 2012): Igeo ≤ 0 = unpolluted; 0 < Igeo ≤ 1 = unpolluted to moderately polluted; 1 < Igeo ≤ 2 = moderately polluted; 2 < Igeo ≤ 3 = moderately to strongly polluted; 3 < Igeo ≤ 4 = strongly polluted; 4 < Igeo ≤ 5 = strongly to extremely polluted; and Igeo > 5 = extremely polluted.

Pollution load index

The pollution load index (PLI) is used to assess the toxicity of metal in the sediment (Tomlinson et al. 1980). The PLI is calculated by obtaining the *n*th root from the contamination factors (CFs) that were obtained for all the metals (Soares et al. 1999). The CF of the metal is obtained by dividing the concentration of each metal measured in the sediment with the background geological reference value of the metal (Tomlinson et al. 1980). The pollution load index (PLI) is determined by the following formula (Tomlinson et al. 1980):

$$\mathrm{PLF} = \sqrt[n]{(\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \ldots \times \mathrm{CF}_n)} \quad (4)$$

where,

$\mathrm{CF} = \mathrm{C}_{\mathrm{mental}}/\mathrm{C}_{\mathrm{background\ reference}}$
CF = contamination factor, n = number of metals
$\mathrm{C}_{\mathrm{mental}}$ = metal concentration in the sediments
$\mathrm{C}_{\mathrm{background\ reference}}$ = background value of each metal
PLI = Pollution Load Index

The pollution load index is classified as follows: no pollution (PLI < 1), moderate pollution (1 < PLI < 2), heavy pollution (2 ≤ PLI < 3), and extremely heavy pollution (PLI > 3) (Harikumar et al. 2009). The PLI value of (PLI > 1) is polluted, whereas PLI < 1 indicates no pollution (Harikumar et al. 2009).

Potential ecological risk index

Potential ecological risk index (PERI) is an index used in the determination of metal pollution (Hakanson 1980; Nobi et al. 2010). The PERI is used to identify toxic substances in aquatic ecosystems to facilitate better pollution management (Hakanson 1980; Nobi et al. 2010). The potential ecological risk (PER) measures a single metal risk whereas the PERI assesses pollution based on multiple metals (Hakanson 1980; Nobi et al. 2010). The sediments give a better representation of spatial and temporal sources of contamination than pollutants in the water column (Özkan 2012). The potential ecological risk index is derived from pollution indices (Hakanson 1980; Nobi et al. 2010) such as (i) contamination factor; (ii) degree of contamination; (ii) toxic response factor; and (iv) potential ecological risk.

Contamination factor

CF is a ratio of the concentration of a metal in sediment to natural abundance (pre-industrial reference value for the same metal) (Hakanson 1980):

$$\mathrm{CF} = \mathrm{C}_{\mathrm{mental}}/\mathrm{C}_{\mathrm{background\ reference}} \quad (5)$$

where C_{metal} is the measured metal concentration in the sediment and $C_{\mathrm{background\ reference}}$ is background value or pre-industrial concentration of the metal (Hakanson 1980). In most studies, the average Shale values (ASV) (Turekian and Wedepohl 1961) and/or average earth's crust abundance data (ACA) (Taylor 1972) are commonly used to provide elemental background concentration for estimation of the contamination factor. The contamination factor is grouped according to the grading system of Hakanson (Hakanson 1980): CF < 1 = low contamination; 1 ≤ CF < 3 = moderate contamination; 3 ≤ CF < 6 = considerable contamination; and CF ≥ 6 = very high contamination (Hakanson 1980).

The degree of contamination

The degree of contamination (DC) in a particular locality is the sum of all CFs of the various heavy metals (Hakanson 1980; Soliman et al. 2015). The DC = Σ CF. The DC is classified as follows (Hakanson 1980; Soliman et al. 2015): DC < 1 = low degree of contamination; 1 ≤ DC < 3 = moderate degree of contamination; 3 ≤ DC < 6 = considerable degree of contamination; and DC ≥ 6 = a very high degree of contamination (Hakanson 1980).

Toxic response factor

The toxic response factor (TRF) is estimated from the sedimentological toxic factor (STF) and the sedimentological sensitivity factor (also known as bioproduction rate (BPR)) (Hakanson 1980, 1984). The sedimentological toxic factor includes the toxicity values, which must reflect the different toxic effects of each metal at natural aquatic ecosystems (Hakanson 1980). The decreasing order of toxicity of metals (standard toxicity values) (Hakanson 1980) were Hg = 40 > Cd = 30 > Cu = Pb = 5 > Cr = 2 > Mn = Zn = 1. Therefore, TRF is calculated as follows (Hakanson 1980): Hg = 40.5/BPR; Cd = $30.5^{1/2}$/$BPR^{1/2}$; Pb = $5.5^{1/2}$/$BPR^{1/2}$; Cu = $5.5^{1/2}$/$BPR^{1/2}$; Cr = $2.5^{1/2}$/$BPR^{1/2}$; and Zn = $1.5^{1/2}$/$BPR^{1/2}$ (Hakanson 1980).

The potential ecological risk and potential ecological risk index

The PER is used to assess the degree of heavy metal pollution in the sediment, according to the toxicity of heavy metals and their response to disturbances in aquatic environment (Hakanson 1980; Cheng et al. 2017). The PER = TRF × CF, where TRF is the toxic response factor and CF is the contamination factor. The PER for each metal is classified as follows (Hakanson 1980): PER < 40 = low risk; 40 ≤ PER < 80 = moderate risk; 80 ≤ PER < 160 = considerable risk; 160 ≤ PER > 320 = high risk; and PER ≥ 320 = very high risk (Hakanson 1980).

PERI is the sum of all PER calculated for each metal in a given ecosystem. The PERI = Σ PER. The PERI is a quantitative method used to assess ecological risks of metal pollution in aquatic environment (Hakanson 1980). The PERI is classified based on the PERI grading system (Hakanson 1980): PERI < 40 = very low ecological risk; 40 ≤ PERI ≤ 80 = moderate low ecological risk; 80 ≤ PERI ≤ 150 = low ecological risk; 300 ≤ PERI < 600 = considerable ecological risk; and PERI ≥ 600 = very high ecological risk (Hakanson 1980).

Statistical analysis

Basic statistics, normality tests and one-way analysis of variance (ANOVA) were computed using the paleontological statistics software package for education and data analysis, (PAST) (Hammer et al. 2001). ANOVA was performed on normally distributed chemical variables to test for spatial variability. Cluster analysis was performed to test the similarities between chemical contaminants. The hierarchical group linking cluster was created by euclidean distance and a SIMPROF test ($\alpha = 0.05$; 999 permutations) of significant similar clusters (Ernst 2004; Clarke et al. 2008; Somerfield and Clarke 2013). The cluster analyses were performed using PRIMER 6 software (Clarke and Gorley 2006). Principal component analyses (PCA) were used to test for spatial variations (Jongman et al. 1995) using Canoco software version 5.03 (Šmilauer and Lepš 2014). Pearson's correlation coefficient (r) was used to determine linear associations using Statistical Package for Social Sciences version 21 (SPSS 21.0). Significant correlation coefficients at p values ($p < 0.05$ and < 0.01) were adopted.

Results

Sediment characteristics (size, organics, sensitivity factor, and metal concentrations)

The sand grains were the most dominant particles in the sediment (Table 2). The percentage dominance order was sand > silt > clay (Table 2). The minimum sand occurrence (53%) was in S4, and the maximum (87%) in S3. The minimum silt (10%) occurred in S3 with the maximum (41%) in S5. The minimum clay content (2%) was recorded in S3 and the maximum (8%) in S4. The organic characteristics of sediment (TN %, TP %, OC %, SOM % carbon-to-nitrogen ratio (C/N) ratio, and LOI %) showed spatial trends from landward towards seaward areas (Table 3). T test showed that sediment organic matter via Walkley-Black methods differs significantly ($p = 0.02$ at one tail and $p = 0.04$ at two-tail) from combustion (LOI). One-way analysis of variance indicated a significant difference ($p < 0.05$) in the sediment organic properties (organic carbon, total nitrogen, sediment organic matter, and loss-on-ignition) between each other and within the stations but no significant variation ($p > 0.05$; $F_{cal\ (0.56)} < F_{crit\ (2.21)}$) for the total percentage of organic properties of sediment in each station.

Table 2 Sediment particle size characteristics of the Densu Estuary, Ghana

Stations	Sand (%)	Silt (%)	Clay (%)
S1	57	40	4
S2	63	32	5
S3	87	10	2
S4	53	41	5
S5	60	32	8
S6	60	39	2
S7	59	39	2
S8	65	33	2
S9	59	36	5
S10	60	34	6
Mean ± SD	62 ± 9.4	34 ± 8.9	4 ± 2.3
Minimum	53	10	2
Maximum	87	41	8

SD, standard deviation

Table 3 Organic characteristics of sediment of the Densu Estuary, Ghana

Stations	OC (%)	TN (%)	C/N (%)	TP (%)	SOM (%)	LOI (%)
S1	1.023	0.090	11.422	1.380	1.764	1.502
S2	0.986	0.098	10.056	0.510	1.699	1.432
S3	1.402	0.132	10.657	0.770	2.418	1.709
S4	1.706	0.064	26.486	0.590	2.941	1.671
S5	1.516	0.056	27.075	0.670	2.614	1.656
S6	0.493	0.062	7.999	0.470	0.850	1.334
S7	0.948	0.098	9.670	0.460	1.634	1.319
S8	1.895	0.148	12.771	0.590	3.267	1.120
S9	2.047	0.059	34.811	0.440	3.529	1.700
S10	0.758	0.062	12.307	1.080	1.307	1.685
Mean ± SD	1.277 ± 0.5	0.087 ± 0.0	16.326 ± 9.4	0.696 ± 0.3	2.202 ± 0.9	1.513 ± 0.2
Minimum	0.493	0.056	7.999	0.440	0.850	1.120
Maximum	2.047	0.148	34.811	1.380	3.529	1.709

SD, standard deviation; *OC*, organic carbon; *TN*, total nitrogen; *C/N*, carbon-to-nitrogen ratio; *TP*, total phosphate; *SOM*, soil organic matter; *LOI*, loss on ignition

The overall, mean sedimentological sensitivity factor ranged from 2.64 to 11.00 with mean ± SD (6.07 ± 1.6) (Table 4. Sedimentological sensitivity factor 1 (SSF_1, TN/SOM*100) did not vary ($p > 0.05$) from sedimentology sensitivity factor 2 (SSF_2, TN/LOI*100). Sedimentological sensitivity factor 1 (SSF_1) significantly ($p < 0.05$) varied from sedimentological sensitivity factor 3 (SSF_3, TN/OC*100).

The decreasing order of mean metal dominance in the sediments was Fe (569.7 ± 176.3) > Mn (90.5 ± 45.7) > Pb (50.9 ± 24.3) > Zn (46.9 ± 45.0) > Cu (10.9 ± 8.5) > Hg (0.020 ± 0.01) (Tables 5 and 6). The maximum mean metal concentration was found in Fe and minimum in Hg. The minimum Fe was recorded at S6 (201.1 mg/kg) and maximum (720.9 mg/kg) at S3. The minimum (40.1 mg/kg) manganese was recorded at S4 and the maximum (152.7 mg/kg) at S7. The minimum (1.9 mg/kg) Pb concentration was recorded at S8 and the maximum (84.7 mg/kg) at S5. The minimum zinc (7.3 mg/kg) was recorded at S6 and the maximum (158.3 mg/kg) at S1. The minimum Cu (3.4 mg/kg) was recorded at S9 and the maximum (23.0 mg/kg) at S6. The minimum (0.00 mg/kg) Hg was recorded in two stations (S5 S8) and the maximum (0.045 mg/kg) at S1 (Table 6). One-way analysis of variance indicated significant variations ($p < 0.05$) in metal (Pb, Hg, Fe, Cu, and Mn) concentrations (mg/kg) and dry weight within the stations. However, there was no significant variation ($p > 0, 05$; $_{(0.27)} < F_{crit\ (2.19)}$) in the total concentration (mg/kg) of metals in the sediment in each station.

Potential ecological risk of metals

The geochemical indices were estimated via comparison with different background materials (geological and local references) (Table 7; Appendices Table 11, 12 and 13). The geochemical indices (enrichment factor, contamination factor, and geoaccumulation index) computed from geological and local background showed lead as the most dominant metal in the sediment (Table 7). The element zinc was the second most dominant metal contaminant in the sediment. The order of dominance for the other metal's (Mn, Hg, Cu, Fe) contamination in the sediment changes depending on background reference material (Table 7). The order of the dominance of metals computed from geological (Shale average and earth's crust) and local preindustrial background were the same for enrichment factor Pb > Zn > Hg > Mn > Cu (Table 7; Appendix

Table 4 Summary of sediment trophic state of the Densu Estuary, Ghana

Sedimentology sensitivity factor	Min	Max	Mean ± SD	Trophic status[a]
SSF_1 (TN/SOM*100)	1.67	7.25	4.48 ± 1.87	Mesotrophic[a]
SSF_2 (TN/LOI*100)	3.38	13.25	6.01 ± 3.05	Eutrophic[a]
SSF_3 (TN/OC*100)	2.87	12.50	7.72 ± 3.23	Hypertrophic[a]
Overall (mean ± SD	2.64 ± 0.9	11.00 ± 3.3	6.07 ± 1.6	Mesotrophic[a]

SD, standard deviation; *Min*, minimum; *Max*, maximum

[a] Trophic state based on mean values, classification of trophic state: ultra oligotrophic > 3.3, oligotrophic, 3.3–4.5; mesotrophic, 4.5–5.5; eutrophic, 5.5–6.5; hypertrophic >6.5

Table 5 Metal concentrations (mg/kg) in the sediments of the Densu Estuary, Ghana

Stations	Zn	Pb	Hg	Fe	Cu	Mn
S1	158.3	47.7	0.0454	N/A	N/A	N/A
S2	21.4	63.3	0.0176	457.8	18.2	43.4
S3	47.7	82	0.0155	720.9	N/A	147.2
S4	27.8	34.1	0.016	719.8	N/A	40.1
S5	25.5	84.7	0.0095	719.8	3.8	152.7
S6	7.3	45.2	0.0263	201.1	23	54.5
S7	9.1	58.5	0.0224	589.9	13.1	83.7
S8	62.8	1.9	0.0077	555.1	4	76.6
S9	32.6	56.3	0.0154	N/A	N/A	N/A
S10	76.8	35.1	0.0287	593.3	3.4	125.6
Mean ± SD	46.9 ± 45.0	50.9 ± 24.3	0.020 ± 0.01	569.7 ± 176.3	10.9 ± 8.5	90.5 ± 45.7
Minimum	7.3	1.9	0.008	201.1	3.4	40.1
Maximum	158.3	84.7	0.045	720.9	23.0	152.7

SD, standard deviation; *N/A*, not available

Table 11). The CF (Table 7; Appendix Table 12) followed the order Pb > Zn > Cu > Hg > Mn > Fe for Shale and local background (pre- and-post-industrial values) (Appendix Table 12) and differed from the earth's crust as background material. However, there was similarity but never the same order for Igeo (Table 7; Appendix Table 13). The geochemical indices (enrichment factor, contamination factor and geoaccumulation index) for the metals computed from Shale average values did not differ significantly ($p > 0.05$) from earth's crust abundance. The contamination factor of pre-industrial Hg varied significantly ($p < 0.05$) from post-industrial Hg. The enrichment factor (EF) for Zn computed from the geological background (Shale average and Earth's Crust values) significantly varied ($p < 0.05$) from the local background (pre-industrial and post-industrial values). Igeo for Zn computed from the geological background (Shale average and Earth's Crust values) showed significant variation ($p < 0.05$) from the local background. Igeo for Hg computed from Earth's Crust significantly varied from pre-industrial value.

The geochemical pollution indices for local background (pre-industrial era as reference (Tables 7, 8, and 9) are stated here: (i) the average enrichment factor of metals was Pb > Zn > Hg > Mn > Cu and (ii) the average contamination factor was Pb > Zn > Cu > Mn > Hg > Fe and the average Igeo was Pb > Zn > Cu > Hg > Mn. The DC ranged from 3.47 to 9.87 depending on the background references (Table 7). The order of PER for the metals was Pb > Hg > Cu > Zn excludes Fe and Mn irrespective of the background reference (Table 7). The PER of Pb (ranged from 17.9 to 44.75) and Hg (ranged from 6.42 to 28.78) made them the most toxic metals with ecological risks compared with other metals (Table 7). The PER of Pb was also higher when estimated with the local background (ranged PER = 32.14–44.75) than with geological reference values (ranged PER = 17.9–21.06) (Table 7). The minimum was recorded for Shale average values and maximum for pre-industrial values (Table 7). Overall, the potential ecological risk index (sum of all PER) ranged from 26.45 to 45.77 depending on the background (Table 7). The potential ecological risk index ranged between 26.45 and 83.42 (Table 7). The minimum was recorded for Shale's average values and the maximum for the pre-industrial background (Table 7). The PLI was ($1 \leq PLI > 3$) depending on background (Table 10). The geological (Shale average and earth's crust) and post-industrial value suggested no pollution ($PLI < 1$) whereas the pre-industrial value showed a higher pollution index ($PLI > 3$) (Table 10).

Multivariate statistics and correlations

There are two main groups of organic properties of sediment: (i) Group 1, SOM, OC, and C/N ratio (SOM, OC, C/N) and (ii) Group 2, TN, TP, and LOI. The corresponding stations are characterized by two major clusters: cluster 1 (S4, S5, S9); cluster 2 is made up of sub-groups (S1, S2, S3, S7) and (S6, S10) and single station S8 (Fig. 2).

There are two hierarchical clusters of metal concentrations, the first group with two sub-groups (copper and lead (Cu–Pb)) and (mercury and zinc (Hg–Zn)) and the second group (manganese and iron (Mg–Fe)) (Fig. 3a). The corresponding stations also formed two major clusters; cluster 1 with two sub-groups (S3, S4, S5, S8) and (S10) and cluster 2 with three sub-groups (S1), (S2 and S7), and (S6 and S9) (Fig. 3a). Cluster analysis of combined organics and metals showed four groups (Fig. 3b). The first group (manganese, iron, and copper (Mg–Fe–Cu)); second group (zinc, total phosphate, and mercury (Zn-TP-Hg)); third group (loss on ignition, carbon to nitrogen ratio and lead (LOI-C/N-Pb)); and fourth groups (sediment

Table 6 Comparison between metal concentrations (mg/kg) obtained from this study and other sources

	Zn	Pb	Hg	Fe	Cu	Mn
This study						
Minimum	7.3	1.9	0.008	201.1	3.4	40.1
Maximum	158.3	84.7	0.045	720.9	23.0	152.7
Mean ± SD	46.9 ± 45.0	50.9 ± 24.3	0.020 ± 0.01	569.7 ± 176.3	10.9 ± 8.5	90.5 ± 45.7
Industrial eras (Mahu 2014)						
Pre-mean	25.19 ± 9.2	8. 00 ± 3.9	0.04 ± 0.0		10.52 ± 3.3	
Post-mean	31.94 ± 3.3	11.14 ± 0.5	0.21 ± 0.2		12.53 ± 1.1	
Wet season (Addo 2017)						
Sediment	28.9 ± 0.9				6.6 ± 0. 2	
Water	2.98 ± 0.4				1.54 ± 0.1	
Dry season (Addo 2017)						
Sediment	30.02 ± 0.9				6.01 ± 0.2	
Water	13.0 ± 0.4				1.1 ± 0.1	
Biota (Addo 2017)						
Fish (Blackchin tilapia)	5.37 ± 0.81				0.14 ± 02	
Fish (*Tilapia zilli*)	4.2 ± 0.6				0.11 ± 0.1	
Bird (Piedkinfisher)	4.36 ± 0.8				1.57 ± 0.2	
Birds (Longtail Cormorant)	12.41 ± 0.0				6.16 ± 0.6	
Bird (Black Heron)	17.58 ± 0.2				11.89 ± 0.2	
Other estuaries (Klub et al. 2018)						
Volta Estuary	21.0 ± 10.0	6.2 ± 3.6	0.075 ± 0.01	29, 000 ± 13,000	6.4 ± 4.3	1800 ± 1500
Pra River Estuary	51.0 ± 13.0	10.8 ± 3.4	0.20 ± 0.17	42, 000 ± 11,000	23.1 ± 7.1	245.0 ± 46.0
Ankobra River Estuary	53.0 ± 15.0	10.6 ± 3.4	0.28 ± 0.10	41,000 ± 13,000	23.8 ± 7.9	261 ± 71.0
Geological background[a]						
Shale average values	95	20	0.18	46,700	45	850
Earth's crust values	65	17	0.05	4000	40	680
Canadian sediment[b]						
CSQGs		123	0.17			
CBSQGs	120	36	0.18	20,000	23	460
SQG[c]						
Non-polluted	< 90	< 40	≥ 1.0		< 20	
Moderately polluted	90–2.0 × 10^2	40–60			25–50	
Heavily polluted	> 2.0 × 10^2	> 60	> 1.0		≥ 50	

SD, standard deviation; *SQG*, Sediment Quality Guidelines

[a] Shale average (Turekian and Wedephol 1961) and Earth Crust values (Taylor 1964)

[b] Canadian sediment: Consensus-Based Sediment Quality Guidelines (CBSQSs) and Canadian Sediment Quality Guidelines (CSGGs)

[c] Fish: *Sarotherodon melantheron* (Blackchin tilapia); *Coptodon zilli* (formerly known as *Tilapia zilli*) (Red belly tilapia); birds: *Cerylerudis* (Piedkinfisher), *Phalacrocorax africanus* (Longtail Cormorant), and *Egrettadesiaca* (Black Heron)

organic matter, organic carbon, and total nitrogen (SOM-OC-C/N)). Principal component analysis of organic properties of the sediment and metal concentration showed four major groups, corresponding stations (Fig. 4): group 1, Hg (S1, S6, 10); group 2, Cu (S2 and S7); group 3, zinc, total nitrogen, sediment organic matter, and organic carbon (Zn-TN-SOM-OC; S3, S8); and group 4: iron, lead, manganese, total phosphate, loss on ignition, and carbon-to-nitrogen ratio (Fe-Pb-Mn-TP-LOI-C/N; S4, S5, S9).

Correlation existed between organic characteristics and metals concentrations in sediment. Pearson's correlation indicated significant negative associations between Cu and Fe ($r = -0.845$; $p = 0.002$), copper and organic carbon ($r = -0.711$; $p = 0.021$), and copper and sediment organic matter ($r - 0.711$; $p = 0.021$). There was positive correlation between carbon-to nitrogen ratio and organic carbon ($r = 0.738$; $p = 0.015$), a strong linear association between sediment organic matter and organic carbon ($r = 1.000$; $p = 0.000$), sediment

Table 7 Summary of mean geochemical indices, potential ecological risk, and degree of contamination computed by geological and local background references

Background references	Geological background		Local background	
	Shale average	Earth crust	Pre-industrial	Post-industrial
Code	1	2	3	4
Geochemical indices				
Enrichment factor	Pb1 (234.5 ± 156.1) > Zn1 (29.6 ± 19.9) > Hg1 (20.6 ± 9.9) > Mn1 (9.1 ± 3.9) > Cu1 (0.0 ± 0.0)	Pb2 (236.4 ± 157.3) > Zn2 (37.02 ± 24.9) > Hg2 (32.64 ± 30.8) > Mn1 (9.1 ± 3.9) > Cu2 (0.0 ± 0.0)	Pb3 (502.2 ± 334.3) > Zn3 (95.5 ± 64.3) > Hg3 (40.8 ± 38.5) > Mn3 (9.8 ± 4.2) > Cu3 (0.0 ± 0.0)	Pb4 (360.7 ± 420.1) > Zn4 (75.3 ± 50.7) > Mn4 (9.8 ± 4.2) > Hg4 (7.7 ± 7.3) > Cu4 (0.0 ± 0.0)
	Pb > Zn > Hg > Mn > Cu	Pb > Zn > Hg > Mn > Cu	Pb > Zn > Hg > Mn > Cu	Pb > Zn > Mn > Hg > Cu
Contamination factor	Pb1 (2.5 ± 1.4) > Zn1 (0.5 ± 0.5 > Cu1 (0.2 ± 0.2) > Hg1 (0.1 ± 0.1) > Mn1 (0.1 ± 0.1) > Fe1 (0.0+ 0.0)	Pb2 (2.9 ± 1.4) > Zn2 (0.7 ± 0.5) > Hg2 (0.4 ± 0.2) > Cu2 (0.2 ± 0.2) > Mn2 (0.1 ± 0.1) > Fe2 (0.0 ± 0.0)	Pb3 (6.4 ± 3.0) > Zn3 (1.9 ± 0.7) > Cu3 (1.0 ± 0.8) > Hg3 (0.5 ± 0.3) > Mn3 (0.1 ± 0.1) > Fe3 (0.0 ± 0.0)	Pb4 (4.6 ± 2.2) > Zn4 (2.5 ± 1.2) > Cu4 (0.8 ± 0.7) > Hg4 (0.1 ± 0.1) > Mn4 (0.1 ± 0.1) > Fe4 (0.0 ± 0.0)
	Pb > Zn > Cu > Hg > Mn > Fe	Pb > Zn > Hg > Cu > Mn > Fe	Pb > Zn > Cu > Hg > Mn > Fe	Pb > Zn > Cu > Hg > Mn > Fe
Geoaccumulation index	Pb1(0.4 ± 1.6) > Zn1 (− 2.15 ± 1.4) > Cu1 (− 3.1 ± 1.3) > Hg1 (− 3.9 ± 0.8) > Mn1 (− 3.9 + 0.8)	Pb2(0.6 ± 1.6) > Zn2 (− 1.6 ± 1.4) > Hg2 (− 2.1 ± 0.8) > Cu2 (− 2.9 ± 1.3) > Mn2 (− 3.7 ± 0.8)	Pb3 (1.7 ± 1.6) > Zn3 (−0.2 ± 1.4) > Cu3 (− 1.0 ± 1.3) > Hg3 (− 1.7 ± 0.8) > Mn3 (− 3.7 ± 0.8)	Pb4 (1.2 ± 1.6) > Zn4 (0.4 ± 1.6) > Cu4 (− 1.2 ± 1.3) > Mn4 (− 3.7 ± 0.8) > Hg4 (− 4.1 ± 0.8)
	Pb > Zn > Cu > Hg > Mn	Pb > Zn > Hg > Cu > Mn	Pb > Zn > Cu > Hg > Mn	Pb > Zn > Cu > Mn > Hg
Potential ecological risk for each metal (PER)				
Zn	0.70	1.02	2.62	2.02
Pb	17.9	21.06	44.75	32.14
Hg	6.40	23.02	28.78	5.48
Fe				
Cu	1.46	1.92	7.27	6.13
Mn				
PER	Pb > Hg > Cu > Zn	Pb > Hg > Cu > Zn	Pb > Hg > Cu > Zn	Pb > Hg > Cu > Zn
Degree of contamination (DC)				
DC	3.47	4.54	9.87	4.54
DC ranking	4	5	10	6
	3 ≤ DC < 6	3 ≤ DC < 6	DC ≥ 6	3 ≤ DC < 6
Classification	Considerable contamination	Considerable contamination	A very high degree of contamination	Considerable contamination
Potential ecological risk index (PERI) for Densu estuary				
PERI	26.45	47.02	83.42	45.77
	PERI < 40	40 ≤ PERI ≤ 80	80 ≤ PERI ≤ 150	40 ≤ PERI ≤ 80
Classification	Very low ecological risk	Moderate low ecological risk	Low risk	Moderate low ecological risk

Table 8 Comparison of average enrichment factor, contamination factor, and geoaccummulation index of metals (estimated using local pre-industrial background)

Metals	Enrichment factor (CF)	Contamination factor (CF)	Geoaccumulation index (*Igeo*)
Pb	502.2 ± 334.3 (extremely severe enrichment)	6.4 ± 3.0 (moderate contamination)	1.7 ± 1.6 (moderately polluted)
Zn	95.5 ± 64.3 (extremely severe enrichment)	1.9 ± 0.7 (considerable contamination)	− 0.2 ± 1.4 (unpolluted)
Hg	40.8 ± 38.5 (extremely severe enrichment)	0.5 ± 0.3 (low contamination)	− 1.7 ± 0.8 (unpolluted)
Fe		0.0 ± 0.0 (low contamination)	
Cu	0.0 ± 0.0 (no enrichment)	1.0 ± 0.8 (moderate contamination)	− 1.0 ± 1.3 (unpolluted)
Mn	9.8 ± 4.2 (significant enrichment)	0.1 ± 0.1 (low contamination)	− 3.7 ± 0.8 (unpolluted)
Overall	Pb > Zn > Hg > Mn > Cu	Pb > Zn > Cu > Hg > Mn > Fe	Pb > Zn > Cu > Hg > Mn

$EF < 2$, no enrichment; $2 \le EF < 3$, minor enrichment; $3 \le EF < 5$, moderate enrichment; $5 \le EF < 10$, moderately severe enrichment; $10 \le EF < 25$, severe enrichment; $25 \le EF < 50$, very severe enrichment; $EF > 50$, extremely severe enrichment; $CF < 1$, low contamination; $1 \le CF < 3$, moderate contamination; $3 \le CF < 6$, considerable contamination; $CF \ge 6$, very high contamination; $Igeo \le 0$, unpolluted; $0 < Igeo \le 1$ = unpolluted to moderately polluted; $1 < Igeo \le 2$, moderately polluted; $2 < Igeo \le 3$, moderately to strongly polluted; $3 < Igeo \le 4$, strongly polluted; $4 < Igeo \le 5$, strongly to extremely polluted; $Igeo > 5$, extremely polluted

organic matter and carbon-to-nitrogen ratio ($r = 0.738$; $p = 0.015$), and positive Hg and total phosphate ($r = 0.723$; $p = 0.018$) (Appendix Table 14).

Discussion

Sediment particle size

The sediment texture was sandy loam at the ten stations. The range of sediment grain size (Table 2) reflects local hydrodynamic conditions from landwards towards the seaward direction. The maximum sandy particle was recorded at S3; this is characterized by a high energy regime. There is river inflow with possible fluvial transport into the Estuary at this station. Coarse grains sediment are normally found in high energy proximal nearshore environment. The maximum silt particles were found at S5, characterized by wetlands. The maximum clay particles were recorded at S4, characterized by mixing of river and marine water. Sediment is generally composed of loose sand, clay, and silt particles that settle at the bottom of a waterbody (Davies and Abowei 2009). Grain size of the deposited sediments act as an indicator of the energy of the bottom of the ecosystem, an attribute of hydrodynamic conditions of the water body (Brookfield and Ahlbrandt 1983; Reading and Collinson 1996; Barcellos et al. 2014). The occurrence of pelitic deposits of silts and clay particles is often linked to a low-energy environment (Barcellos et al. 2014). The psammite sediments including sand grain are due to the proximity of the current source such as crystalline, to past processes and the fragmentation of carbon edifications (Barcellos et al. 2014). Coarse sediment particles tend to remain in the overlying water for a relatively short period and to be transported over only a short distance (Horowitz 1991; Finger et al. 2006). Fine particles are frequently associated with

Table 9 Comparison of geochemical indices (enrichment factor and geoaccumulation index) in this study with other estuaries in Ghana

Pollution indexes	Pb	Zn	Cu	Hg	Mn
Enrichment factor (EF)[a]					
Densu River Estuary (this study)[c]	502.2 ± 334.3	95.5 ± 64.3	0.0 ± 0.0	40.8 ± 38.5	9.8 ± 4.2
Pra River Estuary[d]	1.26 ± 0.0	1.78 ± 0.0	2.75 ± 0.1		1.58 ± 0.0
Ankobra River Estuary[d]	1.29 ± 0.02	1.93 ± 0.0	2.90 ± 0.0		2.35 ± 0.1
Geoaccumulation index (*Igeo*)[b]					
Densu River Estuary[c] (this study)[c]	1.7 (− 2.7, 2.8)	1.2 (− 2.4, 2.1)	0.3 (− 2.2, 0.5)	− 0.9 (− 2.9, − 0.4)	− 2.9 (− 4.7, − 2.7)
Pra River Estuary[d]	0.4 (− 0.7, 1.0)	0.9 (0.0, 1.5)	1.6 (0.2, 2.1)		− 3.0 (− 4.0, − 2.0)
Ankobra River Estuary[d]	0.3 (− 2.0, 1.0)	0.9 (− 1.0, 1.5)	1.5 (− 1.2, 2.2)		− 2.8 (− 3.8, − 2.1)

[a] For EF values, the mean and the standard deviation of the mean are shown

[b] For *Igeo* values, the mean and range (in brackets) are shown; pollution indexes

[c] Densu Estuary estimated based on pre-industrial values with Fe normalization, this study)

[d] Pra River Estuary and Ankobra River Estuary based on Volta lake as background reference with Fe as normalization (Klubi et al. 2018)

Table 10 Pollution load index estimated for the Densu Estuary, Ghana

	Computed from results of the contamination factor			
	Geological background		Local background	
Pollution load index	Shale	Crust	Pre-industrial	Post-industrial
Minimum	2.8×10^{-40}	3.09×10^{-34}	9.67×10^{-26}	5.34×10^{-32}
Maximum	5.64×10^{-4}	0.13	43.11	0.05
Mean ± SD	$8.22 \times 10^{-5} \pm 0.0$	0.02 ± 0.0	4.79 ± 14.4	0.01 ± 0.0
Pollution load index	PLI < 1	PLI < 1	PLI > 3	PLI < 1
Classification	No pollution	No pollution	Extremely heavy polluted	No pollution

SD, standard deviation; *PLI*, pollution load index (no pollution (PLI < 1), moderate pollution (1 < PLI < 2), heavy pollution (2 ≤ PLI < 3), and extremely heavy pollution (PLI > 3))

contaminants (Horowitz 1991; Salomons 1995). The grain size distributions reflect the hydraulic environment in which the grains were transported and deposited (Allen 1971).

Sediment organic characteristics and sensitivity factor

The percentage of organic properties of sediment (Table 3) reflects human activities surrounding the catchment of the Densu Estuary.

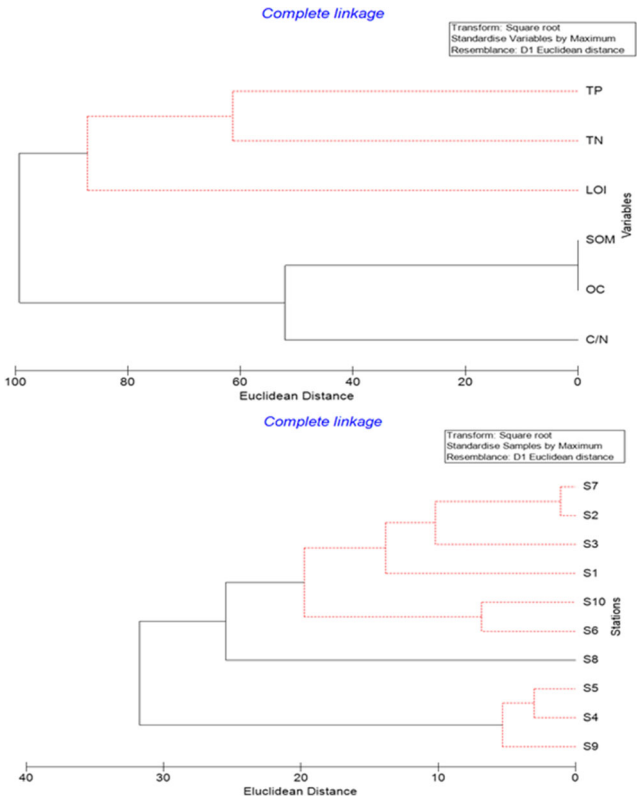

Fig. 2 Hierarchical dendrograms of organic compounds with corresponding stations (S1 to S10). Two dendrograms are discernable. The thin red dotted lines indicate a significant structure of similarity (SIMPROF Test $p < 0.05$). The black thick lines indicate no significant structure. C/N, carbon and nitrogen ratio; OC, organic carbon; SOM, sediment organic matter; LOI, weight loss on ignition, TP, total phosphate; TN, total nitrogen

OC in the sediment obtained by the WB Method ranged from 0.49 to 2.05 (%) with a mean value of 1.28 ± 0.51% (Table 3). TN in the sediment ranged from 0.06 to 0.15% with a mean value of 0.09 ± 0.03% (Table 3). The lowest total nitrogen content was recorded at the stations (S6, S10) and the highest at S8. Wetland zones characterized by mangroves contained nutrient-rich sediment as observed at S8. Mangroves act as a natural barrier against the ocean and are important habitats for shorebirds, nursing grounds for commercially important fin and shellfish. Nitrogen and phosphorus are major nutrients present in water, sediment-water interfaces, and within the sediment (Rysgaard et al. 1993; Cibic et al. 2008). Total dissolved nitrogen occurs as nitrate (NO_3^2), nitrite (NO_2^2), ammonium (NH_4^+), and soluble organic compounds, whereas, total dissolved phosphorous occurs primarily as phosphates in natural waters and wastewaters (Sattayatewa et al. 2011). Increased nutrient loads, particularly N and P induce the growth of opportunistic producers in coastal ecosystems (Elser et al. 2007). Eutrophication (nutrient enrichment) is defined as the increase in organic matter supply to an ecosystem, and this is also associated with extensive ecological and economic costs such as reduced water and sediment quality, altered aquatic communities, and loss of cultural amenity (Nixon et al. 2001; Paerl et al. 2014).

The C/N ratio ranged from 8.00 to 34.81% with a mean value of 16.33 ± 9.42% (Table 3). The lowest C/N ratio was recorded at S6 and the highest at S9. The carbon to nitrogen is higher in sediment from seawards. The natural source of carbon is high in marine waters as found at S9. The C/N ratio may also contribute to the organic matter in the sediment. The C/N ratio values between 4 and 6 are attributed to intense bacterial activity, from 4 to 7 as deriving from plankton and benthos (marine origin); values from 8 to 12 are interpreted as a mixture of marine plankton and terrestrial plants (mixed origin) and above 20 to continental origin (Ruttenberg and Goñi 1997; Jennerjahn et al. 2004; Barcellos et al. 2014). The carbon-to-nitrogen ratio of most sediment is relatively constant, near 12:1.

Sediment TP concentrations ranged from 0.49 to 1.34 (%) with a mean value of 0.70 ± 0.31% (Table 3). The lowest total phosphate concentration was recorded at S9 and the highest at S1. High input of total phosphate originates landwards, caused

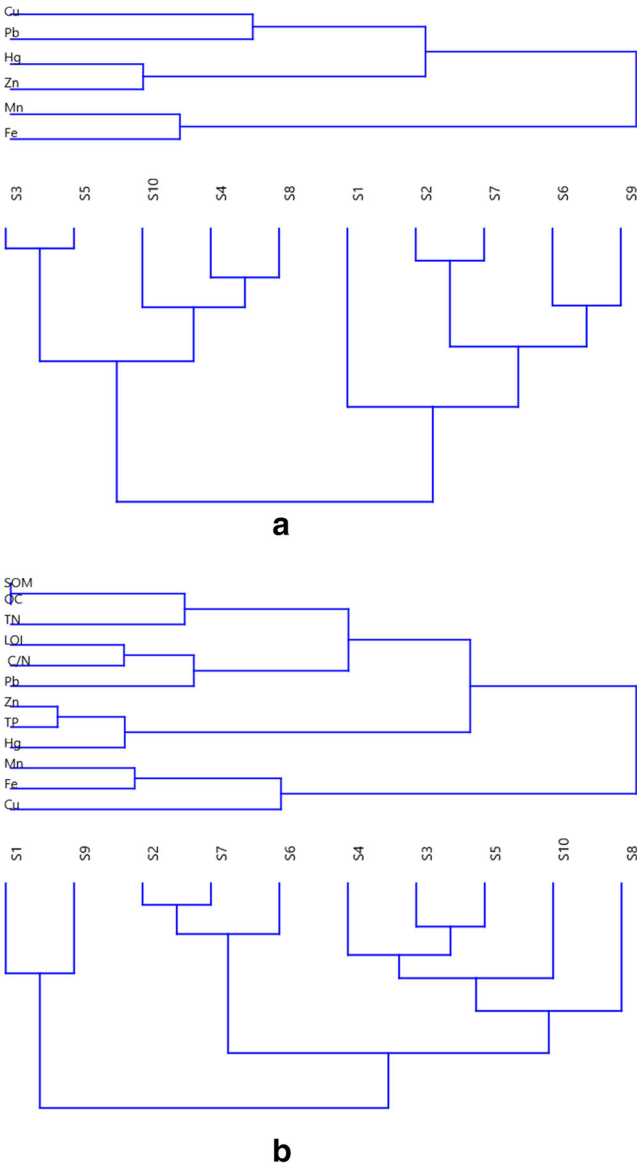

Fig. 3 **a** Hierarchical clustering analysis metals with corresponding stations (S1 to S10). Cu, copper; Pb, lead; Hg, mercury; Zn, zinc; Mn, manganese; Fe, iron. Metals with similar affinity are paired together, suggesting similar sources of geochemical processes. **b** Hierarchical clustering analysis metals and organic integrated. Distance metrics are based on the Euclidean distance on Ward's method (two-way constrained). Cu, copper; Pb, lead; Hg, mercury; Zn, zinc; Mn, manganese; Fe, iron; C/N, carbon-to-nitrogen ratio; OC, organic carbon; SOM, sediment organic matter; LOI, weight loss on ignition, TP, total phosphate; TN, total nitrogen. The integration showed a combined affinity of organic minerals and inorganic (metals) and similar pathways of pollution and geochemical processes

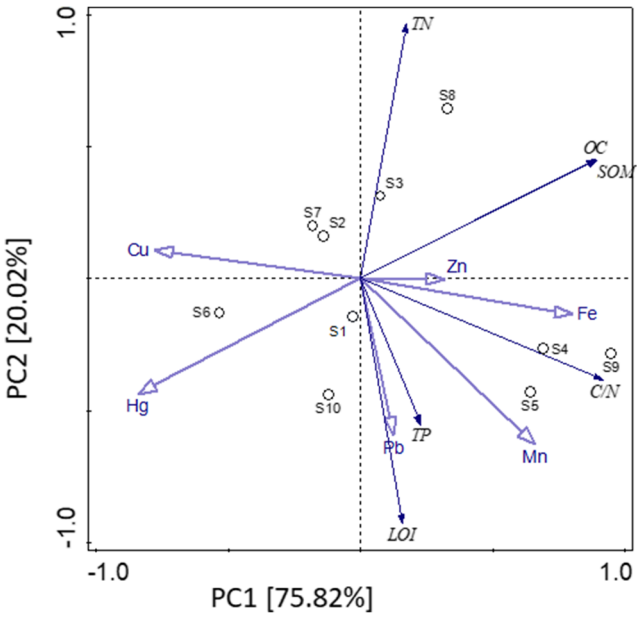

Fig. 4 Principal component analysis (PCA) of organic and metals in the ten sampling stations (S1 to S10). The PCA shows similar groups and sources of variation for metals and organic properties of sediment in the Densu Estuary. The first and second axis contributes to 95.48% of the total variation. Orientations of arrows indicate the correlation between organic and metals in principal component analyses ordination axes. The major contaminants for the cluster of stations are indicated by long arrows. C/N, carbon and nitrogen ratio; OC, organic carbon; SOM, sediment organic matter; LOI, loss on ignition, TP, total phosphate; TN, total nitrogen; Cu, copper; Pb, lead; Hg, mercury; Zn, zinc; Mn, manganese; Fe, iron

by human activities such as domestic waste, sewage effluent, and agrochemicals from farmlands. Phosphorus is a major nutrient, and there are various forms in the soil (Grimshaw 1987). Regeneration of bioavailable dissolved P from particulate matter is an important process of maintaining P availability in estuarine and marine ecosystems (Benitez-Nelson and Buesseler 1999; Karl and Björkman 2002). Sediments act as reservoirs of nutrients such as nitrogen and phosphorous, replenishment and renewal helps to sustain the biological system (Howarth 2008; Parkinson and Dusta 2010). Coastal eutrophication originates from excess nutrients, mainly nitrogen and phosphorus (Howarth 2008; Sattayatewa et al. 2011). The excess nutrients may lead to hypoxia, anoxia, habitat degradation, alteration of the food web structure, loss of biodiversity, and increased algal blooms (Boesch 2002; Howarth 2002).

SOM obtained by the Walkley-Black method ranged from 0.85 to 3.53 (%) with a mean value of 2.20 ± 0.89% (Table 3). The lowest sediment organic matter was recorded at S6 and the highest at S9 (Table 3). Station 6 is characterized by oyster farming and mangroves, a productive zone with higher photosynthetic activities. Whereas, S9 is located seawards. Sediment organic matter obtained by combustion (LOI) ranged from 1.12 to 1.71 (%) with a mean value of 1.51 ± 0.21% (Table 3). The lowest (LOI) recorded at S8 and the highest at S3. Tidal transport from coastal wetlands ("outwelling") (Dittmar and Lara 2001), along with riverine fluxes (Opsahl and Benner 1997), provides the most important sources of terrigenous organic matter to the estuarine and ocean (Dittmar et al. 2006). Organic matter is a major food source of many detritivores and bottom-dwelling organisms

(Anderson 1979; Covich et al. 1999). The SOM is a product from the decomposition of plant residues, roots, and soil organisms whether living or dead (Brady 1974). The major nutrients of sediment organic matter are nitrogen, phosphorus, and sulfur, which become available through decay processes (Brady 1974; Bianchi et al. 2008). Organic matter can retain contaminants in sediments, its break-down products from the degradation processes can mobilize metals (Salomons and Förstner 1984; Garringa 1990; Förstner 2004). The Walkley-Black chemical oxidation and combustion (loss-on-ignition) are common methods used to estimate sediment organic matter in the marine and coastal environment (Frangipane et al. 2009; Wang et al. 2012; Avramidisa et al. 2015). The chemical oxidation methods require pretreatment with acid to remove carbonate for calcareous sediment, whereas the combustion does not involve any pretreatment (Frangipane et al. 2009; Wang et al. 2012; Avramidisa et al. 2015). This may account for the significant difference in the two methods used in the estimation of sediment organic matter (Table 3).

The first sedimentological sensitivity factor 1 (SSF_1) ranged from 1.67 to 7.25 suggest ultra-oligotrophic to the hypertrophic system (Table 4) (da Silveira et al. 2013). The second sedimentological sensitivity factor (SSF_2) ranged from 3.38 to 13.25 and reflects oligotrophic to hypertrophic status. The third sedimentological sensitivity factor (SSF_3) ranged from 2.87 to 12.50 and suggests an oligotrophic to hypertrophic status. Overall, the average values of sedimentology sensitivity factors reflect the mesotrophic status of Densu Estuary (Table 4). The trophic state is associated with the productivity of the ecosystem (Hakanson 1984; Hakanson et al. 2003; da Silveira et al. 2013).

Concentration of metals in sediment

The mean heavy metal concentrations (Table 5) in the sediment of the Densu Estuary were compared with local background levels (Table 6) (industrial mean values; before 1960 and after 1960 during the last 100 to 150 years) (Mahu 2014), other studies from estuaries in Ghana (Klubi et al. 2018), geological background reference values (Shale average and earth's crust values) (Turekian and Wedepohl 1961; Taylor 1964) and sediment quality guidelines (Giesy and Hoke 1990).

The mean concentration of metals (Pb, Zn, Hg, and Cu) in the surface sediment (Table 5) can be compared with past concentration (industrial values) (Table 6) in the sediment cores from the Densu Estuary. The mean concentrations of Pb and Zn (Table 5) in the surface sediments were higher than industrial values (Table 6) from a sediment core (Mahu 2014) and seasonal study (Addo 2017). The mean Pb concentrations (50.9 ± 24.3 mg/kg) (Table 5) were higher than concentrations (mg/kg) found in other estuaries: Volta Estuary (6.2 ± 3.6), Pra Estuary (10.8 ± 3.4), and Ankobra Estuary (10.6 ± 3.4) (Table 7) in Ghana, reflecting urban environmental pollution in Densu Estuary (Klubi et al. 2018). The mean concentrations of five metals (Fe, Mn, Zn, Cu, and Hg) with exception of Pb were below the Shale average and earth's crust values (Turekian and Wedepohl 1961; Taylor 1964, 1972, 1989) (Table 7), suggesting that these contaminants were of natural sources, although anthropogenic sources can also influence their availability and concentration in the sediment. However, the sources of Pb can be associated more with anthropogenic activities such as sewage sludge, fuel combustion and mining, than with natural influence, since the mean concentration was above the benchmarks, local background and geological reference values. The metal, Pb is a toxic element extensively derived from human activities such as sewage sludge, domestic and industrial waste and release from automobile exhaust and direct atmospheric deposition from polluted air (Bowen 1966; Sinex and Helz 1981; Sutherland 1999; Sharma and Dubey 2005; Pan and Wang 2012). Lead contamination in food can affect the lungs and digestive tract via contamination of the blood and can cause cancer (Schwartz 1994; Markowitz 2000; Gupta et al. 2010; Pan and Wang 2012). The lead poisoning is associated with the mental development of miners, women, and their children (Boeckx 1986; Silbergeld 1997; UNEP-UNICEF 1997).

The mean Zn (46.9 mg/kg) concentrations were higher than concentrations found in the wet season (28.9 ± mg/kg) and dry season (30.02 ± 0.9 mg/kg) (Table 6) (Addo 2017) in the same Densu Estuary reflecting the accumulation of metals with time. The mean Zn concentration was higher in Densu Estuary than in Pra River Estuary (51.0 ± 13.0 mg/kg) and Ankobra River Estuary (53.0 ± 15.0 mg/kg), indicating metal pollution in Densu Estuary (Klubi et al. 2018). It was however lower than Zn concentration in the sediment of Volta River Estuary (21.0 ± 10.0 mg/kg) (Klubi et al. 2018). There is a tendency of metals to accumulate in aquatic environments and transfer into the food chain as observed for Zn and Cu in sediment at the Densu Estuary (Table 6) (Addo 2017). The Zn and Cu concentrations were higher in sediment than water and high concentrations were also found in biota (fish and birds) (Table 6) in the aquatic ecosystem of Densu Estuary (Addo 2017). Zinc is an important constituent of cells, metabolic processes and several enzymes depend on zinc as a cofactor (Bowen 1966; Friberg et al. 1974; Kennish 1997). Human activities such as domestic and industrial sewage, runoff from agricultural activities, fossil fuels, and solid waste also release Zn into the sediment (Kennish 2001; Sastre et al. 2002; Pansare and Shaikh 2014). Zn contamination can cause vomiting, diarrhea, and gastric pain (Fosmire 1990; Mudgal et al. 2010). The mean Cu (10.9 ± 8.5 mg/kg) concentration was close to pre-industrial mean values (10.52 ± 3.32 mg/kg) but lower than post-industrial mean values (12.53 ± 1.05 mg/kg) (Table 6). Copper concentrations were lower than concentrations found in the sediment of Volta River Estuary (6. 4 ± 4.3 mg/kg), Pra River Estuary (23.1 ±

7.1 mg/kg), and Ankobra River Estuary (23.8 ± 7.9 mg/kg) (Table 6) (Klubi et al. 2018).

The mean Hg concentration (0.020 ± 0.011) was lower than pre-industrial (0.04 ± 0.0) but higher than post-industrial values (0.21 ± 0.15) (Table 6) (Mahu 2014). Hg is oxidized to mercuric mercury (Hg^{2+}) and methyl mercury (MeHg). These are soluble, mobile, and can quickly enter the food chain (Riisgard and Hansen 1990; Martins et al. 1998; Harris et al. 2003; Pan and Wang 2012). Mercury is extensively used by mankind in gold mining, ship paints, batteries, photographic materials, paper mills, paints, and leather (Bowen 1966; Martins et al. 1998; Scoullos et al. 2001). Mercury is harmful through consumption of methyl mercury-contaminated fish (Hall et al. 1997; Clarkson 2002; Elliott 2003; Sam et al. 2010), and mercury allergen causes contact eczema and accumulates in higher levels in the kidney than the brain and liver (Ullrich et al. 2001; Zahir et al. 2005; Mudgal et al. 2010). The mean Fe concentration (569.7 ± 8.5 mg/kg) was lower than found in Volta River Estuary (29,000 ± 13,000), Pra River Estuary (42, 000 ± 11,000 mg/kg), and Ankobra River Estuary (41, 000 ± 13, 000 mg/kg). Iron is a redox-sensitive element and originates from weathering processes, ore smelting, and scraps (Bowen 1966; Förstner and Wittmann 1983; Salomons et al. 1995). Large doses of iron and its oxide have caused hemorrhage and necrosis of the stomach and intestinal tissue (Bowen 1966; Fine 2000; Morais et al. 2012). The mean concentration of Mn (90.5 ± 45.7 mg/kg) was lower than that found in Volta Estuary (1800 ± 1500 mg/kg), Pra River Estuary (245.0 ± 46.0), and Ankobra River Estuary (261.0 ± 71.0 mg/kg). Manganese is an essential element and major constituent in several enzyme systems including the metabolism of pyruvic acid (Bowen 1966; Stumn and Morgan 1981; Cheng et al. 2017). Manganese is used in ore plants and manganese alloying mining (Bowen 1966; Ozseker et al. 2014). Manganese oxide poisoning results in health implications such as bronchitis, pneumonia, and mental deterioration (Bowen 1966; Ozseker et al. 2014).

Sediment contamination can be assessed according to sediment quality guidelines (SQGs) of the United States Environmental Protection Agency (USEPA) (Giesy and Hoke 1990) and Canadian sediment quality guidelines (CSQGs) (CCME 1995, 1999), Consensus-based sediment quality guidelines (CBSQGs)(Giesy and Hoke 1990). According to SQGs proposed by USEPA (Giesy and Hoke 1990), sediments can be categorized into three classes, non-polluted, moderately polluted, and heavily polluted (Table 7). By comparing the mean concentration of metals measured with the SQGs, the Densu Estuary was moderately polluted with Pb. The SQGs developed by the USEPA do not consider the natural background and multiple metals. The limitation of USEPA SQGs can be overcome by comparing data with geological reference values (Burton 2002). The mean concentrations of metals (Zn, Hg, Fe, Cu, and Mn) except Pb were below geological reference average values (Table 7). The mean metals concentrations in Densu Estuary were below consensus-based sediment quality guidelines (Table 7).

Heavy metals in aquatic environments originate from sources such as effluents, tannery, metallurgy, dyes, explosives, ceramics, paints, and textiles (Athar and Vohora 2001; Gheorghe et al. 2017; Masindi and Muedi 2018). The major anthropogenic sources of metals in the environment are the combustion of fossil fuels, mining and smelting operations, processing and manufacturing industries and waste disposal including dumping, release of domestic sewage and scrap metal handling, and runoff from chemicals used on agricultural farms such as fertilizers and pesticides (Förstner and Wittmann 1983; Kennish 1997). Metal pollution is a global environmental and public health problem (Nelson 1996; Mudgal et al. 2010; Pan and Wang 2012; Maadin et al. 2016). Metals are essential microelements, micronutrients, and macronutrients, and their deficiency can cause impairments of the biological function (Pansare and Shaikh 2014; Simionov et al. 2016). However, high concentrations of metals may become toxic to aquatic organisms and human beings through contamination in the food chain (Underwood 1977; Salomons et al. 1995; Mudgal et al. 2010; Pansare and Shaikh 2014; Stankovic et al. 2014). Sediments act as a pool of metals that can be released to the overlying water from natural and anthropogenic processes such as bioturbation and dredging, resulting in potentially adverse health effects (Kim et al. 2009; McComb et al. 2014). Heavy metal contamination is a critical environmental challenge that threatens animals, plants, and human health (Kim et al. 2009; Nowrouzi and Pourkhabbaz 2014). The presence of heavy metals in sediments is affected by the particle size of the sediments due to sorption, co-precipitation, and complexity of metals on particle surfaces and coatings (Sakai et al. 1986; Krishna and Mohan 2014). Many metals (Cu, Zn, Fe, and Mn) are biologically active elements because they are needed for metabolic activity and physiological functions while other elements such as Hg and Pb are not known to be essential for living organisms (McComb et al. 2014; Pansare and Shaikh 2014). Rare metals (Pb and Hg) with no essential biological functions but are highly toxic to plants and animals in the aquatic environment and humans (Conceiçao et al. 2012; Mohammadnabizadeh et al. 2012; Norouzi et al. 2012). Heavy metals have great economic ecological significance due to their toxicity and tendency to accumulate in the water, sediment, and biota (Kennish 2001and Oyem et al. 2015and Soliman et al. 2015). The metals contaminations in different media (water, sediment and biota) travel through the food chain to the food web and eventually human beings (Rajeswari and Sailaja 2014; Simionov et al. 2016). Heavy metals affect human beings through three major systems, namely the nervous system, the cardiovascular system and the immune system (Kennish 1997; Pansare and Shaikh

2014). Metals become toxic in excess and may lead to human-related illness such as carcinomas, hypertension and heart disease (Diagomanolin et al. 2004; Maadin et al. 2016). Excessive levels of elements in the aquatic environment can affect aquatic life and fish consumers (MacFarlane and Burchettt 2000; Remyla et al. 2008; Öztürk et al. 2009).

Organic properties of sediment and inorganics originate from human activities such as the use of chemical fertilizers in agricultural farmland, discharge of industrial and domestic effluents, use of chemicals in mining and atmospheric depositions of metals (Förstner 1990; Karageorgis et al. 2002; Masindi and Muedi 2018). Metals distribution in sediments can provide evidence of human activities and their effects on ecosystems and it is important for an assessment of the risks associated with human waste discharges (Bowen 1966; Olubunmi and Olorunsola 2010). Organic matter from untreated sewage transforms organic Hg into methyl mercury, which can be transferred into the trophic food web (Berry et al. 1974; Martins et al. 1998). The cluster analysis and principal component analysis suggest similar sources of chemical contaminants and the possibility of co-mobilization of metals showed by the pairing of three major groups of metals. The presence and pairing of redox-sensitive metals (Mn and Fe) suggest insufficient oxygenation within the sediment (Kumar et al. 2011; Özkan 2012). The metals, Fe and Mn mobilization in the sediment at the reducing condition Fe^{2+} rapidly precipitate on the sediment (Matthiesen 1998). The Fe and Mn seem to come from natural sources. But reduced and dissolved Mn diffuses overlying oxic water (Matthiesen 1998). The labile Mn should not be attributed to the possible anthropogenic source, because Mn tends to be present in a less thermodynamically stable form in sediment phases such as Mn^{+2}, easily reducible Mn oxides and Mn enclosed in carbonate minerals (Angelidis and Aloupi 2000).

Potential ecological risk index

The summary of average geochemical indices (enrichment factor, contamination factor and geoaccumulation index, Table 8) based on geological and local background data showed similarity but never the same interpretation (Appendices Table 11, 12, and 13). The enrichment factor analyses showed extremely severe enrichment ($EF > 50$) for Pb and no enrichment for Cu ($EF < 1$) (Table 8; Appendices Table 11 and 14) irrespective of the background references. EF values lower than 1.5 (García et al. 2008) or less than 2.0 (Abreu et al. 2016) indicate that the metal is predominantly from lithogenous material whereas EF values higher than 1.5 or 2.0 suggest the metal is from an increasing portion of the anthropogenic source (Szefer et al. 1996; Zhang and Liu 2002). The metals (Pb, Zn, Hg, and Mn) had enrichment factors greater than 2, suggesting anthropogenic sources such as fuel combustion, agrochemicals, land runoff, and effluents, although they can be originated from natural sources. The high enrichment of sediment with Pb can be attributed to anthropogenic causes, although there can also be natural causes (Özkan 2012).

The decreasing order of the average contamination factor (based on local background) (Tables 7 and 9; Appendices Table 12) was Pb (6.4 ± 3.0) > Zn (1.9 ± 0.7) > Cu (1.0 ± 0.8) > Hg (0.5 ± 0.3) > Mn (0.1 ± 0.1) > Fe (0.0 ± 0.0), suggesting the considerable contamination by Pb ($CF \geq 6$), proceeded by moderate contamination by Zn and Cu ($1 \leq CF < 3$) and low contamination by Hg and Mn ($CF < 1$). There is low ($CF < 1$) to a considerable ($3 \leq CF \geq 6$) metal contamination in the sediment of the Densu Estuary. The high CF value found in Pb ($3 \leq CF \geq 6$) suggested considerable to very high contamination of sediments while five metals (Zn, Hg, Cu Mn, and Fe) exhibited low levels of contamination ($CF < 1$) (Table 8; Appendix Table 12).

The average values of geoaccumulation index of the metals (Pb, 1.7 ± 1.6 > Zn, -0.2 ± 1.4 > Cu, -1.0 ± 1.3 > Hg, -1.7 ± 0.8 > Mn, -3.7 ± 0.8) reflect unpolluted to moderate pollution by Pb and non-pollution by other metals (Tables 9 and 10; Appendices Table 13 and 14) irrespective of the background. The Igeo was negative for all the metals except Pb, indicating the absence of pollution by these metals. The lead had a higher average value ($0 < Igeo \leq 2$) than other metals (Zn, Hg, Cu, and Mn) ($Igeo < 0$) (Tables 7 and 8; Appendices Table 13 and 14). The sediment was unpolluted to moderately polluted by Pb originating from anthropogenic sources, although there can be natural sources, whereas the average of Igeo values ($Igeo < 0$) for the other metals (Zn, Hg, Cu, and Mn) suggest non-pollution (Appendix Table 13) of the sediment. The average geoaccumulation index of the metals (Pb, Zn) was higher in the Densu Estuary (Pb = 1.7, Zn = 1.2) (Table 9) than that found in the Pra Estuary (Pb = 0.4; Zn = 0.9) and Ankobra Estuary (Pb = 0.3, Zn = 0.9) (Klubi et al. 2018). The average Igeo of Mn in the sediment of the Densu Estuary (− 2.9) was close to Igeo of Mn in the Pra Estuary (− 3.0) and Ankobra Estuary (− 2.8) (Table 9) (Klubi et al. 2018). The Igeo of Zn (1.2) in the sediment of Densu Estuary was lower than Pra Estuary (1.6) and Ankobra Estuary (1.5) (Table 9) (Klubi et al. 2018). The negative Igeo means that metal concentrations (Zn, Mn, Hg, Cu) were lower than the geological and local background values and vice versa for positive values observed for Pb (Özkan 2012). The index of geoaccumulation is a quantitative measure of the degree of pollution in aquatic sediments (Singh et al. 2005).

Overall, there is low ($3 \leq DC < 6$) to a very high ($DC \geq 6$) DC (Table 7) of metals in the sediment of the Densu Estuary based on the background reference. The local background reference revealed a very high degree of contamination ($DC = 9.78$, $DC \geq 6$) with a ranking of 10 for the Densu Estuary. The DC (the sum of CF of all the metals) was 9.87, suggesting a very high considerable metal contamination in the Densu Estuary. The very high enrichment of metals in the sediment may impact on bottom-dwelling organisms. The enrichment factor is much less variable than the average concentration of metals (Sinex and Helz 1981). However, it is not sufficient to use enrichment factor only for the evaluation of toxicological risk

at a particular site. Consideration of assessment of CF, PERI, and DC in sediment provided a holistic evaluation of the ecological risk at a particular site (Gong et al. 2008; Wei and Yang 2010). The higher the CF of a metal, the higher the PER as observed for the lead. Pb (< 40 PER < 80) and Hg (ranged PER < 40) are the most toxic metals which contributed to the potential ecological risk (Table 8). The metals Pb and Hg are without any biological significance but extremely toxic (Rajeswari and Sailaja 2014). Copper and Zn in the sediment showed very low potential ecological risk (PER < 40). The potential ecological risk index (sum of all PER) ranged from 40 ≤ PERI < 80 (Table 8). The higher the CF, the higher PER and PERI, and vice versa. Although there is low-risk PERI, the PER showed Pb and Hg as the most toxic metals with potential ecological risk to the ecosystem, which requires further investigation on their pathways through the food chain. Mercury (Hg), although it occurred in minute amount is very toxic. Non-treatment of domestic, industrial and municipal waste discharges, chemicals from agricultural runoff activities contribute to metal contamination in the Densu Estuary.

Clusters, principal component analyses, and correlations

The cluster of organic properties of sediment into two groups showed circulation levels in the sediment (organic matter, organic carbon and carbon-to-nitrogen ratio) and nutrients levels (total nitrogen, total phosphate and loss-on-ignition). The clustering of metals into three major groups (i) (Cu and Pb); (ii) (Hg and Zn) and (Mn and Fe) (Fig. 3a) indicate the binding effect and movement of metals in the sediment from similar sources. Cu moves with Pb, Hg with Zn, and Mn with Fe. Each pair of groups indicate that their availability is from similar sources and similar geochemical processes controlling the occurrence of these metals in the sediment (Soliman et al. 2015). The integrated cluster of organics and metals reflect metal mobility and binding effects with the organic characteristics of the sediment. PCA showed similar sources for each pair of metal contaminants, suggesting similar local geochemical processes controlling the occurrence of these metals, spatial variability and the possibility of human activities surrounding the catchment of the Densu Estuary. Inter-element relationships in the sediment provide information on metal sources and pathways in the geo-environment (Dragovi et al. 2008).

Carbon-to-nitrogen ratio showed significant positive correlation ($r = 0.738$; $p < 0.05$) (Appendix Table 14) with organic carbon suggesting common sources of contamination. The carbon-to-nitrogen ratio increased with an increase in the organic carbon content of the sediment. There was a significant positive correlation ($r = 1.000$; $p < 0.000$) between sediment organic matter and organic carbon, suggesting similar sources of contamination and strong binding effects. The sediment organic matter and organic carbon have a strong relationship (Fig. 5) since they contribute to the carbon cycle of estuarine systems. The significant positive correlation between Hg and Zn ($r = 0.668$; $p < 0.05$) indicated that the two metals accumulate together, have a similar source of contamination, mobility, redistribution, and physical and chemical properties. Cu showed a significant negative correlation ($r = -0.845$; $p < 0.05$) with Fe, which suggests that when Cu concentrations increase, there will be a decrease in Fe concentrations in sediment with dissimilar sources of metal availability and contamination. Hg exhibited a positive correlation ($r = 0.723$; $p < 0.05$) with total phosphates, an indication that total phosphate has an important binding effect to Hg (Hg-TP). There was a significant negative correlation ($r = -0.711$; $p < 0.05$) between Cu and organic carbon and sediment organic matter suggesting the availability of Cu in the sediment decreases with the increase in organic carbon and organic matter concentration in the sediment and these organics properties do not have a binding effect with Cu. The significant Pearson's correlation analysis confirmed the ordination of chemical contaminants in the PCA. The significantly positive correlation indicates that the elements were derived from similar sources and similar mobility in sediment (Benhaddya and Hadjel 2013).

Correlation matrix combined with multivariate principal component analysis and cluster analysis suggested that three metals (Zn, Hg, Cu) originated from proximal sources such as landfill sites, agrochemicals, effluents, mining, whereas the other three metals (Pb, Fe, and Mn) primarily originating from distal sources of contaminants with contributions from anthropogenic and natural activities are possible. Since the Pb concentration was higher than the natural geological reference values, this may suggest anthropogenic inputs into the Densu Estuary. Heavy metal sources in coastal environment originate from natural sources such as atmospheric deposition, weathering of rocks, and coastal erosion (Yusof and Wood 1993; Nobi et al. 2010), whereas anthropogenic sources include agriculture activities, disposal of liquid effluents, and urban and industrial emission (Rivail Da Silva et al. 1996; Pekey et al. 2004). The sources of Fe could

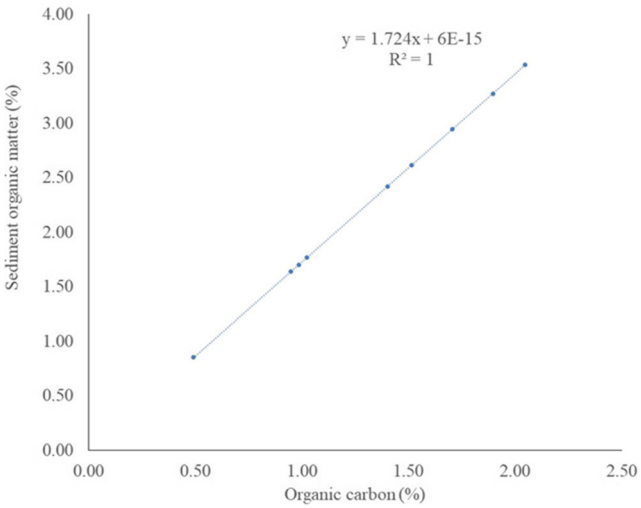

Fig. 5 Linear relationship between sediment organic matter (%) and organic carbon (%) at the Densu Estuary, Ghana.

be local weathering of rocks, which form in the sediments, corrosive processes, and anoxic conditions. The high mean concentration of Fe could be due to weathering of granite rocks within the Densu basin since the Densu basin is composed of granite with 2.8% Fe_2O_3 (Kerbyson and Schandorf 1966) and 2.67% FeO (Kesse 1985).

Conclusions

Densu Estuary is an important socio-economic ecosystem situated in the urban center of Accra, surrounded by industrialization and agricultural activities in the densely populated coastal area of the Gulf of Guinea, Ghana. The study assessed the spatial distribution of organics and concentrations of metals and their potential ecological risk assessment to understand environmental risks towards sustainable management of the estuarine. The potential ecological risk of metals was evaluated using multiple geochemical indices (EF, Igeo, PLI, CF, and PERI) for quantitative assessment of sediment quality. Overall, the Densu Estuary is a mesotrophic ecosystem with moderate to low ecological risk of geochemical contaminants.

The sediment was dominated by sand (62.2 ± 9.37%) > silt (33.57 ± 8.87%) > clay (4.13 ± 2.25%). The means of organic characteristics of the sediment in [%] were organic carbon, 1.28 ± 0.51; 354; total nitrogen ± 0.09; carbon-to-nitrogen ratio, 16.33 ± 9.42; total phosphate, 0.70 ± 0.31; sediment organic matter, 2.20 ± 0.89; and loss on ignition, 1.51 ± 0.21. Cluster analyses showed two groups of organic properties of the sediment. The first group was made up of sediment nutrients, mainly total nitrogen, total phosphate, and loss on ignition, whereas the second group consisted of sediment organic matter, organic carbon, and carbon-to-nitrogen ratio. The percentage of organic characteristics of the sediment of the Densu Estuary may not be too harmful to ecosystem health.

The decreasing order of mean concentrations of metals (mg/kg) in sediment were Fe (569 ± 176.27) > Mn (90 ± 45.68) > Pb (50.88 ± 24.33) > Zn (46.93 ± 45.01) > Cu (10.92 ± 8.47) > Hg (0.02 ± 0.01). The descending order of the average enrichment factor of metals was Pb > Zn > Mn > Hg > Cu. The sediment was severely enriched by Pb compared with other metals (Zn, Hg, Mn, and Cu). Metal enrichment in the sediment was in the order of extremely high enrichment with Pb (EF > 50) and very high enriched by Zn (EF = > 50), significantly enriched by two metals (Hg and Mn; EF = 5–20) and no enrichment for Cu (EF < 1). Only Cu had an EF of less than 1, suggesting natural origin. The decreasing order of mean contamination factors was Pb > Zn > Hg > Cu > Mn > Fe. The descending order of the mean contamination factors was Pb (6.4 ± 3.0) > Zn (1.9 ± 0.7) > Cu (1.0 ± 0.8) > Hg (0.5 ± 0.3) > Mn (0.1 ± 0.1) > Fe (0.0 ± 0.0). Five metals (Zn, Hg, Fe, Cu, and Mn) exhibited low contamination (CF < 1) while there was considerable contamination for Pb (3 ≤ CF ≥ 6). The decreasing order of average Igeo was Pb > Zn > Hg > Cu > Mn. The order of PER for the metals was Pb > Hg > Cu > Zn (Table 10) excluding Fe and Mn. Although sediment contained a high mean concentration of Fe due to anoxic conditions in Densu Estuary, the elevated mean metal concentration and mean values of geostatistical analyses (EF, Igeo, and CF) suggested considerable pollution of the surface sediment of Densu Estuary by Pb and Zn irrespective of the background reference. The mean concentration of Pb exceeded the local background and geological reference values suggesting anthropogenic inputs via sewage effluents and domestic and industrial waste discharges into the Estuary.

The decreasing order of PER of metals was Pb (PER = 44.75) > Hg (PER = 28.78) > Cu (PER = 7.29) > Zn (PER = 2.62). The risk assessment showed that Pb had the highest ecological risk, followed by Hg while Zn had the lowest risk. The DC (DC = 9.87) indicated a very high considerable contamination (DC ≥ 6) of metals at the Densu Estuary with a DC ranking of 10 based on local pre-industrial background values. The potential ecological risk of Pb exceeded 40 (PER = 44.75) with local background references. The PERI (the sum of potential ecological risk of each metal) for Densu Estuary based on the local background was 82.42 (80 ≤ PERI ≤ 150), suggesting low ecological risk. The PLI (4.79 ± 14.4; PLI > 3) indicated extremely heavy pollution in the Densu Estuary.

Multiple geostatistical analyses provided quantitative sediment quality assessment. The Densu Estuary is known for its oyster aquaculture and fishing activities. The study contributes to the understanding of chemical contaminants in the sediment from the tropical estuarine system, the basis for the reconstruction of past pollution in coastal systems. Enforcement of existing legislation should be taken to reduce the accumulation of metal pollutants to promote the eco-sustainability of the system.

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Author' contributions Lailah Gifty Akita: conceptualization, investigation, methodology, formal analysis, funding acquisition, and writing-original draft preparation. Laudien Juergen: conceptualization, funding acquisition, and writing-original draft preparation. Nyarko Elvis: methodology, funding acquisition, writing-review, and editing.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Appendix

Table 11 Enrichment factors estimated for the metals measured at the Densu Estuary, Ghana

Parameter	Min	Max	Mean ± SD	Classification[a]
Zn1	7.58	63.63	29.57 ± 19.9	Very severe enrichment
Zn2	9.49	79.66	37.02 ± 24.9	Very severe enrichment
Zn3	24.50	205.55	95.53 ± 64.3	Extremely severe enrichment
Zn4	19.32	162.11	75.34 ± 50.7	Extremely severe enrichment
Pb1	7.99	524.82	234.54 ± 156.1	Extremely severe enrichment
Pb2	8.05	528.86	236.35 ± 157.3	Extremely severe enrichment
Pb3	17.11	1123.82	502.24 ± 334.3	Extremely severe enrichment
Pb4	12.29	807.05	360.67 ± 240.1	Extremely severe enrichment
Hg1	3.42	33.93	10.58 ± 9.9	Severe enrichment
Hg2	10.56	104.62	32.64 ± 30.8	Extremely severe enrichment
Hg3	13.20	130.78	40.80 ± 38.5	Extremely severe enrichment
Hg4	2.51	24.91	7.77 ± 7.3	Severe enrichment
Cu1	0.00	0.00	0.00 ± 0.0	No enrichment
Cu2	0.00	0.00	0.00 ± 0.0	No enrichment
Cu3	0.00	0.00	0.00 ± 0.0	No enrichment
Cu4	0.00	0.00	0.00 ± 0.0	No enrichment
Mn1	3.06	14.89	9.13 ± 3.9	Severe enrichment
Mn2	3.30	20.00	9.61 ± 5.0	Severe enrichment
Mn3	3.28	15.94	9.78 ± 4.2	Severe enrichment
Mn4	3.28	15.94	9.78 ± 4.2	Severe enrichment

Min, minimum; *Max*, maximum; *SD*, standard deviation

[a] Classification based on the mean values: EF < 2 = no enrichment; 2 ≤ EF < 3 = minor enrichment; 3 ≤ EF < 5 = moderate enrichment; 5 ≤ EF < 10 = moderately severe enrichment; 10 ≤ EF < 25 = severe enrichment; 25 ≤ EF < 50 = very severe enrichment; EF > 50 = extremely severe enrichment. Estimated: 1 = shale average; 2 = earth crust; 3 = pre-industrial; 4 = post-industrial

Table 12 Contamination factors estimated for the metals measured at the Densu Estuary, Ghana

Parameters	Min	Max	Mean ± SD	Classification[a]
Zn1	0.08	1.67	0.49 ± 0.5	Low contamination
Zn2	0.11	2.44	0.72 ± 0.7	Low contamination
Zn3	0.29	6.28	1.86 ± 1.8	Moderate contamination
Zn4	0.23	4.96	1.47 ± 1.4	Moderate contamination
Pb1	0.10	4.24	2.54 ± 1.2	Considerable contamination
Pb2	0.11	4.98	2.99 ± 1.4	Considerable contamination
Pb3	0.24	10.59	6.36 ± 3.0	Considerable contamination
Pb4	0.17	7.60	4.57 ± 2.2	Considerable contamination
Hg1	0.04	0.25	0.11 ± 0.1	Low contamination
Hg2	0.15	0.91	0.41 ± 0.2	Low contamination
Hg3	0.19	1.14	0.51 ± 0.3	Low contamination
Hg4	0.04	0.22	0.10 ± 0.1	Low contamination
Fe1	0.00	0.02	0.01 ± 0.0	Low contamination
Fe2	0.00	0.02	0.01 ± 0.0	Low contamination
Fe3	0.01	0.02	0.01 ± 0.0	Low contamination
Fe4	0.01	0.02	0.01 ± 0.0	Low contamination
Cu1	0.00	0.51	0.18 ± 0.2	Low contamination
Cu2	0.00	0.58	0.20 ± 0.2	Low contamination
Cu3	0.32	2.19	1.04 ± 0.8	Moderate contamination
Cu4	0.27	1.84	0.87 ± 0.7	Moderate contamination
Mn1	0.00	0.18	0.09 ± 0.1	Low contamination
Mn2	0.00	0.22	0.11 ± 0.1	Low contamination
Mn3	0.06	0.22	0.13 ± 0.1	Low contamination
Mn4	0.06	0.22	0.13 ± 0.1	Low contamination

Min, minimum; *Max*, maximum; *SD*, standard deviation

[a] Classification based on mean values: CF < 1 = low contamination; 1 ≤ CF < 3 = moderate contamination; 3 ≤ CF < 6 = considerable contamination; CF ≥ 6 = very high contamination. Estimated: 1 = shale average; 2 = earth crust; 3 = pre-industrial; 4 = post-industrial

Table 13 Geoaccumulation indices estimated for the metals measured at the Densu Estuary, Ghana

Parameters	Min	Max	Mean ± SD	Classification[a]
Zn1	− 4.29	0.15	− 2.15 ± 1.4	Unpolluted
Zn2	− 3.74	0.7	− 1.6 ± 1.4	Unpolluted
Zn3	− 2.37	2.07	− 0.23 ± 1.4	Unpolluted
Zn4	− 2.71	1.72	− 0.57 ± 1.4	Unpolluted
Pb1	− 3.98	1.5	0.36 ± 1.6	Unpolluted to moderately polluted
Pb2	− 3.75	1.73	0.59 ± 1.6	Unpolluted to moderately polluted
Pb3	− 2.66	2.82	1.68 ± 1.6	Moderately polluted
Pb4	− 3.14	2.34	1.2 ± 1.6	Moderately polluted
Hg1	− 5.13	− 2.57	− 3.9 ± 0.8	Unpolluted
Hg2	− 3.28	− 0.72	− 2.05 ± 0.8	Unpolluted
Hg3	− 2.96	− 0.4	− 1.73 ± 0.8	Unpolluted
Hg4	− 5.35	− 2.79	− 4.12 ± 0.8	Unpolluted
Cu1	− 4.31	− 1.55	− 3.06 ± 1.3	Unpolluted
Cu2	− 4.14	− 1.38	− 2.89 ± 1.3	Unpolluted
Cu3	− 2.21	0.54	− 0.96 ± 1.3	Unpolluted
Cu4	− 2.47	0.29	− 1.21 ± 1.3	Unpolluted
Mn1	− 4.99	− 3.06	− 3.99 ± 1.8	Unpolluted
Mn2	− 4.67	− 2.74	− 3.67 ± 0.8	Unpolluted
Mn3	− 4.67	− 2.74	− 3.67 ± 0.8	Unpolluted
Mn4	− 4.67	− 2.74	− 3.67 ± 0.8	Unpolluted

Min, minimum; *Max*, maximum; *SD*, standard deviation

[a] Classification based on mean values: Igeo ≤ 0 = unpolluted; 0 < Igeo ≤ 1 = unpolluted to moderately polluted; 1 < Igeo ≤ 2 = moderately polluted; 2 < Igeo ≤ 3 = moderately to strongly polluted; 3 < Igeo ≤ 4 = strongly polluted; 4 < Igeo ≤ 5 = strongly to extremely polluted; Igeo > 5 = extremely polluted. Estimated: 1 = shale average; 2 = earth crust; 3 = pre-industrial; 4 = post-industrial

Table 14 Pearson's correlation for organics and metals concentrations in the sediment of the Densu Estuary, Ghana

	OC	TN	C/N	TP	SOM	LOI	Zn	Pb	Hg	Fe	Cu	Mn
OC	1											
TN	0.201	1										
C/N	*0.738**	− 0.505	1									
TP	− 0.259	0.004	− 0.246	1								
SOM	*1.000***	0.201	*0.738**	− 0.259	1							
LOI	0.178	− 0.524	0.548	0.260	0.178	1						
Zn	− 0.035	0.178	− 0.177	*0.923***	− 0.035	0.067	1					
Pb	− 0.124	− 0.236	0.140	− 0.060	− 0.124	0.543	− 0.248	1				
Hg	− 0.628	− 0.224	− 0.410	*0.723**	− 0.628	0.038	*0.668**	− 0.048	1			
Fe	0.584	0.121	0.455	0.065	0.584	0.524	− 0.016	0.250	− 0.456	1		
Cu	*− 0.711**	− 0.071	− 0.575	0.019	*− 0.711**	− 0.465	0.036	0.054	0.575	*− 0.845***	1	
Mn	0.096	0.045	0.098	0.107	0.096	0.415	− 0.095	0.476	− 0.344	0.559	− 0.593	1

OC, organic carbon; *TN*, total nitrogen; *C/N*, carbon-to-nitrogen ratio; *TP*, total phosphate; *SOM*, sediment organic matter; *LOI*, loss on ignition; *Zn*, zinc; *Pb*, lead; *Hg*, mercury; *Fe*, iron; *Cu*, copper; *Mn*, manganese

*Correlation is significant at the 0.05 level (2-tailed); **correlation is significant at the 0.01 level (2-tailed)

The italics showed significant Pearson Correlations, thus the potential associations between the geochemical contaminants

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