Pollution fingerprinting of two southwestern estuaries in Ghana

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ABSTRACT

The present study assessed the pollution fingerprints of two estuaries (Pra and Ankobra) in the Southwestern region of Ghana. Contaminations of sediments in the two estuaries were evaluated for particle size distribution, total organic matter, microplastics, nitrate-nitrogen, phosphorous, and metals. The results revealed the mean concentration of microplastics particles in Pra as follows: fibre (14.22 ± 4.99); sheet (24.44 ± 13.21); fragment (38.00 ± 25.47); bead (4.22 ± 4.84); and in Ankobra as follows: fibre (13.00 ± 7.56); sheet (20.60 ± 12.59); fragment (8.70 ± 11.22); bead (3.30 ± 4.14). Metal concentrations were in the order Fe > As > Zn > Cu > Pb; concentrations of Cd and Hg were below the detection limit. Pb, Cu, and Zn were within Interim Marine Sediment Quality Guidelines except for Fe and As. The respective order of contamination factor and geo-accumulation index of the metals were As > Fe > Zn > Pb > Cu and As > Fe > Pb > Cu. The pollution load index recorded for Pra and Ankobra estuaries were 1.94 and 2.71, respectively, suggesting deterioration of the estuaries due to metal pollution. The principal component analysis indicated that pollution fingerprinting is strongly influenced by Fe, Cu, As, Zn, silt, and sand associated with illegal artisanal gold mining activities. Thus, the findings from this study imply that the levels of pollution recorded could have deleterious impact on human health and the communities that depend on the services rendered by the estuaries. There is the need to adopt strategies for pollution control to protect these fragile ecosystems that support livelihoods.

1. Introduction

Estuaries are transition water bodies that border freshwater bodies and the ocean. They provide several ecosystem services for humans like water purification, flood mitigation, and they serve as nesting grounds for several species of fish(es) (Maanan et al., 2018; Pinto et al., 2010; Rodrigues et al., 2018; Scanes et al., 2017). The services provided by estuarine ecosystems are constantly threatened by anthropogenic activities (e.g. agricultural practices, improper waste disposal, open defecation, mining activities, e.t.c) that introduce contaminants such as plastics, heavy metals, excessive nutrient, polycyclic aromatic hydrocarbons (PAHs), pesticides, etc. into estuaries, which eventually accumulate in biota and the sediments (Klubi et al., 2018; Edet et al., 2018; Ribeiro et al., 2016; Rodrigues et al., 2018).

In Ghana, the major threats to estuaries are mining activities, illegal fishing practices, improper waste disposal, sewage discharges, open defecation, and the use of chemicals in agricultural activities that lead to estuarine pollution (Yelelire et al., 2018; Faseyi, 2021).

Gold mining activities in the Western region of Ghana account for about 81% of the entire goldfields output in the country. Majority of the mining activities are from artisanal small-scale mining industries that occur occur in this region of the country. Alluvial mining is done on rivers in the region, using water for processing the gold. The resultant wastewater from the processing is also discharged into water bodies. These mining activities have been reported on river Pra and Ankobra leading to several environmental and health issues in the region (Duncan et al., 2018; Gbogbo et al., 2017).

Pra and Ankobra estuaries are two major estuaries in the Southwestern region contributing to the sediment delivery to the coast of...
Ghana (Mahu et al., 2016). Discharge of pollutants into these estuaries can provide information on contaminant types, source, deposition history, and effects on ecosystem health. This study broadly sought to use integrated multiple approaches to assess levels of contamination in the two estuaries, and specifically aimed to evaluate (i) particle size of the sediments influencing contaminant's transport and deposition (ii) sediment total organic matter (iii) microplastics distribution and abundance, and (iv) nutrients and heavy metal contamination status of the Pra and Ankobra estuaries.

2. Materials and methods

2.1. Study sites

Pra estuary is one of the Southwestern estuarine systems in Ghana (Figure 1). It supports non-commercial fishing activities and serves as a source of water for households within the surrounding communities along its banks. The estuary is formed at the point of entrance of river Pra into the Gulf of Guinea at Shama District (N05.02698, W001.625768) in the western part of Ghana. It stretches for about 8 km inland from the sea and it is the second-largest coastal estuary in Ghana (Tufuor et al., 2007; Okyere and Nortey, 2018). Ankobra estuary is also an important estuary in the Southwestern region of Ghana (Figure 1) and covers an area of about 12 km within the mangrove ecosystem. It discharges into the Gulf of Guinea at Asanta (Ellemelbe district, N04.896146, W002.270845), which is a few kilometers westward of Axim, the Western Region of Ghana. The entire Western region is known to have the highest gold deposit in the country, and it is the largest producer of rubber, cocoa, coconut, and palm oil in the country. The region is also known for oil production in Ghana. Hence, this region contributes largely to the Gross Domestic Production (GDP) of the country (Gbogbo et al., 2017; Ghana Chamber of Mines, 2013; Ghana Statistical Service, 2013; NCAI Policy Research Center, 2014).

2.2. Sediment sampling and analysis

Sediment samples were collected bimonthly from July 2020 to July 2021 from 9 sites on Pra estuary and 10 sites on Ankobra estuary. The sites were selected based on the estuarine classification in the region (i.e., marine/lower estuary, middle estuary, and upper/fluvial estuary) by Fairbridge (1980). Three composite surface sediment samples (5 cm) were collected from each sampling site at random using Ekman grab sampler. The samples were placed into appropriately pre-labelled zip-lock bags and transported to the Coastal Research Laboratory, Department of Fisheries and Aquatic Sciences, University of Cape Coast, Ghana. Samples for microplastics analysis were air-dried in the Laboratory for a month and crushed with a mortar and pestle, after which they were sieved through a 4 mm mesh and stored in aluminum foil pending analysis. Samples for analyses of nutrients, total organic matter (TOM), heavy metals, and particle size distribution were dried at room temperature, crushed with a mortar and pestle, sieved through a 125 μm mesh, and stored in zip lock bags for analysis.

2.3. Determination of sediment particle size

Determination of particle size of sediments was done by sorting out foreign materials from the collected samples to ensure effective analysis and were oven-dried at 100 °C overnight. The samples were crushed with a mortar and pestle, after which 100 g was weighed using ADAM tabletop scale (HCB602H) and dispensed into a set of US-Tyler sieves comprising...
4000 μm, 2000 μm, 500 μm, 250 μm, 125 μm, 63 μm and with a receiving pan. The samples on the test sieves were shaken vigorously in a shaker (Model: RX-812-3, US) for 15 minutes. The sieves of different mesh sizes were removed and the particles retained on each sieve were weighed and recorded in grams against the sieve size. This procedure was repeated for all the samples. The results were estimated and expressed in percentage, cumulative weight retained was estimated, and classification of the sediments was done using Blott and Pye’s (2012) methods.

2.4. Total organic matter (TOM)

Total organic matter was determined using Loss-on-Ignition (LOI) procedure by Schulte and Hopkins (1996). Five grams of prepared samples were weighed using a balance (HC8602H) into crucibles and oven-dried in Genlab Oven at 105 °C for 2 h, cooled in a Boekel desiccator (Boekel Scientific-1342), and weighed before they were combusted at 550 °C for 2 h in Muffle Cole-Parmer furnace. After 2 h, the temperature of the furnace was reduced and the samples were transferred to a desiccator and weighed the second time. The TOM was estimated as follows:

\[
\text{TOM (\%)} = \frac{\text{Weight loss on ignition (g)}}{\text{Weight of dry sediment (g)}} \times 100
\] (1)

2.5. Microplastics analysis

Sediment analysis for microplastics was performed using the protocol of Willis et al. (2017) with some modifications. Samples and equipment were wrapped in aluminum foil to prevent contamination from airborne microplastics. To digest the samples, 10 g of the prepared samples were transferred into a glass beaker and 50 mL of hydrogen peroxide (H₂O₂) was added and placed in an oil bath at 75 °C, stirred, and heated for 30 min. After the digestion of the samples, 100 mL of 25% zinc chloride solution was added and stirred for about 20 min using a magnetic stirrer covered with aluminum foil. Thereafter, the mixture was allowed to settle for about 2 h and the supernatant was collected into a centrifuge tube and centrifuged at 3500 rpm for 5 min. After centrifugation, the supernatant was filtered through Whatman glass-fibre paper (47 mm diameter, 1.6 μm pore size) using a vacuum filter. The 25% ZnCl₂ was collected and poured back into the beaker containing the sample, stirred, and allowed to settle, after which the same process of filtration was repeated twice to extract the remaining microplastics. This process of microplastic extraction was carried out for each sediment sample. The glass-fibre papers, after the extraction, were oven-dried in glass Petri dishes at 50 °C for 24 h, after which they were observed on OPTIKA dissecting microscope at 40x magnification for microplastics particles. Microplastics were identified using the classification criteria by Willis et al. (2017) and categorized as fibres, sheets, fragments, and beads. For proper identification, forceps were used to rub the objects before being identified (non-microplastic objects would break when rubbed or pressed with metals). The results were presented as the number of microplastic particles per 10 g mass of dried sediment samples. Precautionary measures were taken by wearing clothing made of natural fiber and laboratory coats were worn throughout the analysis to reduce the introduction of microplastics from synthetic sources.

2.6. Nitrate-nitrogen (NO₃-N) and total phosphorous determination

Nitrate-nitrogen in the sediments was determined by Cadmium Reduction Method using HACH NitraVer 5 nitrate reagent powder. Ten grams of prepared sample was measured into a pre-labelled sample bottle, 0.10 g of Calcium sulphate (CaSO₄) was added and 20 mL of distilled water was added using a graduated cylinder and then capped. The sample was shaken vigorously for 1 min using a vortex. The mixture was filtered using HM Filter paper (diameter 125 mm, No 10) through a glass funnel into a conical flask. Ten milliliters of the extract were dispensed into a cuvette and a content of NitraVer 5 extract of 10ml was taken into a cuvette and a reagent pillow was added and shaken for 1 min. The mixture obtained was set aside for 5 min for the pillow to react with the extract. Another 10 mL cuvette was filled with the same extract to blank the equipment. After the 5 min reaction time lapsed, (NO₃-N) content of the sediment was measured using a HACH DR-900 colorimeter at an absorbance of 520 nm.

The total phosphorous was determined by Ascorbic Acid Method using HACH PhosVer3 Phosphate reagent powder. Mehlich-2 soil extractant was used to extract the phosphorous content from the sediment sample. The Mehlich-2 solution was prepared by measuring 20 mL of the extractant into a conical flask and 180 mL of distilled water was added and mixed thoroughly. Two grams of the sediment sample was measured into a round bottom sample bottle and 20 mL of Mehlich-2 solution was added and shaken vigorously for 5 min using a vortex, and thereafter filtered using HM Filter paper (diameter 125 mm, No 10) through a glass funnel into a conical flask. The filtrate was transferred into a cuvette and the content of PhosVer3 Phosphate reagent powder was added and shaken for 30 s and left to react for 2 min. After ending the reaction time, the total phosphorous in the sediment was determined using HACH DR-900 colorimeter at an absorbance of 880 nm.

2.7. Metal concentration

The determination of Cd, As, Pb, Hg, Zn, Cu, and Fe concentrations were obtained using the US-EPA 3050B method (EPA, 1996). 2.00 ± 0.01 g (dry weight) sample was weighed using AND GF-3000 weighing balance into a digestion tube. 2.5 mL of concentrated HCl and 2.5 mL of concentrated HNO₃ (both were analytical reagent grade) were mixed by swirling until effervescence ceased. An Environmental Express Hot-Block Pro was used in the digestion and was pre-heated to 110 ± 4 °C, the temperature was monitored using a calibrated thermometer. The samples were digested at 110 ± 4 °C for 40 min, the tubes were later removed from the digestion block and 10 mL of de-ionized water was added and digested further for another 20 min. The tubes were removed finally from the block and allowed to be cooled. The samples were marked up to 50 mL with de-ionised (DI) water, and the tube caps were placed and they were inverted 3–4 times. The samples were allowed to settle for about 30 min, the clear samples were decanted for analysis. The heavy metal concentrations in the samples were measured using Inductively Coupled Optical Emission Spectrometer (Optima 5300DV) and the detection limits (DL) for each of the elements were presented in Table 2.

2.8. Data analysis

Data from sediment analysis was subjected to statistical analysis for the Mean (X) ± Standard Deviation (SD), range and presented in Table 2. One-way Analysis of Variance (ANOVA) was used to test for the significant differences among the means of the sediment variables. Pearson Correlation and Principal Component Analysis were performed for establishing a possible relationship between the various sediment variables. The data analysis and charts were performed and presented using Microsoft Excel version 2019, IBM SPSS Statistics Version 21, and R-Studio Version 3.6.0.

2.9. Quality assurance and quality control (QA/QC)

Instrumental and analytical quality assurance and quality control (QA/QC) was done for laboratory analyses through replicates, spikes, and blanks. The MB blank result was further cross-checked by comparing it to the Limit of Reporting. Laboratory control samples and matrix spike recoveries were also measured by computing the analyte percentage recovered from the sample by comparing it to the amount of analyte that was spiked into the sample. Duplicate and MSD relative percent differences were also measured and compared to the original native samples.
according to the formula: the absolute difference between the two results was divided by the average of the two results as a percentage (EPA, 1996).

2.10. Assessment of sediment contamination by heavy metals

Pollution fingerprints due to the levels of heavy metals contamination in the estuaries were assessed using the contamination factor (CF) by Eshhaimi et al. (2012), geo-accumulation index (Igeo) by Muller (1969), pollution load index (PLI) by Tomlinson et al. (1980), and they were estimated as follows:

\[
\text{Contamination Factor (CF)} = \frac{C_{\text{metal}}}{C_{\text{background}}} \tag{2}
\]

where \(C_{\text{metal}}\) is the concentration of the individual elements in the sediment sample, \(C_{\text{background}}\) is the background value for individual elements in sediment. Sediment background value after Turekian et al. (1961).

\[
\text{Geo – accumulation Index (Igeo)} = \log_2 \left( \frac{C_n}{1.5 \cdot B_n} \right) \tag{3}
\]

where; \(C_n\) is the concentration of the metal in the sediment, \(B_n\) is the geochemical background value and 1.5 is a constant factor accounting for geological background variations.

\[
\text{Pollution Load Index (PLI)} = \sqrt{(CF_1 \cdot CF_2 \cdot CF_3 \ldots CF_n)} \tag{4}
\]

where CF is Contamination Factor as is described above.

The pollution indicators (CF, Igeo and PLI) and their corresponding scales and variables are presented in Table 1.

3. Results and discussion

3.1. Particle size distribution

The results of the sediment particle size classifications are presented in Tables 1 and S1 and the percentage classification is presented in Figure 2.

Particle size distribution as described by the Canadian Soil Information System (Day, 1983) is the amount of different soils separated from a soil sample mostly expressed as weight percentages (Gregorich et al., 2001). They are essential characteristics of sediments and soils which affect several other characteristics including predisposition to entrainment, transference, deposition, permeability, loading, chemical reaction and agricultural productivity (Blott and Pye, 2012; Delgado et al., 2010).

The percentage sediment classification of Pra and Ankobra estuaries are as follows: Gravel (0.81%), Sand (64.04%), Silt (35.16%), and Gravel (2001) sediment classification grades (Gravel > 2000 \(\mu\)m, Sand: 63 \(\mu\)m-2000 \(\mu\)m, and Silt < 63 \(\mu\)m). This implies that the sediments of Pra and Ankobra estuaries are predominantly sand-silt. The particle size distribution reported in the current study is similar to the predominant silty-sand sediments in Lagos Lagoon reported by Ajao and Fagade (1990) but in contrast to silty-clay sediment dominating tropical Cochin estuary in India as reported by Balachandran et al. (2005) and sandy loam particles reported by Akita et al. (2020) from Densu estuary, Ghana. The sand sediment particles reported in this study were lower than the reports of Chico-Ortiz et al. (2020) who recorded higher sand particles (78.47–100%) from Mukwei and Kpeshie lagoons in Ghana.

3.2. Total organic matter (TOM)

The mean values and the ranges of the total organic matter percentages in the estuaries are shown in Table 2. The ranges of TOM recorded in Pra and Ankobra estuaries were 0.00–30.72% and 0.20–15.50% respectively. The maximum TOM recorded in Pra (30.72%) was higher than the maximum TOM recorded in Ankobra (15.50%) estuarine sediments. The organic matter content in this study is higher than the contents reported by Kubí et al. (2021) who reported 2.28 ± 1.95% from Songor Wetland in Ghana, 2.20 ± 0.90% reported by Akita et al. (2020) from Densu estuary in Ghana, and 3.00–4.00% reported by Balachandran et al. (2005) from Cochin estuary in India. Nutrients are made available in sediments by organic matter and serve as a habitat and food for organisms and also improve sediment holding capacity by binding soil particles into aggregates (Ayag et al., 2013; Bot and Benites, 2005). Organic matter gives important information in understanding the changes caused by both natural and anthropogenic activities in aquatic ecosystems (Bot and Benites, 2005; Maslennikova et al., 2012). The presence of high TOM in this study can be ascribed to several factors like the sediment moisture content and water saturation, salinity, and mangrove biomass production (Bot and Benites, 2005). According to Ayag et al. (2013), high content of organic matter can reduce the oxygen concentration in the water and sediment, which is detrimental to aquatic organisms.

3.3. Microplastic particles in sediments

Microplastics were observed in all sampling stations within the Pra and Ankobra estuaries. This observation indicates the occurrence and contamination of the coastal waters of Ghana by microplastics. The total number of the various microplastic types extracted from the estuaries is 1184. The concentration and abundance of the microplastics in the sediments are presented in Table S2. Figure 3 shows the mean concentration of microplastic particles from the estuaries while the percentage composition of microplastic particles is shown in Figure S1 and the images of some of the particles in Plates S (1–6). The Pearson correlation of microplastic particles with other sediment variables is presented in Figure 4.

In this study, four main classes of microplastics were identified using the classification criteria by Willis et al. (2017) into fibre, sheet, fragment, and bead according to their shape, structure, and colour. Pra estuary recorded higher microplastic contamination (728 particles/10 g of the entire 1184 particles/10 g) compared to Ankobra estuary which recorded microplastic contamination of 456 particles/10 g (Table S2). This is an indication of the high rate of microplastic contamination in Pra estuary than in Ankobra estuary. The contamination rate of microplastics recorded in the Pra estuary could be because there are more communities along the Pra estuary than in the Ankobra estuary that disposes their plastic wastes into or around the water banks. Desforges et al. (2014), and Benson and Fred-Ahmadu (2020) suggested that the population growth and activities of resident communities along the watercourse are frequently related to microplastic abundance.

The microplastics concentration in the Pra and Ankobra estuaries are higher compared to findings of Chico-Ortiz et al. (2020) who reported a total number of 964 microplastics particles per 10 cm\(^3\) of sediment samples from Mukwei and Kpeshie lagoons in Ghana, but lower than the number reported by Benson and Fred-Ahmadu (2020) who reported 3424 particles/m\(^2\) from 150 sampling stations in five beaches located

| Contamination Factor | Geo-accumulation Index | Pollution Load Index (PLI) |
|----------------------|------------------------|--------------------------|
| CF < 1 - Low contamination | <0, Unpolluted | PLI-value < 1, No contamination, |
| 1 < CF < 3 - Moderate contamination | >0–1, Unpolluted to moderately polluted | PLI = 1, Pollution at a baseline level |
| 3 < CF < 6 - Considerable contamination | >1–2, Moderately polluted | PLI >1, Site deterioration |
| 6 > CF - Very high contamination | >2–3, Moderately polluted | |
| >5 Very highly polluted | |

CF, Eshhaimi, et al. (2012), Igeo, Muller (1969), PLI, Tomlinson, et al. (1980).
along the coast of Nigeria. A comparison was also made with the study conducted by Alam et al. (2019) who reported 3.03 ± 1.59 particles per 100 g of dry sediment from the Ciwalengke River in Indonesia, and Sembiring et al. (2020) that reported 16.67 ± 0.58 particles/100 g mean concentration of microplastics in the sediment of Citarum River, Indonesia which was lower compared to the concentrations reported in this study. Peng et al. (2017) reported a mean concentration of microplastics of 121.00 ± 9.00 items per kg of dry sediment from Changjiang estuary, China. Willis et al. (2017) reported 87% of fibre recovered from different sediment depths in a typical estuary in Australia, which was higher than the fibre (24%) reported in this study.

The result of the one-way ANOVA showed significant differences in the means of all the microplastic particles at a 95% confidence level (Table S3) across all the stations from the two estuaries. Similar significant differences were reported by Sembiring et al. (2020) in sediments from the Citarum River in Indonesia, and Chico-Ortiz et al. (2020) reported similar significant differences from Mukwei and Kpeshie lagoons in Ghana. The Pearson correlation between the sediment variables and microplastics showed a positive significant correlation of fragments with the sheet (r = 0.62, Figure 4). There were significant correlations of the bead with gravel (r = 0.76) which implies that the size of the sediment particles does influence the distribution and abundance of the microplastics in Pra and Ankobra estuaries. This finding is comparable to the reports by Peng et al. (2017) from Changjiang estuary, China, and Sembiring et al. (2020) from the Citarum River in Indonesia.

3.4. Nitrate-nitrogen (NO₃⁻N)

The mean, standard deviation, and the ranges of the nitrate-nitrogen concentrations of Pra and Ankobra estuaries are presented in Table 2.
The ranges of concentration of NO₃⁻N recorded in Pra and Ankobra estuaries were <0.30–18.30 mg kg⁻¹ and <0.30–12.90 mg kg⁻¹ with mean concentrations of 3.68 ± 4.40 mg kg⁻¹ and 3.40 ± 3.82 mg kg⁻¹ respectively. The maximum value recorded in Pra was found higher than the maximum value recorded in the Ankobra estuary. The mean concentrations in both estuaries were low when compared to the concentration of 18.13 ± 16.68 mg kg⁻¹ reported by Ogbeibu et al. (2014) from Benin River, Nigeria. The low concentrations recorded from both estuaries could be as a result of the sand-silt nature of the estuarine sediments which limits nutrient retention in the sediment. In addition, the low concentrations of NO₃⁻N in the estuaries could also be a result of denitrification which limits NO₃⁻N availability in the sediment due to oxygen depletion in the water column and the saline nature of the environment (Dahnke et al., 2008; Ogilvie et al., 1997). Generally, nitrogen is known to be limiting in coastal or marine ecosystems including estuaries (Harrison et al., 1990; Slomp, 2012). The low nitrate concentrations in the sediments pose a serious consequence on the entire ecosystem and could affect the productivity of the estuaries.

### 3.5. Total phosphorous

The mean total phosphorous concentration in the Pra (1.00 ± 0.45 mg kg⁻¹ P) was slightly above the concentrations in Ankobra (0.80 ± 0.48 mg kg⁻¹ P). The ranges of the total phosphorous concentration were 0.29–2.49 mg kg⁻¹ and 0.28–3.56 mg kg⁻¹ for Pra and Ankobra estuaries, respectively. The concentrations reported in the present study were lower than the 6.96 ± 3.00 g kg⁻¹ mean concentrations reported by Akiya et al. (2020) from Densu estuary, Ghana, but higher when compared to 2.19 ± 2.01 mg kg⁻¹ reported by Ogbeibu et al. (2014) from Benin River, Nigeria. Low concentrations of total phosphorus in the two estuaries have implications on the productivity of the estuaries, this is a result of distortion to the phosphorous biogeochemical cycling and salinity gradient which affect phosphorous availability in the sediments (Lee and Oh, 2018; Slomp, 2012). High organic matter content recorded in the sediments could also lead to a low concentration of phosphorous in estuarine sediments (Slomp, 2012). Organic matter could affect the adsorption of phosphate either by direct (competing for adsorption sites or indirect inhibition of iron oxide crystalization in the sediments) according to Borggaard (1986). In addition, the sand-silt nature of the sediments could affect the availability of phosphorous in the estuarine sediments. Estuaries are known to play a key role in nutrient biogeochemical cycling (Meire et al., 2005), hence a disturbed estuarine ecosystem would have reduced nutrient cycling.

### 3.6. Metals concentration

The mean, standard deviation, and the ranges of the heavy metal concentration in the estuaries are presented in Table 2. The concentrations found in the sediments were compared with the Canadian Interim Marine Sediment Quality Guidelines-ISQGs (Canadian Council of
Ministers of the Environment, 2001). Cadmium (Cd) and Mercury (Hg) were below the ICP-MS detection limit of 0.30 mg kg\(^{-1}\) and 1.00 mg kg\(^{-1}\) respectively. The metal concentrations in Pra and Ankobra estuaries were in the order of Fe > As > Zn > Cu > Pb (see values in Table 2). Concentrations of As, Zn, and Fe were above the ISQGs at 7.24 mg kg\(^{-1}\), 35.00 mg kg\(^{-1}\), and 9.00 g kg\(^{-1}\), respectively while Pb and Cu concentrations were within the ISQGs limits. The mean concentrations of As were 23.10 ± 8.75 mg kg\(^{-1}\) and 59.43 ± 29.83 mg kg\(^{-1}\) for Pra and Ankobra respectively. The Pb mean concentrations recorded in Pra and Ankobra were 7.38 ± 2.27 mg kg\(^{-1}\) and 7.71 ± 2.99 mg kg\(^{-1}\) while the mean concentrations of Zn were 33.67 ± 3.51 mg kg\(^{-1}\) and 35.00 ± 1.00 mg kg\(^{-1}\) respectively. The maximum value of Fe recorded in Pra (26.00 g kg\(^{-1}\)) was lower than the 36.00 g kg\(^{-1}\) recorded in Ankobra. Generally, the mean concentrations of all the metals were higher in Ankobra estuarine sediments than in the Pra estuarine sediments. This is an indication of more metal pollution in the Ankobra estuary than in the Pra estuary. Lead and Zn concentrations in the present study were lower, while As, Fe, and Cu were similar to their findings from Klubi et al. (2021) recorded in Songor Wetland, Ghana. Arsenic and Fe concentrations were higher than the concentrations reported by Klubi et al. (2018) while Pb, Zn, and Cu were similar to their findings from Pra and Ankobra estuaries. Although Hg concentrations were below the detection limit in this study, Gbogbo et al. (2017) reported 1.60 μg kg\(^{-1}\) of Hg from Ankobra estuarine sediments.

Furthermore, the mean concentrations of all the metals recorded in this study were above the levels reported by Conrad et al. (2019), except Pb which was fairly below the reported levels. The Pearson correlations of the heavy metals with other sediment variables are presented in Figure 4. There were no correlations of metals with the sediment particles size due to the sand-silt nature of the sediments which does not allow the accumulation of metals by the sediments. Iron had a strong significant correlation with Zn (r = 0.66) while there were significant correlations between Cu and Zn (r = 0.81), Cu and Fe (r = 0.93).

### 3.7. Pollution indications and contribution of sediment variables to the contamination of Pra and Ankobra estuaries

The pollution indications and contributions of each of the sediment variables especially the heavy metals and microplastics particles to the contamination of Pra and Ankobra estuaries were estimated by ecological risk indicators (contamination factor, geo-accumulation index, pollution load index), and principal component analysis (Figure 5, Table S4, and Figure S2).

The Contamination Factor (CF) and Geo-accumulation Index (Igeo) which are indicators of pollution and ecological risk by these metals were in the order of As > Fe > Zn > Pb > Cu and As > Fe > Pb > Cu respectively. Their respective values are shown in Table 3, while their classes and categorization are shown in Table 3. The contamination factor indicated that Pra and Ankobra estuarine sediments were highly contaminated with As and Fe. Geo-accumulation index employed to measure the contribution of the individual heavy metals in the contamination of the estuaries indicated that the estuaries were strongly to

**Table 3. Pollution status of the Pra and Ankobra estuarine sediments.**

| Elements | CF |         | Igeo |
|----------|----|---------|------|
|          | Pra | Ankobra | Pra   | Ankobra |
| As       | Very high contamination | Very high contamination | Strongly contaminated | Extremely contaminated |
| Pb       | Low contamination | Low contamination | Uncontaminated to moderately contaminated | Uncontaminated to moderately contaminated |
| Zn       | Low contamination | Moderate contamination | Uncontaminated to moderately contaminated | Uncontaminated to moderately contaminated |
| Fe       | Moderate contamination | High contamination | Uncontaminated to moderately | Moderately contaminated |
| Cu       | Low contamination | Low contamination | Uncontaminated to moderately contaminated | Uncontaminated to moderately contaminated |

CF, Igeo values are shown in Table 2, PLI for Pra and Ankobra estuaries are 1.94 and 2.71 respectively.
extremely contaminated by As, while Fe contributed moderately to the estuarine contaminations (details in Table 3). Alagarsamy (2006) also reported Fe contamination of Mandovi estuarine sediments from the west coast of India. The geo-accumulation index recorded for all the elements was higher than the report of Klubi et al. (2021). The pollution load index (PLI) in Ankobra (2.71) was higher than that of Pra (1.94) estuarine sediments which indicate more pollution rate in the estuary than the Pra. The PLI values of heavy metals were higher than 1 and it is an indication of the deteriorating condition of the Pra and Ankobra estuaries caused by the mining activities around the water bodies. The values of the pollution load index from this study were higher than those reported by Bentum et al. (2011), Akoachere et al. (2019), Klubi et al. (2021), similar to some of the PLIs reported by Eshshaimi et al. (2012).

The principal component analysis is a dimension reduction statistical tool employed to reduce several variables into simpler components or dimensions without compromising their importance. In this study, all the sediment variables were used for PCA analysis with the exceptions of Cd and Hg which were below the equipment’s detection limit. The analysis was done to extract seven (7) components which accounted for about 80.43% (Table S4) of the cumulative variance in the sediment samples at a 95% confidence limit. The first two components (Figure 5) accounted for 50.60% of the total variance in the sediments of both Pra and Ankobra estuaries.

The first component (Dim 1) explained 34.3% and the second component (Dim 2) explained 16.3% of the total variance. In Pra estuary, TOM, Pb, Fe, Cu, Zn, and microplastic fragments were highly loaded in the two components while Zn, phosphorous, and all the microplastic particles (beads, fibres, sheets, and fragments) were highly loaded in the extracted components from Ankobra estuary. Considering the component matrix generated, the PCA revealed that all the metals (Fe, Cu, As, Zn) except Pb were highly loaded in the first component (dimension). This shows that the metals had the same anthropogenic source. Iron, Cu, As, Zn and fragments contributed more to the variance in sediment samples and contamination in the two estuaries (Figure S2). The main anthropogenic activity as reported in the southwestern region of Ghana is that of the gold mining activities that introduce foreign elements into the associated water bodies such as the Pra and Ankobra. The water from these water bodies is used in the processing of the gold mined in these water bodies and the discharge is thrown back into the water bodies. Kumah and Nyarko (2018) reported alluvial gold mining activities on Pra and Ankobra rivers that have introduced mining deposits into the water bodies. The contamination of these estuaries with heavy metals has serious implications on the health status of these water bodies and also poses threats to the health of coastal communities that depend on these water bodies for drinking and harvesting fishes (Maslennikova et al., 2012).

4. Conclusions

This paper presents the findings of multiple assessment methods used to determine the state of sediment contamination of the Pra and Ankobra estuaries in Ghana. The two estuaries play major roles in the livelihood of the coastal communities in the western region of the country. Microplastic particles were observed in all sampling stations within the Pra and Ankobra estuaries, indicating contamination of the coastal waters of Ghana. The low nutrient concentrations in the sediments pose a serious threat to the entire ecosystem and could affect the productivity of the estuaries. The pollution indicators suggested that Pra and Ankobra estuarine sediments were highly contaminated with As and Fe, which impact the deteriorating condition of the estuaries as a result of mining activities around the water bodies. The principal component analysis indicated that pollution fingerprinting is strongly influenced by Fe, Cu, As, Zn, silt, and sand associated with illegal artisanal gold mining activities. Thus, the findings from this study imply that the levels of pollution recorded could have deleterious impact on human health and the communities depending on the services rendered by the estuaries. Furthermore, there is the need to adopt strategies for pollution control to protect these fragile ecosystems that support livelihoods.

Declarations

Author contribution statement

Charles Abimbola Faseyi: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Michael Miyittah & Levi Yafetto & Akindayo Sowumi: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

George Lutterodt: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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