



The Impact of Anthropogenic Activities on the Fosu Lagoon in the Central District of Cape Coast: Integrated Assessment of Heavy Metal Contamination

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Authors' contributions

This work was carried out in collaboration between all authors. Author GAA designed the study. Authors JKB and GYH performed the statistical analysis and wrote the first draft of the manuscript.

Author CKA and GAA managed the analyses of the study. Author CKA and GYH managed the literature searches. Author EMA performed the lab work, wrote the protocol. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/BJAST/2017/31275

Editor(s):

(1) Dr. Teresa De Pilli, University of Foggia, Department of Science of Agriculture of Food of Environment (SAFE).

Reviewers:

(1) Egwumah, Francis Attah, University of Agriculture, Nigeria.

(2) Raul S. Lavado, University of Buenos Aires, Argentina.

(3) Steve Pothoven, National Oceanic and Atmospheric Administration, USA.

(4) Floarea Damian, North Centre University of Baia Mare, Romania.

Complete Peer review History: <http://www.sciencedomain.org/review-history/19416>

Short Research Article

Received 29th December 2016

Accepted 18th February 2017

Published 8th June 2017

ABSTRACT

Effluents from humans and industrial discharges into the environment pose a serious threat to human health and aquatic life. In view of this, levels of some heavy metals Zn, Pb, Cu, Ti, V and Mn were determined in sediment samples collected from one of the most polluted water bodies (Fosu Lagoon) in the central region of Ghana using Atomic Absorption Spectrophotometer (AAS) - (Varian

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– AA240 FS). The average concentrations of lead (Pb), zinc (Zn), manganese (Mn), copper (Cu), Titanium (Ti) and Vanadium (V), from the various sites ranged from 138.75 mgkg⁻¹ (Ti) to 4.90 mgkg⁻¹ (Zn). Among the concentrations of heavy metals found in the sediment samples, Ti recorded the highest concentration of 4600 mgkg⁻¹ followed by Mn (290.00 mgkg⁻¹) and then Cu (235.93 mgkg⁻¹). The sequence of distribution followed Ti>Mn>V>Cu>Pb>Zn. The mean concentration of Mn, Cu, Ti and V exceeded the USEPA and WHO standard guideline while Pb and Zn were below the standard regulation limits. The Pearson correlation analysis between the heavy metals at the various sampling points was generally weak, with both positive and inverse correlations demonstrating that heavy metals may be coming from different anthropogenic sources. Comparing results from this study with previous works in the same Lagoon showed increased anthropogenic activities around the lake which pose potential pollution threats to the lagoon especially, the heavy metal pollutants which may be toxic to humans and aquatic life.

Keywords: Heavy metal pollution; Fosu Lagoon; metal distribution; anthropogenic activities.

1. INTRODUCTION

Heavy metals are discharged into the environment through several anthropogenic sources such as the burning of fossil fuels, transportation, industrial effluent discharge and indiscriminate waste dumping. Heavy metals can build-up in sediment components and interact with other aquatic organisms through ion exchange, absorption and precipitation [1]. Heavy metals are of particular concern due to their toxic effect at certain levels of exposure and ability to bio-accumulate in aquatic ecosystems, body tissues and organs [2-3].

The occurrence of toxic metals in pond, stream and river water affects the lives of humans and animals that depend upon these water sources for their daily life. The consumption of aquatic resources containing toxic metals may cause serious health hazards through food chain magnification [4]. Heavy metals are more highly accumulated in sediments than in fish tissue/organs and water, because most of the heavy metals are insoluble in water but bound to sediments. In addition, the metals in the aquatic ecosystems are mainly deposited in sediment, and sediment acts as a source and as a sink. As a consequence, benthic biota living in metal polluted environment can have very high level of metals. Heavy metal intake by fish in polluted aquatic environments vary and depend on ecological requirements, metabolism and other factors such as salinity, water pollution level, food and sediment [5-10]. A study in 2014 observed a trend in heavy metal accumulation in sediment to be higher than that in fish tissues and the amount in fish tissue higher than that in water [11]. The results from their findings showed significant accumulation of heavy metals in the tissue of fish, indicating the ability of aquatic organisms to accumulate high concentrations of

metals many times higher than present in water. Fish are known for their ability to concentrate heavy metals in their muscles and since they play an important role in human nutrition, they need to be carefully screened to ensure that high levels of toxic trace metals are not being transferred to humans through consumption [11-12]. Pollutants like heavy metals in aquatic ecosystems precipitate on sediments surface and form as deposited pollutants [13].

The amount of absorption and assembling depends on ecological, physical, chemical and biological factors and also the kind of element and physiology of the organisms [14]. The metals, on accumulation by the aquatic organisms, enter into the food chain and are finally consumed by humans [15]. Effects of these metals on consumers depend on the concentration, physiochemical properties, chemical bonds and their distribution in the body [16]. Studies have shown that decreased content of antioxidative elements, such as zinc (Zn), selenium (Se), manganese (Mn) and increased content of some elements including copper (Cu), cobalt (Co) and arsenic (As), which probably elevate the oxidative stress, can cause some inflammatory diseases and cardiac functional disorders [17-22]. On the other hand, lead (Pb) toxicity can lead to growth retardation, neuronal defects and anemia in children. Hepatotoxicity, nephrotoxicity and neurotoxicity can occur as a result of Pb chronic toxicity [23]. Heavy metals discharge into a river system by natural or anthropogenic sources are distributed between the aqueous phase and bed sediments [24]. Sediment can provide a deeper insight into the long term pollution state of a water body [25].

Sediments from Ghanaian rivers, lakes and oceans have been contaminated by pollutants and the method employed in their analysis is a

useful tool to study the metal pollution in an area. Some of these pollutants are directly discharged by industrial plants and municipal sewage treatment plants; others come from polluted runoffs in urban waste, agricultural and residential waste products. The problem of heavy metal pollution is attracting the attention of people around the world, due to its negative effects on the environment and on human health [26]. The issue of Fosu lagoon came into the spot light about six years ago as a result of its suspected heavily polluted nature. In 2008, the Environmental Protection Agency (EPA) Ghana, advised that all activities in the Lagoon be put to a halt, due to its highly polluted nature [27]. According to the EPA, test performed on the lagoon water revealed that the water was highly polluted with most of the commonly known cations and anions measured [28].

The commonest sources of pollutants into the Fosu Lagoon are the various automobile garages at Siwdu, Cape Coast District Hospital and some palm kernel oil producers at the Adisadel village. There are also lots of residential settlements which are close to the lagoon. Wastes from all these human activities flow directly into the lagoon without any prior treatment. This increases the influx of metals, which can be transported by wind and water and thus become available to aquatic plants and fishes in the lagoon. These heavy metals gradually accumulate to higher concentrations in different parts of plants and finally pose serious health hazard to human beings and the animals through biomagnification [29].

Due to the polluted nature of the lagoon, the Fosu lagoon is now one of the water bodies referred to as 'Dead zones' in the world [30-31]. Sediments naturally consist of a complex mixture of organic and inorganic components like clays, silicates, carbonate, sulphide, minerals and bacteria. Contaminated sediments do not always remain at the bottom of a water body. Anything that stirs up the water, such as dredging can re-suspend sediments. Re-suspension may mean that all of the animals in the water and not just the bottom-dwelling organisms will be directly exposed to toxic contaminants [32].

The accumulation of these elements, many of which are highly toxic to animals, aquatic plants life and lower forms of marine animals is one of man's less praiseworthy influences on the biosphere. The six elements considered in this study are zinc, manganese, titanium, vanadium, copper and lead. The detection and

determination of these in natural waters are of considerable importance not only as a means of establishing their influence on various ecosystems but also for monitoring and controlling the pathways by which they reach the hydrosphere.

2. MATERIALS AND METHODS

2.1 Study Area

The Fosu Lagoon is located in the Cape Coast municipality in the central region of Ghana. The Municipality occupies an area of 122 Km² and is dominated by batholiths. The geographical coordinates of the Fosu lagoon are 50 7'N and 10 16'W. The map showing the lagoon and the sampling points is shown in Fig. 1. Some economic activities (automobile garage, car washing, palm kernel oil making, metal scrappers activities etc.) also go on at sites very close to the banks of the lagoon. There are valleys of various streams between the hills, with Kakum being the largest stream. The small streams end in wetlands, the largest of which drains into the Fosu Lagoon at Bakano, a suburb of Cape Coast. The soils of the municipality are generally lateritic and are derived from the weathered granite and schist. The soil profile shows a topsoil of about 0.33 m. In the valleys and swampy areas, fine sandy deposits occur extensively [33].

Two major and other minor drainages lead through the township into the lagoon which increases the domestic sewage contamination in the lagoon. Although no industrial activities exist in the immediate area of the lagoon, there are human activities such as metal scrappers, mechanical shops both private and government and a motor bicycle repair shop near the lagoon. The District has double maxima rainfall totaling between 750 mm and 1000 mm. The major rainy season occurs between May to July and the minor around September to October. Cape Coast is a humid area with mean monthly relative humidity varying between 75% and 85%. The sea breeze has a moderating effect on the local climate. The major economic activity in the southern coast is fishing [34]. Eight sampling points were chosen for this research based on the activities in and around the area. These points are as follows: sampling sites A, B, C and D are located at the Bakano end—an estuary with lots of refuse dumping activities; Sampling site F is located at mechanical shop at Siwdu; Sampling site E is located at the municipal

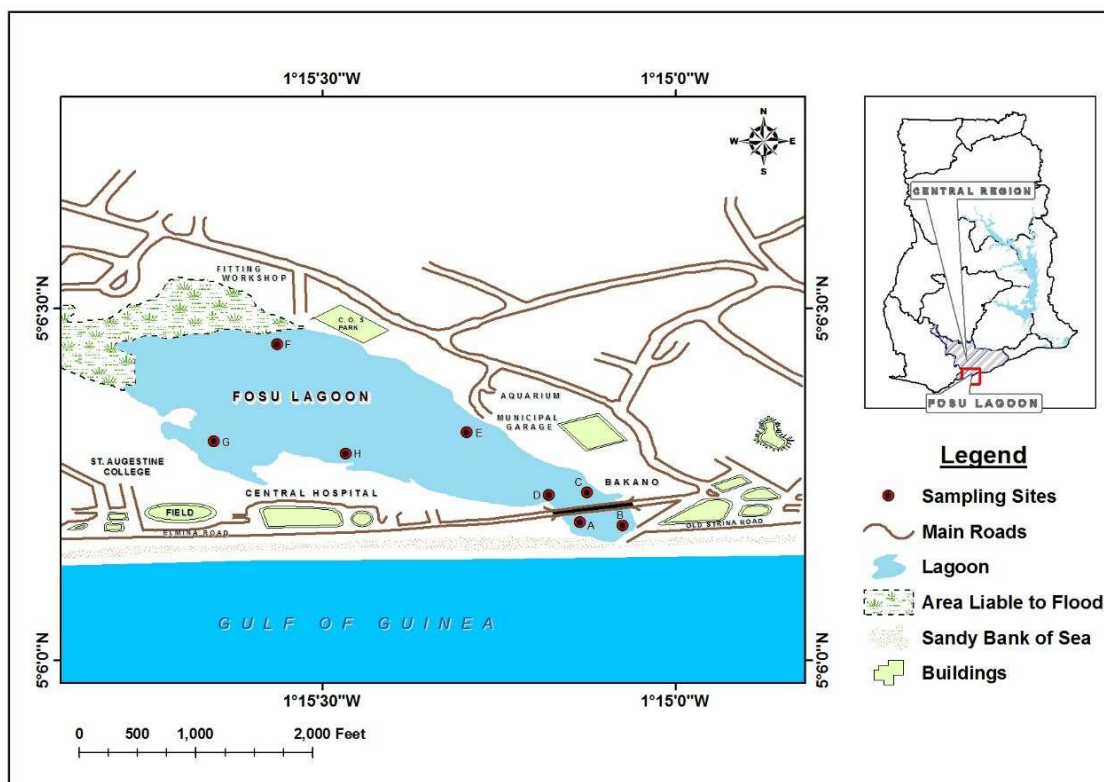


Fig. 1. A map showing the eight sampling sites within the Fosu lagoon

automobile garage; Sampling site H and G are located at the southern sector of the lagoon, at the Cape Coast District Hospital and St. Augustin’s College, respectively.

2.2 Sample Collection and Preparation

All the Eight sediment samples for the study were collected from eight sampling points in the lagoon. The choice of the eight sampling points was based on their accessibility, nearness to human activity and their suitability for future survey. Some of the points were accessible through navigation by boats, others by just walking through the lagoon.

Sediment samples were taken in the Lagoon at 1m depth with the aid of improvised hollow sampling gauge into black polyethylene bags and labelled immediately on the field. Sediment samples were collected 100 m apart in replicates at two weeks’ interval over two months (February to March) at the designated points. The sediment samples were air dried for three days and further dried at 105 °C for 48 hours before they were transported to the Nuclear Chemistry Department

of Ghana Atomic Energy Commission where they were pulverised, sieved and analysed using Atomic Absorption Spectroscopy.

2.3 Sample Digestion and Analysis

1.5 g of the pulverized and sieved soil samples was weighed into a previously acid washed labeled 100 mL polytetrafluoroethylene (PTFE) Teflon bombs. The samples were digested by adding 6 mL of concentrated nitric acid (HNO₃, 65%), 3 mL of concentrated hydrochloric acid (HCl, 35%) and 0.25 mL of hydrogen peroxide (H₂O₂, 30%) to each sample in a fume chamber. The samples were then loaded on the microwave carousel. The vessel caps were secured tightly using a wrench. The complete assembly was microwave irradiated for 26 minutes using milestone microwave labstation ETHOS 900, INSTR: MLS-1200 MEGA. The digestate was made up to 20 mL with double distilled water and assayed for the presence of zinc (Zn), Manganese (Mn), Titanium (Ti), Vanadium (V) lead (Pb) and copper (Cu) using VARIAN AA 240FS- Atomic Absorption Spectrometer in an acetylene- air flame. Blanks and duplicates of

samples were digested under the same conditions as the samples. These served as internal positive controls.

Reference standards (SQC001) used are from FLUKA ANALYTICAL, Sigma-Aldrich Chemie GmbH.

2.4 Quality Control

In sample preparation, contamination is of prime concern and to avoid that high standard quality measures were taken to eliminate sample contamination during packaging, storage and transport of samples. To ensure high surface area exposure to the nuclear reactor, samples were crushed with a laboratory pulverize at Ghana Atomic Energy Commission Center through 250 µm. The devices were fed into a machine that crushed it to powder. The powders were of the order of a few microns. Other quality assurance measures taken were: duplication of analysis, preparation of blank, the use of standard reference material.

2.5 Recovery and Reproducibility Studies

Recovery study was conducted by adding a known amount of certified reference standard soil material to three different sediment samples and digested the same way as other samples and the responses were compared based on values calculated from the standard curve. The recovery study was performed to help determine the validity of the sensitivity and efficiency of the method used. The recovery values for the reference material (FLUKA ANALYTICAL, Sigma-Aldrich Chemie GmbH, a product of Switzerland) and the heavy metals are given below. The measured concentration for the spiked QC certified standard (from FLUKA ANALYTICAL) ranged between 4.839 and 4.979 mg/L as against the certified value of 5.000 mg/L. The percent recovery was calculated to be 98.2%. Similar average percent recovery estimates for the metals in the spiked water samples were obtained as; Zn, 100.4%, Cu, 100.1%, Mn, 96.4%, V, 100.1%, Ti, 92.5% and Pb, 95.7%.

2.6 Data Analysis

Statistical analysis on the data from the study was done using Excel Analysis Tool Pack. The Pearson's correlation was used to examine correlation between the metals from the various sampling points studied for possible distribution of the metals present in the Lagoon.

2.7 Enrichment Factor (EF) Calculations as Evidence of Anthropogenic Origin of the Heavy Metals

In order to segregate the fraction of the element concentration originating from natural sedimentary sources from the anthropogenic fraction, normalizing tools are normally employed [35]. Geochemical normalization has been used to reduce the heavy metal erraticism caused by grain size and mineralogy of the sediments to identify anomalous metal [36]. In this case various conservative metals including Fe, Al etc. have been used for this purpose [37]. In this analysis, heavy metal concentrations in the Fosu lagoon sediments are normalized using Al as a conservative element to evaluate anthropogenic sources of the metals.

The enrichment factor (EF), which is the index of contamination formula for the sediment samples, was calculated using the heavy metal average concentrations at various sites A to H and the average earth or crustal levels (Table 1) as baseline levels according to Equation below.

$$EF = \frac{([M]/[Al])_{\text{target site}}}{([M]/[Al])_{\text{base line}}}$$

Where [M] is the metal studied.

Table 1. Metal concentrations in average continental shale

Element	Average continental shale [38]
Cu	45
Pb	20
Zn	95
Mn	850
V	130
Ti	4600

3. RESULTS AND DISCUSSION

The mean values of heavy metals analyzed in the sediment samples from the eight sampling points of the Lagoon are presented in Table 2. Heavy metals concentration was determined from sediment samples. The results clearly indicate that concentration were high in the sediment samples from all the eight points. In general, metal content in the sediment samples is indicative of the extent of pollution and serves as a source of solubilization into the water when all the physico-chemical circumstances such as pH and temperature are favourable and the uptake by benthic organisms. At sampling point

A in the Lagoon, Ti and Mn were more concentrated in the sediment sample. The same trend was also observed all other sampling point H. The highest concentration of 4600.00 mg/kg recorded in the samples came from Ti at point A followed by Mn with concentration of 900.00 mg/kg at sampling point H. The high concentration of these two metals is not surprising due to their abundance nature in the earth crust [38]. There was an increased in metal concentration especially, in the case of Cu, Zn and Pb at sampling point G and H. This may be due to gradual deposition of the metals from effluent from anthropogenic sources (e.g. Cape Coast district hospital and St. Augustine's college). The concentration of Cu recorded in all the sites studied in this research is far higher than interim marine sediment quality guidelines (ISQGs) value for marine environment protection (Table 2). The increase concentration is anticipated in regard to reports that demonstrated the general increasing trend for average Cd levels over the 8-month survey period in the same lagoon [39].

The presence of high concentration of heavy metals in sediment from this study is in agreement with other related studies at the same site. A study carried out by Eshun in 2011 [27], showed similar high levels of heavy metals in the lagoon. From the study, sediment samples contained concentrations of Mn, Zn and Pb to be 543.50 mg/kg, 22.72 mg/kg and 14.22 mg/kg respectively. He further indicated that the geoaccumulation indices showed that the lagoon sediments were highly contaminated with Mn, Zn and Pb. The high level of Mn, Zn and Pb found in the tissue of fish samples is indicative of the degree of dissolution of the metals in the water body itself [27]. Another study in the same lagoon by Bentum and co-workers [40], also showed elevated levels of heavy metal, notably Pb (28.1 mg/kg), Cu (26.4 mg/kg) and Zn (20.90 mg/kg) in the sediment samples. In their assertion, the heavy metal burden showed significant variations in their distribution with Pb showing the greatest variation.

High levels of heavy metals in sediments were found to be around 10,000 times higher than in water in Lake Balaton [41]. A study conducted by Jumbe and Nandini in 2009 on urban lake in Bangalore to determine heavy metals concentration and sediment quality, showed persistent high levels of heavy metals in the bed sediments despite all attempts made to reduce

the effect [42]. Lake sediments are therefore regarded as important abiotic environmental monitoring tool for heavy metal contaminants, providing a unique medium to assess the impact of anthropogenic pollutants on freshwater systems. Results from this study further indicates higher levels of heavy metals in the sediment compared with the previous results from the same lagoon, suggesting high and continual burden of pollutants in the water body.

Correlation analysis to study the relation between the metals and their source apportionment shows that a very strong and positive correlation was observed between the sites indicating similar concentration of metal distribution at all the eight sites. The strongest correlation was observed between site A and E with the r- value at 0.998 and the weakest correction between site H and F with the r-value at 0.625. However, the correlation between the heavy metals at the various sampling points was low, with both positive and inverse associations. Correlation between Mn, Ti and V, showed weak but positive correlation indicating their common distribution in the water body. Cu correlated inversely with Ti, V and Mn but positively with Pb and Zn. The strongest correlation existed between Cu and Zn while the weakest existed between Pb and Zn. The details of the correlation patterns can be seen in Tables 3 and 4.

The calculated EF values of the studied heavy metals as normalized to Al for the various anthropogenic sites is shown in Fig. 2. Even though the calculated EF could be underestimated, the values would allow us to ascertain places where anthropogenic contributions of particular metals were discharged (i.e., $EF > 1$) [43]. This is clearly demonstrated in all the sampling sites showing some form of anthropogenic input of all the metals studied with EF values >1 , except Zn (Fig. 2). The reason for underestimated values of EF are that, the use of average earth or crustal levels ignores natural geochemical variability and also the fact that crustal values are bulk concentrations, this undermines comparison with "fine fraction" sediment concentrations [44].

The industrial activities at the eastern sector of the lagoon, especially the cluster of mechanical shop at Siwidu (sampling site F) is the main source of Cu and Mn to the lagoon. At the southern sector of the lagoon, especially,

sampling site at Cape Coast District Hospital (sampling site H), and St. Augustin's College sampling site (G) showed EF>20 (EF is only slightly greater than 20 at G, and not at H, where it was only about 13) for Cu (Fig. 2) demonstrating anthropogenic input of Cu at these sites. This is not surprising and strongly be attributed to effluents from the Cape Coast District Hospital and St. Augustin's College.

These two institutions do not have any treatment plant for treating waste and emptied their waste directly into the lagoon. Moderately Cu and Pb EF values between 4-6 were also observed at the sampling sites A, B and C (Bakano where the lagoon meets the sea) which may be due to flow of effluent downstream Bakano. The situation is worrying looking at the level of EF values of Cu and Pb.

Table 2. Mean concentrations (mgkg⁻¹) of heavy metals in sediment samples measured in this work and reported mean concentration of heavy metals from Fosu Lagoon with Marine sediment quality guidelines levels

Sites	Al	Mn	Ti	V	Cu	Pb	Zn
A	1497.00	210.00	4600.00	189.80	43.74	21.02	4.02
B	2789.00	700.00	3200.00	237.00	94.62	15.75	4.82
C	4165.00	100.00	3200.00	300.00	96.76	8.78	5.18
D	4723.00	120.00	3600.00	299.00	33.26	13.43	4.91
E	5210.00	170.00	3700.00	151.33	29.73	13.13	4.66
F	5871.00	290.00	2800.00	178.67	89.05	31.67	4.98
G	1512.80	600.00	3700.00	103.75	178.33	26.21	4.84
H	3176.00	900.00	2500.00	226.50	236.69	23.72	5.81
ISQG*	-	-	-	-	18.70	30.20	124.0
PEL *	-	-	-	-	108.00	112.0	271.0
Conc. reported		2.66 ^[39] 543.50 ^[27]			1.50 ^[27] 26.40 ^[40]	18.90 ^[27] 28.10 ^[40]	1.15 ^[39] 20.90 ^[40]

Interim marine sediment quality guidelines (ISQGs) dry weight, probable effect levels (PELs) dry weight [45].*

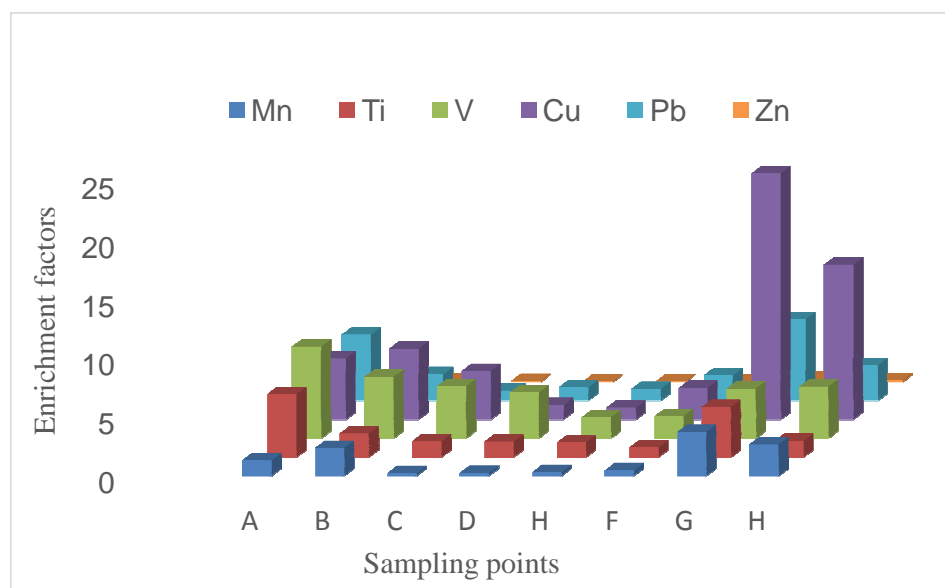


Fig. 2. Enrichment factor values of heavy metals calculated using average continental shale values

Table 3. Correlation matrix between sites for heavy metals in sediment at Fosu Lagoon

	A	B	C	D	E	F	G	H
A	1							
B	0.935	1						
C	0.958	0.995	1					
D	0.992	0.964	0.974	1				
E	0.998	0.932	0.955	0.989	1			
F	0.873	0.734	0.796	0.813	0.882	1		
G	0.844	0.975	0.962	0.883	0.844	0.662	1	
H	0.661	0.831	0.829	0.683	0.661	0.625	0.919	1

Table 4. Correlation matrix between heavy metals in sediment at Fosu Lagoon

	Mn	Ti	V	Cu	Pb	Zn
Mn	1					
Ti	0.118	1				
V	0.210	0.523	1			
Cu	-0.466	-0.584	-0.390	1		
Pb	0.419	-0.214	-0.270	0.452	1	
Zn	-0.372	-0.908	-0.455	0.716	0.068	1

4. CONCLUSION

To determine the status of metal contamination in Fosu lagoon sediments, Pb, Zn, Cu, Mn Ti and V concentrations were estimated in eight sampling points. The sequence of the mean concentrations of tested heavy metals follows; Ti > Mn > V > Cu > Pb > Zn. The correlation analysis of mean concentrations showed weak with positive and inverse correlations among the metals suggesting that these metals may be introduced into the lagoon from different sources. WHO quality guidelines for sediments and USEPA enrichment factor were applied to assess the extent of metal contamination [46-47]. According to sediment quality guidelines, sediments in the Fosu lagoon are polluted by Mn, Ti, V, Pb and Cu which could be attributed indicator to intensification of socioeconomic activities around the lagoon.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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