Levels and Distribution of Heavy Metals in Weija Reservoir, Accra, Ghana

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Abstract

Reservoirs are normally subjected to various forms of degradation due to pollution arising from anthropogenic activities. Heavy metals are of particular concern because of their potential toxic effect and ability to bio-accumulate in aquatic ecosystems. Agricultural activities around the Weija reservoir and municipal waste leachate intrusion have been reported. Investigations were therefore conducted to determine the levels and distribution of heavy metals in the Weija reservoir. Specific heavy metals were determined in water, suspended particles, sediments and fish species using Flame Atomic Absorption Spectrophotometry. Mercury was analysed with a mercury analyser, which uses cold vapour. The result showed that the concentrations of metals were greater in sediment than the suspended particles and reservoir water; Cd, Cu, Ni, Pb and Zn were all below the chronic freshwater quality criteria for aquatic life. Iron (Fe) and Mn were the most abundant elements associated with the suspended solids, whiles Cd was the least. With the exception of Cu and Cd that were not detected in the fish species, the other metals were found at varying concentrations, but within acceptable thresholds. The concentrations of heavy metals in the various fish and prawn species were ranked in the following order: Parachanna obscura > Macrobrachium rosenbergii > Chrysicthys nigrodigitatus > Clarias batracus > Clarias gariepinus > Hemichromis faciatus > Sarotherodon melantheron. There were significant positive correlation between the following metals in water; Pb and Zn (r=0.66), Cr and As (r=0.52). Evidence from principal component analysis (PCA) suggested that two key source factors, characterised as related to mining and municipal solid wastes, underpinned heavy metal contamination in the Weija reservoir. Thus, illegal small-scale mining along the tributaries feeding the Weija reservoir affected the quality of water received in the reservoir.

Introduction

The accumulation of heavy metals and nutrients in reservoirs has become a public health concern in both the developed and developing world. This is so because most reservoirs serve as the main source of drinking water in most developing countries. Heavy metals are distributed among aqueous phase, suspended particles and sediments in reservoirs (Wang *et al.*, 2012).

Rapid urbanisation, industrial development and agricultural practices have given rise to significant concerns for the release of pollutants into the environment. Heavy metals contamination and nutrient enrichment of surface and coastal waters may originate from both point and non-point sources. Point sources include wastewater treatment facilities; non-point sources include diffuse inputs from the atmosphere and agriculture (including land drainage and animal wastes) (Allan & Castillo, 2007).

The main anthropogenic sources of heavy metal contamination in reservoirs are mining, waste disposal of untreated and partially treated effluents that contain toxic metals, as well as metal chelates from different industries and indiscriminate use of heavy metal-containing fertilisers and pesticides in agricultural fields within the catchment of reservoirs. Rivers in urban areas are prone to water quality problems because of the practice of discharging untreated domestic and small scale industrial waste into them, leading to elevated levels of contaminants such as heavy metals. (Sekabira *et al.*, 2010).

Study of reservoirs is very important, because they are normally subjected to various forms of degradation due to pollution arising from activities such as stone quarrying, dumping

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of domestic wastes, industrial effluents and agricultural run offs (Asante et al., 2010). Among these pollutants, metals are of particular concern because of their potential toxic effect and ability to bio-accumulate in aquatic ecosystems. Heavy metals are of public health concern particularly as most have no biological role in humans (Censi *et al.*, 2006).

The Weija reservoir currently provides drinking water to the Western parts of Accra, as well as provides fisheries resources (Karikari *et al.*, 2006). The reservoir has contributed significantly to the national fish production stock in the past. As a result of increase in population and urbanisation, portions of the dam have been encroached and have been reclaimed and used for residential and agricultural purposes, thereby influencing the dam with various activities including the release of waste effluent from industries, which release various forms of heavy metals into the reservoir (Ameko *et al.*, 2012).

The Densu River, which feeds the Weija reservoir, receives storm run-off and waste materials deposited in the catchment areas. These usually find their way into the Weija reservoir by the action of run-off especially during heavy down pour. These anthropogenic activities carried out around the catchment of the reservoir have a very high propensity to impact significantly on the physico-chemical parameters of the reservoir. Heavy metals, when discharged persist in the aquatic bodies and bioacummulate along the food chain. A study by Tiimub and Afua (2013), of the Densu River at Weija revealed varying concentrations of heavy metals in two common fishes (Tilapia and catfish).

The use of fertilisers in farming within a dam and reservoir’s catchment is a potential source of heavy metal discharge into water bodies (Anim *et al.*, 2011). Farming along the Weija reservoir is rampant and application of inorganic fertilisers and fungicides containing heavy metals such as Mn, Fe, Zn Cd, Co, Cu, Ni and Pb may pollute the reservoir water.

The need therefore to determine the levels and distribution of heavy metals in water, sediments and fish species in the Weija reservoir is very important to help establish the heavy metals pollution status of the reservoir. The findings would have implications for the hundreds of thousands of people living in Accra and its environs who depend on the reservoir as a source of drinking water and for the fisheries resources, as well as biodiversity conservation. Although water quality of the reservoir has been monitored and researched by various research scientists (Ansa-Asare and Asante, 1998; Akpabli & Drah, 2001; WRC, 2003; Tiimub, & Afua, 2013), the fate of the metals with regards to their distribution among the water, suspended particles, bottom sediment and fish species have not been investigated. It is against this backdrop that this study sought to determine the levels of selected heavy metals (Cu, Pb, Zn, Fe, Ni, Cr, Cd, As, Hg and Mn) in the reservoir, assess their concentrations in suspended solids and bottom sediments, evaluate the concentrations of these metals in fishes from the reservoir and finally explore potential factors influencing the contamination from these metals.

Materials and Methods

Study Area

The study was conducted at the Weija Reservoir in Accra. (0 °20’ W 0 25’ W and 5 30’ N 5 45’ N). The reservoir was created in 1977 as a replacement for an earlier one which was washed away in 1968 by

Ghana Water Company Limited (GWCL) through damming River Densu mainly to satisfy the demand for potable water supply (Quarcoopome & Amevenku, 2010). The Weija Reservoir, located about 17 km west of Accra, is almost at the mouth of the 116 km long River Densu which takes its source from the Atewa-Atwiredu mountain range in the Eastern Region of Ghana. The current reservoir provides water to western parts of Accra, supports irrigation projects, as well as fisheries. The Weija Reservoir is 14 km long, 2.2 km wide and has total surface area of 38 km2 with mean depth of 5 m (Vanden Bossche & Bernacsek, 1990).

The reservoir area is low lying with undulating topography and isolated ridges. Climatic conditions are tropical with temperature averaging 27 oC. Rainfall is moderate with the seasonal average being 65.5 mm. The catchment of the reservoir lies in the coastal savanna zone where rainfall is seasonal, with two rainfall peaks in June and September, while dry periods span between December and March. The main economic activities in the catchment are fishing and crop farming. Major crops include maize, cassava, sugarcane and vegetables. Untreated domestic waste waters are discharged into the Reservoir.

Sample collection

Water and sediment samples were collected from sixteen (16) selected sampling sites (Fig 1). A geographical positioning system (GPS), GARMIN *etrex* 20 model was used for recording the geographical coordinates of the sampling sites.

All the water analyses were determined using appropriate certified and acceptable international procedures outlined in the standard methods for the examination of water and waste water (APHA, 1998) and AWWA & WEF (2012). The physical parameters such as temperature, dissolved oxygen, pH, conductivity, total dissolved solids, salinity and turbidity were measured in situ using HORIBA model multi-probe meter (U-50 series). Water and fish samples collected were all kept on ice at a temperature of about 4°C and transported to the Ecological Laboratory

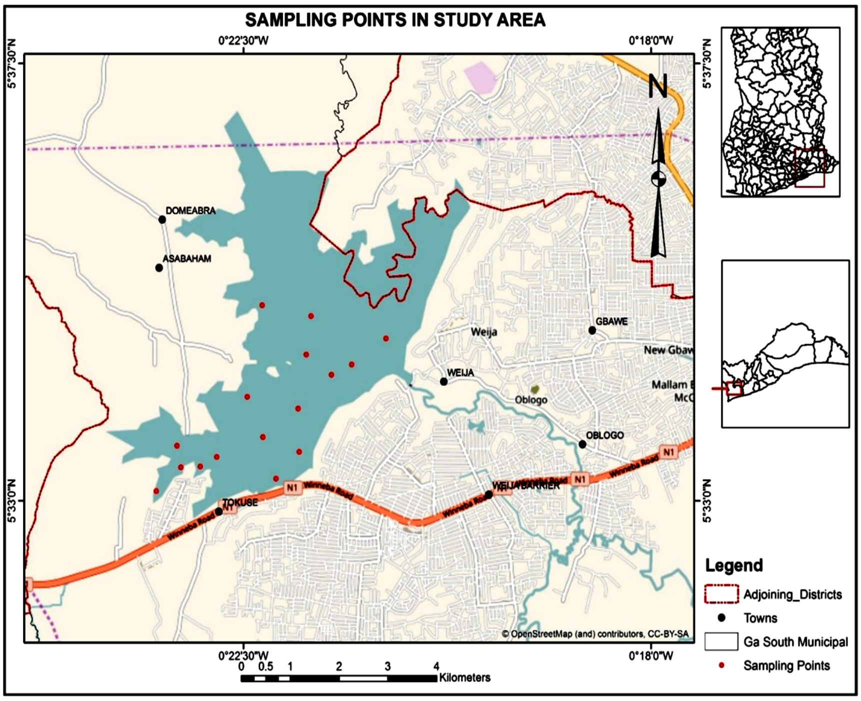

Fig 1 A map showing sampling point of the Weija Reservoir

of the University of Ghana for analysis

Water sampling and analysis

Water samples were collected from all the respective sampling sites of Weija Reservoir. At each sampling site, two separate water samples were taken using polyethylene bottles. Few drops of nitric acid were added to the samples for dissolved metal analysis whilst the other for suspended particles, no acid was added. Samples were kept on ice and transported to the laboratory.

Concentrations of heavy metals in water samples were determined using Perkin Elmer Atomic Absorption Spectrophotometer (ASS) (PinAAcle 900T) with a specific wavelength for each metal. Average values of three replicates were taken for each determination. Appropriate drift blank was taken before the analysis of samples. The working wavelength for the heavy metals were 248.3 nm for Fe, 279.5 nm for Mn, 213.9 nm for Zn, 324.7 nm for Cu, 232 nm for Ni, 228.8 nm for Cd, 357.9 nm for Cr, 217 nm for Pb, 193.7nm for As and 253.7nm for Hg.

Suspended solids sampling and analysis

To determine the levels of heavy metals in the suspended particles in the water column, 250 mL of the water samples were filtered through 0.45 µm membrane filter. The filtrate was acidified with 3mL nitric acid while the suspended solid on the filter paper was dried to constant weight at 70°C and retained for metal analysis. Filter loaded with suspended solids were digested in nitric acid and perchloric acid in the ratio of 3:4 for 1-2hours at 75-80 oC till clear solution was obtained.

Sediment sampling and analysis

The sediment samples were taken at a depth of about 25-30 cm using Ekman grab. At each site, a composite sample of three subsamples were collected and mixed, to ensure that the sample was representative for this site. The sediments were put in air-sealed plastic bags and kept on ice in the field. The sediment samples were air-dried, pulverised using mortar and pestle and sieved through 2 mm particle size. One gram (1g) of soil sample was digested with a mixture of concentrated nitric acid (3 ml), perchloric acid (4 ml) at 75-80 °C for 1-2 hours on heating mantle till a clear solution was obtained.

Fish sampling and analysis

Six edible fish species as well as a prawn species were collected from commercial catches made by the local fishermen. A total of 83 samples comprising the six fish species and the one fresh water prawn were obtained and identified using a fresh water fish identification key (Dankwa *et al.*, 1999). The seven (7) species were, *Parachanna obscura* (n=13), *Clarias batrachus* (n=11), Clarias gariepinus (n=9) *Hemichromis fasciatus* (n=14), *Chrysichthys nigrodigitatus* (n=13), *Sarotherodon melantheron* (n=12) and one fresh water prawn; *Macrobrachium rosenbergii* (n=11).

Each fish sample was dissected using stainless steel scalpels, forceps and scissors in a dissecting tray to separate muscles and gills. Fish muscles and gills were dried in labelled pre-washed crucibles at 70 °C for 24 h in an oven. Each dried sample was then pulverised, homogenized with porcelain mortar and pestle and stored in labelled pre-treated specimen bottles. Each sample was transferred to pre-weighed crucibles and dried again in the oven until constant weight was obtained. One gram of the dry sample, placed in a Teflon beaker, was digested with 10 mL analytical grade nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) (1:1) on a hot plate at 100 °C to near dryness when a clear solution was obtained. The solution was then diluted up to 25 mL with distilled water. The concentrations of trace elements in each sample were determined using atomic absorption spectrophotometer. Blank experiments were run to check for background contaminants by the reagents and apparatus used. The values obtained from running blank experiments were subtracted from the analyte values as applicable.

The Atomic Absorption Spectrophotometer (AAS) was pre calibrated. The calibration was done with 10, 8, 6, 4, 2 and 0 ppm solution of the metals obtained by serial dilution of 1000 ppm of the stock standard metal solution. Analysis of each sample was carried out in duplicate and results expressed in µg/g (ppm or mg/kg). Data obtained was analysed and the results were expressed as mean ± Standard Error. The mercury and arsenic analyses were however carried out by Flow Injection Assemble System (FIAS). This system uses cold vapour with quartz cell when measuring mercury.

A standard blank solution was made by measuring 10 mL of deionised water. Also, a series of calibration solutions containing known amounts of analyte element (the standards) were made. The blank and standards were atomized in turn and the response for each solution measured. The concentration of the sample from the calibration was then determined based on the absorbance obtained for the unknown.

Data Analysis

Pearson's product moment correlation (PPMC) was also carried out to establish association between heavy metals and pH and intermetals relationship in water, suspended solids, sediments and biota. The physicochemical and heavy metal data were subjected to principal component analysis for exploration of the extent of metal pollution and source identification.

Results

Heavy metal concentration in sediment

The heavy metal variations in sediment revealed that copper (Cu) exhibited highest concentrations of all the investigated heavy

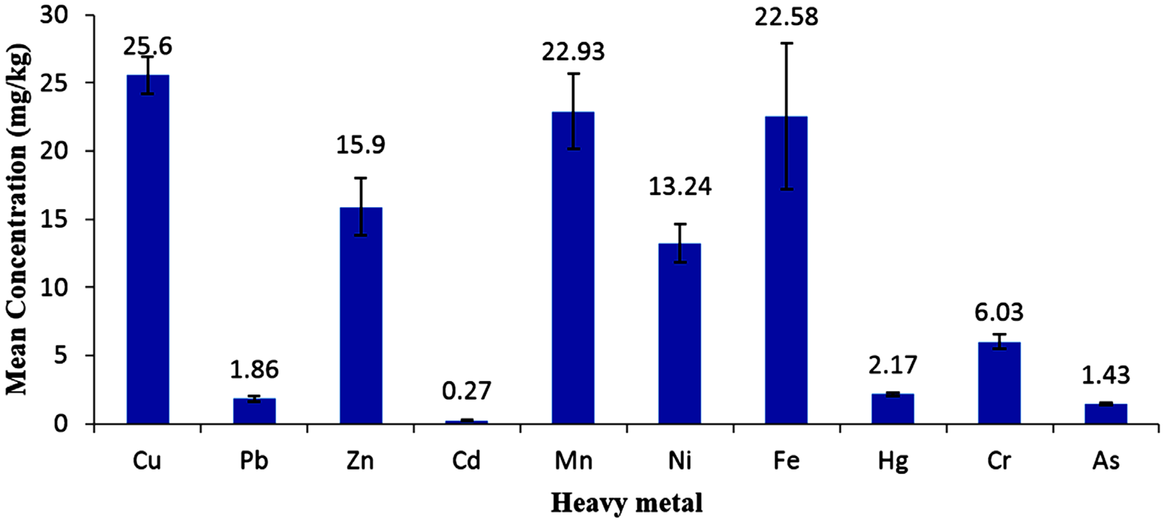

Fig. 2: Concentrations of heavy metals in sediment from the Weija Reservoir in Ghana

metals in the sediment. The mean values are illustrated in Fig 2. The concentrations of Cu ranged from 10.6 to 45.2 mg/kg with mean value of 25.60 mg/kg. This was followed closely by Mn and Fe with mean values of 22.93 and 22.58 mg/kg, respectively. Mercury (Hg) and Pb concentrations were relatively lower in sediment, with mean concentrations of 0.67 and 1.86 mg/kg respectively. The heavy metal with least concentration in the sediment was Cd, whose concentration ranged from non-detection to 1.3 mg/kg with a mean value of 0.27 mg/kg. The concentrations of heavy metals in sediments from the Weija Reservoir followed the decreasing order of ranking; Cu >Mn > Fe >Zn >Ni >Cr > Pb > As > Hg >Cd (Fig. 2).

Heavy metal concentrations in water

The results of the heavy metal analysis in water sample from the Weija reservoir are illustrated in Fig. 3. With the exception of Cr and As that were below detection limit, all other heavy metals studied were detected at various concentrations. Nickel (Ni) exhibited relatively higher concentrations among the analysed heavy metals and ranged from 0.04 to 3.44 mg/L with a mean value of 0.21 mg/L. Zinc concentrations in the reservoir water also ranged from 0.002 to 0.51 mg/L with mean value of 0.16 mg/L. This was followed by Cd (0.01-0.32) and Mn (0.02-0.22) mg/L with mean values of 0.07 and 0.06 mg/L, respectively. The least metal concentration in the reservoir water was recorded for Hg and it ranged from non-detection to 0.1 mg/L with a mean value of 0.002 mg/L. It was observed that Cu and Pb concentrations were also relatively lower with Cu levels ranging from non-detection to 0.32 mg/L with mean value of 0.02 mg/L, whilst Pb levels also ranged from a minimum of non-detection to 0.04 mg/L with mean value of 0.01 mg/L. The order of heavy metal accumulation in the water from the Weija Reservoir followed the decreasing order of ranking; Ni > Fe = Zn > Cd > Mn > Cu > Pb > Hg. This is an indication that Ni was highly concentrated in the reservoir water whilst Hg was the least concentrated (Fig 3).

Heavy metal concentrations in suspended particles

With the exception of Cr, all other heavy metals studied were detected at varying concentrations within the suspended particles, which normally serves as a chelating substance in the water

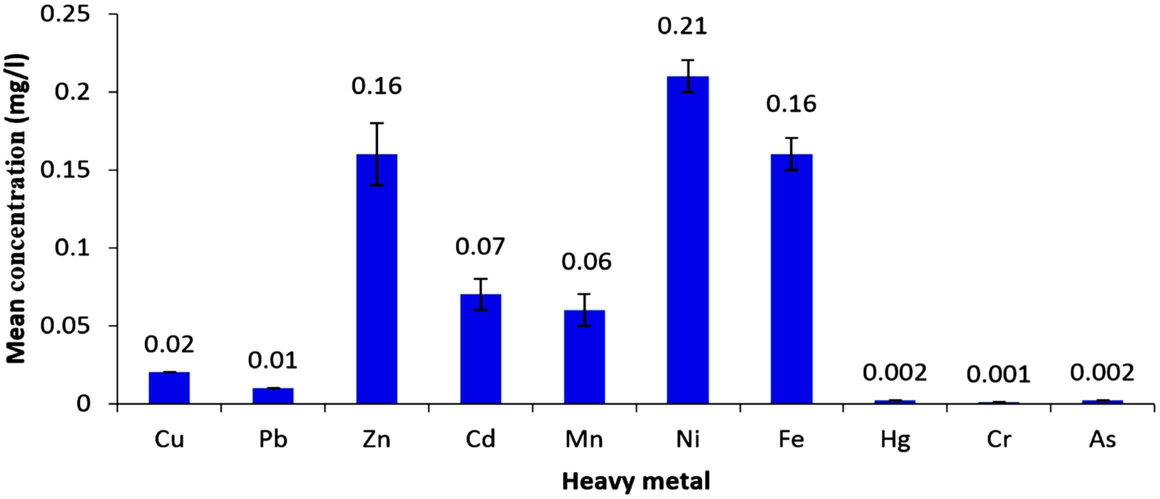

Fig. 3: Concentrations of heavy metals in water from the Weija Reservoir in Ghana

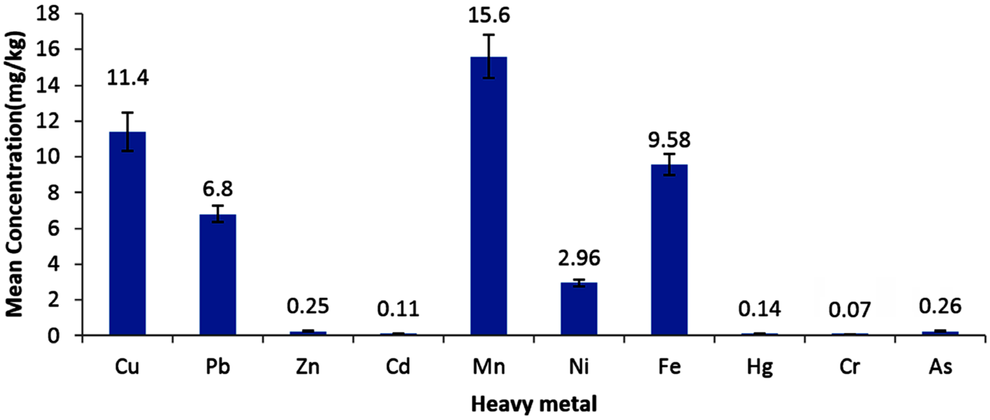

Fig. 4: Concentrations of heavy metals in suspended particles from Weija reservoir in Ghana

column. Manganese (Mn) exhibited higher concentrations among all the examined heavy metals in the suspended particles and ranged from 4.3 to 36.2 mg/kg with a mean value of 15.6 mg/kg. The Cu levels also ranged from 2.2 mg/kg to 45.6 mg/kg with mean value of 11.4 mg/kg and Fe ranged from a minimum of 2.3 to 17.2 mg/kg with mean value of 9.58 mg/kg. The lead levels in the suspended particles ranged from 2.2 to 14.2 mg/kg with a mean concentration of 6.8 mg/kg in the suspended particles. It was observed that Hg, Zn, Cd and As levels were relatively lower compared to other heavy metals studied in the suspended particles. The accumulation of heavy metals in suspended particles from the Weija Reservoir was observed to follow the decreasing order of ranking: Mn > Fe > Cu > Pb > Ni >As > Zn > Hg > Cd (Fig 4).

Heavy metal distribution in sediment, water and suspended solids

The heavy metal distribution and fate in sediment, water and suspended solids were assessed and the results showed that Ni accumulation was high in the reservoir water and its concentration was significantly lower in both sediment and suspended particles. The Fe accumulation was high in sediment followed by suspended particles and the least levels recorded in the water. Sediment samples recorded the highest concentration of Cu with mean value of 25.6 mg/kg and this was followed by suspended solids with mean value of 11.4 mg/kg and least recorded in water samples with mean of 0.02 mg/kg. The concentration of heavy metals such as Cu, Mn, Fe and Zn were higher in the sediment compared to the suspended solids and water and followed the order of ranking: Sediment > suspended solids > water

Chromium and arsenic were below detection limit in water samples, however, they were detected in sediment samples with mean values ranging from 6.02 mg/kg for chromium and 1.44 mg/kg for Arsenic. Lead was however highest in suspended particles with mean value of 6.8 mg/kg and followed by sediment with mean value of 1.86 mg/l and least in water samples with mean value 0.01 mg/l. The accumulation and distribution of Pb in the Reservoir followed the order; suspended particles > sediment > water. Fe concentration in sediment with mean value of 22.5 mg/kg was higher than in both suspended solids and water samples. The concentrations of heavy metals in sediment were found to be generally greater compared to the levels in suspended solids and water.

Principal component analysis of heavy metal in water, suspended particle and sediment

The mean concentrations of the heavy metals in the water, suspended particles and sediments samples were subjected to factor analysis using Principal Component Analysis (PCA) with varimax rotation as the extraction technique. Two major principal components were extracted, which accounted for a total of 71.30 % of the total variance, with the first component explaining 60.63% and the second component explaining 10.66% of the variance. The results indicated that component 1 was significantly enriched with Cu, Pb, Zn, Mn, Ni, Fe, Hg, Cr and As when there is a significant decrease in hydrogen ions in the sediment, water and suspended particles (Table 1). Component 2 significantly correlated with only Cd.

In order to determine the individual variance contributed by the studied heavy metals in the water, sediment and suspended particles, communalities were extracted, the results showed that Cu, Fe, Hg and As contributed more than 80% each of the total variance of heavy metals in the reservoir. Lead (Pb) and Cd also contributed 73% and 72% respectively of the distribution of heavy metals in the Reservoir whilst Mn produced the least variance with 67% of the total variance of heavy metal accumulation.

TABLE 1
Rotated Component Matrix of factor analysis of heavy metals and pH in the Weija Reservoir

Variable	Communalities	Component 1 (60.63%)	Component 2 (10.66%)
pH	0.639	-0.797	0.053
Copper	0.818	0.868	0.255
Lead	0.712	0.695	-0.478
Zinc	0.559	0.643	0.382
Cadmium	0.725	0.495	0.693
Manganese	0.474	0.676	-0.131
Nickel	0.671	0.726	-0.379
Iron	0.885	0.939	-0.050
Mercury	0.848	0.919	-0.055
Chromium	0.674	0.788	0.231
Arsenic	0.838	0.899	-0.175

Heavy metal in fish and prawn samples

The heavy metal concentrations in the muscles and gills of six different species of fish and one prawn species namely; *Parachanna obscura*, *Macrobrachium rosenbergii* (prawn), *Chrysicthys nigrodigitatus*, *Clarias batracus*, *Clarias gariepinus*, *Hemichromis faciatus* and *Sarotherodon melanotheron* were determined. With the exception of Cu and Cd that were not detected in all the species of fish studied, all other heavy metals were detected at varying concentrations. The mean concentration of heavy metals in the fish species ranged from a minimum of 0.06 mg/kg (As) in Hemichromis faciatus to a maximum of 11.3 mg/kg (Zn) in Clarias batracus. The levels of heavy metal concentrations in the

TABLE 2
Heavy metal concentration in fish and prawn species in the Weija reservoir (in mg/kg)

Variable	Cu	Pb	Zn	Cd	Mn	As
Parachanna obscura	ND	1.3±0.21	5.5 ±0.67	ND	8.5±0.15	ND
Macrobrachium rosenbergii	ND	1.6±0.06	9.0±0.11	ND	4±0.56	0.1±0.05
Chrysicthys nigrodigitatus	ND	2.2±0.10	4.4±0.05	ND	5.2±0.13	ND
Clarias batracus	ND	0.43±0.15	11.3±0.57	ND	8.4±0.14	0.13±0.06
Clarias gariepinus	ND	1.5±0.15	4.4±0.11	ND	1.53±0.06	ND
Hemichromis faciatus	ND	1.23±0.15	6.9±0.61	ND	8.6±0.15	0.06±0.01
Sarotherodon melanotheron	ND	0.6±0.20	4.3±0.12	ND	8.2±0.30	0.27±0.06

	Ni	Fe	Cr	Hg
Parachanna obscura	2.3±0.05	1.4±0.06	ND	0.1 ±0.05
Macrobrachium rosenbergii	1.2±0.05	5.5±0.32	0.1±0.00	0.2±0.01
Chrysicthys nigrodigitatus	1.2±0.10	3.7±0.05	0.1±0.05	0.1±0.05
Clarias batracus	3.2±0.05	4.8±0.06	ND	0.2±0.05
Clarias gariepinus	1.8±0.10	8.5±1.09	ND	0.5±0.01
Hemichromis faciatus	1.2±0.05	0.6±0.06	0.1±0.00	0.1±0.00
Sarotherodon melanotheron	4.3±0.10	6.53±0.06	4.3±0.10	0.4±0.10

ND-Not detected

various fish and prawn species followed the decreasing order of ranking; *Parachanna obscura >Macrobrachium rosenbergii > Chrysicthys nigrodigitatus >Clarias batracus > Clarias gariepinus > Hemichromis faciatus> Sarotherodon melanotheron* (Table 2).

Physicochemical parameters of water

The pH of the water sample ranged from 7.22 to 8.52 with a mean value of 7.53±1.20 indicating a slightly alkaline environment. The conductivity of the water sample ranged from 224 to 482 µS/cm with mean value of 350.3±68.3 µS/cm. The total dissolved solids ranged from a minimum of 122 to a maximum 281 mg/l with mean value of 211.1±42.48 mg/l. The total suspended solids ranged from 68 to 154 mg/l with mean value of 122±42.4 mg/l. The temperature of the water also ranged from 27.8 °C to 32.5 °C with mean value 27.81±4.45. The turbidity also ranged from 8 to 74 NTU with mean value of 40.96±25.51 NTU. The dissolved oxygen of the water sample ranged from 3.2 mg/l to 16.4 mg/l with mean value of 10.4±3.78 mg/l. The salinity also ranged from 0.10 to 0.20 ppt with mean value of 0.14±0.05 ppt. The Biochemical oxygen demand (BOD) ranged from 2.1 to 14 mg/l with mean value of 5.6±2.65mg/l.

Intermetals Relationship

Statistical analysis was conducted to determine the correlation between the different heavy metals in water, sediment and suspended solids using Pearson's Product Moment Correlation Coefficient (PPMC). In the water, apart from Pb and Zn, Cr and As that showed a significant correlation, all other heavy metals in water registered a weak correlation between each other. A significant positive correlation was found between Pb and Zn with a correlation coefficient of 0.663 at 95% confidence level. There was also positive correlation between Cr and As ($r=0.521$, $p<0.05$). There was however very weak correlation between the other heavy metals at 95% confidence level.

Discussion

Heavy metals in large amounts are usually present in fresh waters due to the weathering of rocks and soils (Al-Juboury, 2009). Changes in the physico-chemical parameters of water such as pH, temperature, dissolved oxygen, presence of chelating material, salinity and rainfall significantly influence the concentrations and mobility of metals. Reservoirs or water bodies are also normally subjected to various forms of degradation due to pollution arising from stone quarrying, dumping of domestic wastes and industrial effluents. However, these metals could also be present as a result of anthropogenic activities mainly from industrial and domestic effluent discharges (Anim *et al*., 2011). Considerable accumulation and variation in heavy metals were found in the sediments and suspended particles as compared to the reservoir water during the entire study period. The findings of the study confirm the earlier work of Aderinola *et al.* (2009) and Wufem (2009) who reported that heavy metals in the aquatic environment can be found in sediments and suspended particulates. Sediments normally act as a sink for pollutants such as heavy metals which are transported by rivers and by atmospheric precipitation or runoff to the sediments where they are finally deposited and accumulated (Censi *et al*., 2006). The heavy metal variations in sediment revealed that, copper (Cu) exhibited higher concentrations of all the investigated heavy metals and the concentrations ranged from 10.6 to 45.2 mg/kg. According to Aderinola *et al.* (2009), the major source of copper in the environment is industrial activities, which include scrap smelting, electroplating, manufacture of paints and pigments. Other sources are landfill leachates, mining effluents, manufacture and application of fertilizer and biocides. The possible sources attributed to the accumulation of Cu included application of fertilizer and pesticides in farming activities by some encroachers within the catchment of the Weija reservoir.

Heavy metals while migrating from the environment are deposited in bottom sediments where they are temporarily immobilized and may pose a hazard to biological life in a given ecosystem especially bottom feeding organisms (Anim *et al*., 2011). There was a very weak positive correlation between the heavy metals in suspended solids and that of the sediments. This therefore meant that the heavy metals in suspended solids and sediment sources are different. The heavy metals in sediments reflect many years of accumulation and depositions from the suspended materials. Secondly, through turbulent mixing, suspended solids could be transported from an area with high concentration to that with lower concentration (Censi *et al*., 2006). There may also be resuspension of metals from sediments into the sediment-water interface. For these reasons, it is unlikely that concentration of heavy metals in suspended solid would relate directly to the concentration of the metals in bottom sediments.

The chromium levels in the sediment were higher compared to suspended solids and the reservoir water. Chromium exists in water in two forms, trivalent and hexavalent but it is the speciation of the metal or the form that it exists that determines its toxicity and mobility. The hexavalent state is highly toxic but due to its poor solubility it is not detected in water (Besser *et al.*, 2004). The concentrations of heavy metals in bottom sediment were found to be comparatively higher than those obtained in the water and this may partly be attributed to the neutral to alkaline nature of the riverine water, since most of the heavy metals have precipitated and settled as carbonates, oxides and hydroxide bearing sediment and elevated levels can significantly impact on the benthic biota of the river. The sources implicated in the higher levels of heavy metals in the bottom sediment include industrial discharges from diverse sources such as untreated sewage, municipal waste and the use of agrochemicals in farming activities within the catchment of the reservoir. Runoff from rains could also be a major contributing factor which results in the transport of nutrient detritus, silt, industrial and domestic wastes into the reservoir.

The concentrations of heavy metals in the suspended particles were also higher compared to the reservoir water. This is so because when heavy metals are discharged into water systems, they generally show a large tendency to bind to suspended matter, which normally acts as scavenges, and thus, through sedimentation before they finally accumulate in aquatic sediments (Giguere *et al.*, 2004). Surface waters, depending on their geological structure, substratum type and land development are characterized by varied chemical composition and metals such as Cd, Cr, Cu, Fe, Pb, Ni or Zn and they enter into water as a result of natural processes as well as direct and indirect human activity. With the exception of Ni in the reservoir water that was above the WHO guideline limit of 0.02 mg/l, all other heavy metals Cd, Cu, Zn and Mn in the Weija Reservoir were below the chronic freshwater quality criteria for aquatic life. These phenomena is not surprising since the pH of the water ranged from 7.22 to 8.52 with a mean value of 7.53 which indicate a slight alkaline condition; heavy metals are not released into solution in alkaline medium. The pH level of the reservoir corroborated the work done by Amuzu (1975), who determined the physical and chemical properties of the Weija reservoir and reported that mean pH was about 7.0.

Two major principal components were extracted as affecting the dataset, with principal components 1 and 2 accounting for 60.63% and 10.66%, respectively, of total variance. With the exception of Cd, all the other metals were regulated by principal component 1 (Table 1). Fe, Hg and As contributed largely to principal component 1. These metals are associated with gold mining in Ghana. The Densu River and its tributaries, which feeds the Weija Reservoir, passes through areas in the Eastern Region of Ghana where water sources are heavily contaminated by illegal small-scale gold mining activities. Considering that the gold ore is arseno-pyrite in nature, it is likely to release As. The small-scale miners mostly use Hg to extract the gold, which may lead to the release of Hg into the water course. Water sources from the illegal mine sites were highly turbid and visibly contaminated and brown in colour, which suggested release of Fe compounds into the water that eventually arrived at the Weija Reservoir. Consequently, principal component 1 was associated with mining operations. It was presumed that principal component 2, which related mostly to Cd, was derived from Cd cell batteries in that waste stream that easily contaminated the Densu River along its tributaries. Hence, principal component 2 was deduced as a source factor related to the municipal waste stream. With the exception of Cu and Cd that were not detected in fish species, all other heavy metals were detected in at least one species of fish. These heavy metals accumulate significantly in the muscles and gills of fish species. According to Burger (2002), there are two main routes of heavy metals exposure. The primary route of intake of these metals is through the gills or transport of dissolved contaminants in water across biological membranes and ionic exchange. The secondary route is through ingestion of food or sediment particles with subsequent transport across the gut. The aquatic microflora or microfauna which constitute the food chain for fish species accumulate these metals in their living cells from the environment. The fishes consume them and gradually get enriched with heavy metals through bioaccumulation which may subsequently affect man through the food chain. These metals are known to produce adverse effects on aquatic biota and human health (Newman, 2012). According to Oguzie, *et al.*, (2010), fish has been reported to be very much sensitive to Pb and its uptake increases with increasing concentration in the environment. Unlike findings of the present study, fish living in contaminated sediment showed higher concentration of Pb in gills and muscles (Hewit and Servos, 2012). However, Cr levels were higher in most fish species especially *Sarotherodon melantheron* and far exceeded the recommended limit of 0.02 set by the EU. Beyer et al. (2000) postulated that Cr at sublethal concentrations in fish decreases survival growth and productivity and mainly accumulates in gills and liver. The effects of these metals in fish include reduction of growth and reproductive capacity. These heavy metals penetrate the mucous membrane of the bronchia, from where they move in the body through the circulatory system and accumulate in the liver and kidney (Fleischer *et al.*, 2011). The increase in contamination of metals in fish may be due to metals contaminated diet, which comes from discharge of effluent into the Reservoir from residential apartments and industries in the form of particulates and solutions from the catchment of the reservoir. Higher levels of Mn were observed in *Hemichromis faciatus, Sarotherodon melanotheron, Parachanna obscura* and *Clarias batracus* (table 2) which exceeded the WHO/FAO maximum permissible limit (MPL) of 5.5mg/kg (Tiimub and Afua, 2013). Further, the study recorded higher levels of Pb in all fish species studied than the WHO/FAO maximum permissible limit of 1mg/kg except for *Sarotherodon melanotheron* and *Clarias batracus* which recorded values within the WHO/FAO maximum permissible limit (table 2).

High concentrations of metals such as Ni in sediment and the fish tissues such as liver muscles and gills have been reported in a study by Newman (2012). This is so because these fishes are bottom feeders and feed on sediments and can accumulate higher concentrations of heavy metals. The findings of the study confirmed similar work done by Tiimub and Afua (2013), which recorded iron levels ranging from 44mg/kg to 53mg/kg and low level of Lead, Mercury and Arsenic in the fish species.

Conclusions

This study has established that the concentrations of heavy metals accumulation in sediments from the Weija reservoir followed the decreasing order of ranking; Cu > Mn > Fe > Zn >Ni >Cr > Pb > As > Hg > Cd. The sediment was contaminated in relatively high concentration with Cu and minimally with Cd; these concentrations were however, below the EU standard for sediment samples. The possible sources attributed to the accumulation of Cu included application of fertiliser and pesticides in farming activities by some farmers within the catchment of the Weija reservoir.

With the exception of Cr and As that were below detection limit in the reservoir water, all other heavy metals studied were detected at various concentrations, with Nickel (Ni) exhibiting highest concentrations of all the analyzed heavy metals and ranged from 0.04 to 3.44 mg/l, with a mean value of 0.21 mg/l, which exceeded the recommended limit set by the WHO standard for drinking water quality. The order of heavy metal accumulation in the reservoir water from Weija followed the decreasing order of ranking; Ni > Fe = Zn > Cd > Mn > Cu > Pb > Hg. This is an indication that Ni was highly contaminated in the reservoir water whilst Hg was the least contaminated. With the exception of Cu and Cd that were not detected in all the species of fish studied, all other heavy metals were detected at varying concentrations in the muscles and gills with some of the metals like Mn and Pb exceeding the WHO/FAO maximum permissible limit for human consumption. With continuous anthropogenic release of waste into the reservoir water, the accumulation of these metals in fish may increase beyond acceptable limit in the medium to long term. Evidence from principal component analysis (PCA) suggested that two key source factors, characterised as related to mining and municipal solid wastes, underpinned heavy metal contamination in the Weija reservoir.

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