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Distribution of heavy metals in sediments, physicochemical and microbial parameters of water from River Subin of Kumasi Metropolis in Ghana

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ABSTRACT

The River Subin, which serves as a source of direct drinking water downstream, flows through the Metropolis of Kumasi in Ghana, making it vulnerable to pollution due to human activities. In this study, we assessed the heavy metals content in the sediment of the Subin River as well as the physicochemical properties and microbial load in the river. Water and sediments were sampled from Race course upstream and downstream, Asafo, and Abinkyi upstream and downstream, Kaase, Asokwa and Wood village with a sampling distance of 100 m. Index of Geoaccumulation (*I*geo), contamination factor (CF), contamination degree (CD) and pollution load index (PLI) were used to assess the level of heavy metal enrichment and contamination in the sediments of River Subin. Analysis showed that temperature of the river ranged between 31.23 to 31.40 °C, pH ranged between 6.62 and 7.52, conductivity ranged between 1.16 and 4.67 µS/cm, total hardness ranged from 0.65 to 3.82 mg/L, Ca ranged from 0.26 to 1.22 mg/L, alkalinity ranged from 324 to 711 mg/L, Mg from 0.24 to 3.35 mg/L and Cl ranged from 56.76 to 99. 30 mg/L. The microbial load assessment indicated that the River Subin is highly polluted by *E. coli*, Faecal Enterococci, Total coliform and faecal coliform, which generally increased as the river flows downstream since more solid waste from domestic and industrial effluents enter the river. *I*geo data suggested that the river was highly contaminated by Ag and Cd and moderately polluted by Pb and Co. The CF, CD and PLI, results showed high levels of Ag, Cd, Cr, Cu, Fe, Hg, Co, and Zn, indicating a progressive deterioration of water quality at the various sites. Our results suggest that the River Subin is highly polluted and thus, urgent management strategies are needed to mitigate further deterioration of the river.

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Introduction

Water is considered one of the most important resources found on Earth and its quality is essential for life [8,16]. Waterbodies such as river are subjected to pollution mainly through human activities, thus affecting its quality [36,50]. Most rivers are polluted mainly by domestic, industrial, mining and agricultural activities, which affects the properties of water bodies biologically, physically and chemically [8,30,51]. In most developing countries, faecal contamination of rivers plays a major role in the quality of water. In most cases, development of water collection and treatment does not correspond to population growth [34]. The microbial parameters of water can be used to test for pathogens, which are disease-causing microorganisms and thus as a tool for assessing water quality.

The River Subin, which flows through the metropolis of Kumasi in Ghana, is surrounded by communities making it vulnerable to contamination and the level of contamination could increase substantially by heavy rainfall, which easily transports them into the river. Previous work by Obiri-Danso et al. [34] reported that the bacterial indicator numbers varied from 1.61×10^9 to 4.06×10^{13} for total coliforms, 9.75×10^8 to 8.98×10^{12} for faecal coliforms and 1.01×10^2 to 6.57×10^6 for enterococci in the River Subin an indication of pollution. The river constantly receives untreated waste from manufacturing industries, a teaching hospital, an abattoir, wood processing plants, and refuse from the city leading to possible contamination [34]. The river serves as a source of drinking water without processing for communities downstream as well as their domestic and agricultural usage. Disposal of wastewater and sludge, industrial activities and agricultural activities have led to contamination by pesticides and heavy metals in water bodies [17]. River's sediments get contaminated either from point sources such as industrial waste or non-point sources, including runoff from excavated lands, smelting of metalliferous ores and leachate from landfills [17]. The pH, temperature, and the water disturbance affect the levels of these heavy metals in an aquatic environment [9,41]. For example, heavy metals are released more easily into the water at lower pH and higher temperatures. Although many metals are considered essential, they become toxic at higher concentrations due to their ability to cause oxidative stress by forming free radicals, which can react with cellular structure proteins, enzymes and membrane systems [29]. The levels of heavy metals in sediments can be the basis for predicting the extent of pollution of the overlying water [17]. In a previous study, heavy metals in sediments and waters of River Subin were identified as Al, As, Cd, Cr, Cu and Zn using instrumental neutron activation analysis (INAA). The concentrations of Al, As, Cd, Cr, Cu and Zn in the water sample were in the range 4.02–15.18, 0.007–0.16, 0.002–0.05, 0.001–0.019, 1.32–7.04 and 4.28–10.2 mg/L, respectively an indication of pollution by these metals [2]. Poor water quality has been reported to contribute about 80% of all diseases in human beings [24]. In view of this, it is, therefore, necessary for research to be conducted frequently on the water quality of the River Subin. Therefore, this current study examined the levels of heavy metals present in the sediment, physicochemical parameters and the microbial contamination levels of the water from the River Subin.

Study area and sampling

The River Subin rises out of spring at an abandoned Racecourse (6° 45′ N 1° 38′W) north of Kumasi and runs southwards through the city centre (Fig. 1) and merges with the River Oda at Asago (6°45′N 1° 36^1 W). The Subin river covers about 230 km^2 and has a mean flow rate of 0.243 m^3/s [34].

About 500 g of sediments were taken from 0 to 10 cm depths using plastic trowel. A total of three sediment samples were collected per site and placed into ziploc bags and transported into the laboratory. Sediments were taken from Race course upstream, Race course downstream, Asokwa and Wood village due to accessibility and concreting of some parts of the river.

Twenty-four water samples were taken from 8 different sites into 1 L polyethylene plastic bottles previously washed with deionised water. Bottles were rinsed with water from the river at the sampling point before bottles were filled to the brim and covered tightly. Samples were taken from Race course downstream and upstream, Asafo, Abinkyi upstream, Abinkyi downstream, Kaase, Asokwa and Wood village. Three water samples were taken from each location. Water samples and sediments were collected in January 2020. The samples were kept at a low temperature of 4 °C and conveyed to the laboratory for analysis.

Physicochemical parameters

The temperature of the water samples was measured *in situ* using a calibrated field-portable PCSTestr35 multi-parameter probe (Oakton waterproof Multiparameter). Whilst in the laboratory, the PCSTestr35 multi-parameter probe (Oakton waterproof Multiparameter) was calibrated and used to determine pH, turbidity and conductivity of the water samples.

Microbiological analysis

A 1 ml of each water sample was pipetted with a micropipette into test tubes containing the MacConkey Broth solution after the tubes had been sterilised. The solutions were then incubated for 24 h at a temperature of 44 °C. Total Coliform present was determined by pipetting 1 mL of the sample into test tubes containing the MacConkey Broth solution. The solutions were then incubated for 24 h at a temperature of 37 °C. The presence of *Escherichia coli* in the water sample was determined as follows, Tryptophan Broth was prepared by dissolving 16 g of Kovac's reagent in 1 litre of water and

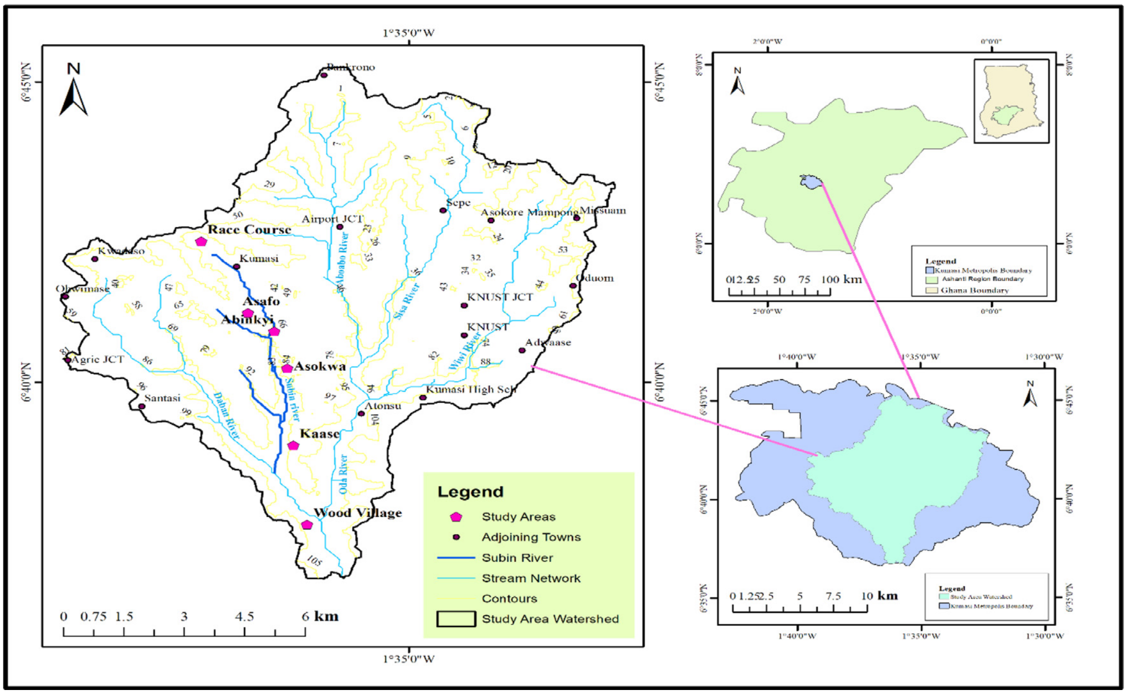

Fig. 1. Map of River Subin and sampling points in Kumasi of Ghana.

distributed into test tubes which were sterilised in an autoclave at 121 °C for 15 min. About 1 litre of the Tryptophan Broth was equally distributed in each of the tubes containing MacConkey Broth for the Total Coliform. A reddish ring at the meniscus of the tubes confirms the presence of *E. coli*.

Analytical method

Deionised water was used throughout the analysis. All field and laboratory determinations were carried out according to the standard methods for the analysis of water and wastewater [7]. Total hardness was determined by complexometric titration, calcium and magnesium by EDTA titrimetric method, chloride using the Mohr's method and total alkalinity using acid-base titration.

Determination of heavy metals in sediments

The concentration of heavy metals in sediments was determined using X-ray fluorescence (XRF) Spectrophotometer. Samples of sediments were air-dried in the sun to ensure that they were free from moisture. Each dried sediment was sieved to $< 250\ \mu$m particle size using a USA Standard Testing Sieve (ASTM E11). Samples of sediments were analysed using a Niton XL3t GOLDD+ X-ray fluorescence (XRF) analyser (ThermoFischer Scientific, Manitoba, USA). About 2 g of the sieved sample was placed in a small (approximately 30 mm) polyethylene container, so it was three-quarters full and sealed at both ends using a mylar film. The sample was then placed in the XRF shroud and scanned for 180 s to determine the concentration of heavy metals. The XRF instrument was calibrated using NIST 2711 standard reference material and system checked prior to sample analysis.

Pollution assessment of heavy metals

*Geo-accumulation index (*Igeo*)*

This index was used to measure the anthropogenic effects of the metals and was obtained by using Eq. (1) [21,40,42].

$$Igeo = log_2 \frac{Cn}{1.5} * Bn \tag{1}$$

where Cn is the measure of heavy metal concentration, Bn is the background concentration of metals [45] and 1.5 is the background factor due to lithogenic effects [43]. *I*geo classification of heavy metals were, *I*geo < 0 (class 0, uncontaminated), 0 < *I*geo < 1 (class 1, uncontaminated to moderately contaminated), 1 < *I*geo< 2 (class 2, moderately contaminated), 2 < *I*geo < 3 (class 3, moderately to strongly contaminated), 3 < *I*geo < 4 (class 4, strongly contaminated), 4 < *Igeo*< 5 (class 5, strongly to extremely contaminated) and 5 < *I*geo < 6 (class 6, extremely contaminated).

Contamination factor (CF)

Contamination factor of the heavy metals was calculated by comparing the mean concentration of trace metal with average shale concentration provided by Turekian and Wedepohl [45]. The CF of the heavy metals was obtained by using Eq. (2).

$$\mathrm{CF} = \frac{Average\ concentration\ of\ heavy\ metals\ at\ a\ site}{Average\ metal\ shale\ concentration} \tag{2}$$

Grouping of metal CF into class was achieved by using the Hakanson [19] classification method, which puts CF into four classes (CF $<$ 1 (class 1), 1 $\leq$ CF $<$ 3 (class 2), 3 $\leq$ CF $<$ 6 (class 3) and CF $\geq$ 6 (class 4) and it means the contamination degree is low, moderate, considerable and very high, respectively.

Contamination degree (CD)

Contamination degree of a sampling site was calculated by adding all individual metal CF of that site [21,42]. Classification of CD in terms of four grade ratings (Class 1, 2, 3 and 4) of sediments was done according to the method described by Ahdy and Khaled [3]. CD $<$ 6 (class 1, indicates a low contamination), 6 $\leq$ CD $<$ 12 (class 2, indicates moderate level of contamination), 12 $\leq$ CD $<$ 24 (class 3, suggests a considerable level of contamination) and CD $\geq$ 24 (class 4, indicates a very high level of contamination).

Pollution load index (PLI)

Pollution load index for each sampling site was determined by using Eq. (3) [42].

$$\mathrm{PLI} = n\sqrt{(\mathrm{CF1}} \times \mathrm{CF2} \times \mathrm{CF3} \times \mathrm{CF}n) \tag{3}$$

where CF is the contamination factor and n is the number of heavy metals under consideration. A PLI = 0 indicates a perfect state of no pollution; PLI = 1 indicate only baseline levels of pollutants present and PLI $>$ 1 indicate progressive deterioration of the site.

Statistics analysis

IBM Statistical Package for Social sciences (SPSS) 20.0 and Microsoft Excel version 2010 were used for the statistical analysis. Pearson's correlation matrix was performed to study the relationship between variables. Significance levels are described as non-significant ($p > 0.05$) and significant ($p < 0.05$) and were determined by One-way analysis of variance (ANOVA) test performed using Microsoft excel 2010 version. ANOVA is important in finding out significant differences between the different sampling points for a particular parameter.

Results and discussion

Physicochemical parameters

The mean values of the physicochemical parameters for the water sampled from eight different sites of the River Subin are presented in Table 1. Water quality can be considerably linked to its physicochemical parameters such as pH, temperature, conductivity, turbidity, etc. Also, aquatic ecology can be significantly influenced by these physicochemical properties, especially temperature and pH [5]. To assess the physicochemical parameters of River Subin, we measured temperature, pH, conductivity, turbidity, total hardness, alkalinity and nutrients such as calcium, magnesium and chlorine. We observed a temperature range of 31.23 to 31.40 °C, which was slightly above the permissible limits of 25 to 30 °C [48]. The river receives direct sunlight activity, which may have led to a higher temperature. Vegetation along the river banks has been destroyed to make way for infrastructure for housing and industrial activities. Water temperature is influenced by the local climate and is an important condition in aquatic ecosystems. It influences the reproduction and metabolism of many aquatic organisms and can alter most physicochemical variables of the water body [32]. This current study shows that all the water samples have acidic pH except from Wood village and Race course upstream. We also observed a significant difference in pH between different points ($p < 0.01$) which may be due to the geology of the riverbed and the extent of pollution through surface runoff. However, the pH values for the different sites were all within the WHO limits (6.5 to 8.5) for potable water [48]. A previous study by Ali et al. [5] reported an average pH of 7.89 and 8.17 for River Karnaphuli during the summer and winter. The measured pH agrees well with Adiyiah et al. [1] study in the Oti river in Ghana but is higher than pH recorded by Boateng et al. [12].

Electrical Conductivity (EC) values for the water ranged from 1.16 to 4.67 µS/cm and were all within the WHO acceptable limits (700 µS/cm) for portable water. Dissolved ions influence EC in surface water and may come from natural and anthropogenic origins. A lower value of EC indicates the presence of low concentration of dissolved ions such as inorganic salts. Higher turbidity in water increases the cost of purification processes such as flocculation and filtration [23]. We observed a significant difference ($p < 0.01$) in turbidity between the water sample. Turbidity in surface water is an indication of the presence of suspended solids and organic matter. Water sampled from Race course upstream recorded the lowest turbidity of 1.79 ± 0.05 NTU, lower than the WHO guideline value of 5 NTU. Water from Asafo had the highest value of 166.6 ± 7.63 NTU, which exceeds the guideline value. This observation may be that at Race course upstream where the river starts its

Table 1
Results for Physicochemical parameters of River Subin ($n = 3$).

Sample	Racecoursedownstream	Race courseupstream	Asafo	Abinkyidownstream	Abinkyiupstream	kaase	Asokwa	Wood village
Temperature (°C)	31.33 ± 0.50	31.36 ± 0.12	31.4 ± 0.7	31.26 ± 0.20	31.26 ± 0.21	31.33 ± 0.15	31.36 ± 0.12	31.23 ± 0.06
pH	6.75 ± 0.27	7.24 ± 0.24	6.71 ± 0.12	6.78 ± 0.02	6.62 ± 0.08	6.85 ± 0.01	6.84 ± 0.03	7.52 ± 0.09
Conductivity (µS/cm)	3.36 ± 0.14	2.48 ± 0.07	4.67 ± 0.24	2.06 ± 0.03	3.90 ± 0.04	2.54 ± 0.005	2.54 ± 0.10	1.16 ± 0.16
Turbidity (NTU)	6.93 ± 0.06	1.79 ± 0.05	166.6 ± 7.63	49.16 ± 0.36	55.06 ± 1.00	34.39 ± 0.433	34.69 ± 0.07	81.33 ± 7.09
Total Hardness (mg/L)	3.82 ± 0.06	2.80 ± 0.05	0.68 ± 0.04	0.65 ± 0.02	0.72 ± 0.04	0.76 ± 0.02	0.68 ± 0.085	0.67 ± 0.21
Calcium (mg/L)	0.66 ± 0.04	1.22 ± 0.19	0.26 ± 0.05	0.26 ± 0.02	0.37 ± 0.07	0.42 ± 0.03	0.42 ± 0.11	0.63 ± 0.22
Alkalinity (mg/L)	575 ± 3.78	711.33 ± 11.93	324 ± 5.56	540.33 ± 15.01	967 ± 16.86	476.33 ± 6.11	451 ± 78.17	491.33 ± 49.57
Magnesium (mg/L)	3.35 ± 0.09	1.61 ± 0.11	0.38 ± 0.03	0.24 ± 0.04	0.40 ± 0.1	0.423 ± 0.08	0.29 ± 0.02	0.5 ± 0.31
Chloride (mg/L)	56.80 ± 0.3	56.76 ± 0.55	99.30 ± 0.93	72.83 ± 1.76	82.93 ± 6.79	89.73 ± 3.61	78.96 ± 1.09	73.66 ± 10.26

Table 2
Result showing mean ± standard deviation of microbial indicator counts from the eight sampling sites on the River Subin in Kumasi (n = 3).

Sampling sites	Total coliform	Faecal coliform	E. coli	Faecal Enterococci
Racecourse upstream	$2.67 \times 10^{10} \pm 9.67$	$1.48 \times 10^{7} \pm 5.9$	$9.28 \times 10^{6} \pm 5.35$	$1.51 \times 10^{2} \pm 1.4$
Racecourse downstream	$9.18 \times 10^{10} \pm 8.66$	$2.31 \times 10^{8} \pm 7.22$	$3.94 \times 10^{6} \pm 5.52$	$5.61 \times 10^{2} \pm 1.64$
Asafo	$2.31 \times 10^{10} \pm 9.19$	$2.3 \times 10^{8} \pm 7.3$	$2.5 \times 10^{6} \pm 5.26$	$8.32 \times 10^{2} \pm 1.31$
Abinkyi upstream	$2.53 \times 10^{10} \pm 8.90$	$5.71 \times 10^{8} \pm 7.21$	$3.63 \times 10^{6} \pm 5.64$	$8.86 \times 10^{2} \pm 1.61$
Abinkyi downstream	$3.16 \times 10^{10} \pm 8.89$	$2.81 \times 10^{8} \pm 6.76$	$1.93 \times 10^{6} \pm 4.77$	$4.56 \times 10^{2} \pm 1.61$
Kaase	$4.23 \times 10^{11} \pm 9.93$	$9.16 \times 10^{8} \pm 6.7$	$2.34 \times 10^{6} \pm 5.06$	$1.4 \times 10^{3} \pm 2.25$
Asokwa	$9.11 \times 10^{11} \pm 10.8$	$2.97 \times 10^{8} \pm 7.31$	$4.4 \times 10^{6} \pm 5.67$	$1.68 \times 10^{3} \pm 2.82$
Wood village	$1.57 \times 10^{10} \pm 9.06$	$4.26 \times 10^{8} \pm 7.31$	$9.29 \times 10^{6} \pm 4.12$	$6.22 \times 10^{2} \pm 1.34$

flow, it experiences less soil erosion and water runoff compared to Asafo where human activities may have led to an increase in runoff and soil erosion. The degree of hardness and alkalinity greatly influences the quality of water supplied and is attributed to the chemical composition of water bed, which may be carbonate, bicarbonate and hydroxide compounds or borates and silicates. We recorded a range of 0.65 ± 0.02 to 3.82 ± 0.06 mg/L for total hardness of the River Subin, which was below the WHO limits of 500 mg/L. Hardness in water is due to the presence of cations such as Ca^{2+} and Mg^{2+}; and anions such as HCO_3^-, Cl^- and SO_4^{2-} in the water [37]. The river water is classified as soft water according to the WRC [49] standards. In the present study, alkalinity ranged from 324 ± 5.56 to 967 ± 16.86 mg/L, which was above the suitable range of 20–300 mg/L for fish [22]. Alkalinity refers to the waters ability to neutralise acids. For the ions present in the river, Ca ranged from 0.27 ± 0.02 to 1.12 ± 0.19 mg/L, Mg level ranged from 0.21 ± 0.04 to 3.27 ± 0.09 mg/L and Cl level ranged from 56.76 ± 0.55 to 99.30 ± 0.93 mg/L. Ca, Mg and Cl concentrations were below the WHO [47] permissible limit of 75, 50 and 250 mg/L, respectively.

Microbial analysis

The results for mean values of microbial indicator load at the eight different sampling sites of the River Subin are presented in Table 2. Total coliform levels ranged from 1.57×10^{10} to 9.11×10^{11}Cfu/ml while faecal coliform levels ranged from 1.48×10^{7} to 9.16×10^{8} Cfu/ml, however, for water to be considered safe, it must have zero total coliform [23]. Our microbial results also showed that E. coli ranged from 2.34×10^{6} to 9.29×10^{6} Cfu/ml, while the levels of Faecal Enterococci ranged from 4.56×10^{2} to 1.68×10^{3} Cfu/ml. We observed a significant difference in bacterial load between the eight sampling sites of the River Subin ($P < 0.001$) and this may be due to the differences in levels of disposal of waste product either directly or indirectly into the river by the surrounding communities. Faecal enterococci showed a very strong correlation with total coliform. Microbial contamination of rivers has become a major water quality issue mainly due to the fast-growing population. Indeed, while population is increasing in cities, development of wastewater collection and treatment facilities has not been increased to meet the demand. The poor collection and treatment facilities have resulted in the direct disposal of waste products into river bodies, which affect the quality of the river. This current study shows that the River Subin has a high microbial load, which generally increases as the river flows from its source to downstream. For example, total coliform load at Racecourse upstream (source of the river) had an average load of 2.67×10^{10} Cfu/ml but increased to 9.18×10^{10} Cfu/ml at Race course downstream and a load of 9.11×10^{11} at Asokwa. Faecal coliform average load at Race course upstream was 1.48×10^{7} Cfu/ml but increased to 4.46×10^{8} CFU at Wood village. Race course upstream had faecal enterococci load of 1.51×10^{2} Cfu/ml but was increased to 8.86×10^{2}Cfu/ml at Abinkyi upstream. The general increase of microbial load from upstream to downstream can be attributed to increased community size and industrial activities coupled with poor waste treatment facilities. Our result agrees with a previous study that reported that microbial load in the River Subin increases as it flows from the source through the commercial centres of Kumasi to downstream [34]. We observed that E. coli load was higher at the Race course upstream with an average load of 9.28×10^{5} and was reduced to 1.93×10^{6}Cfu/ml at Abinkyi downstream. However, at Wood village average E. coli load was again increased to 9.29×10^{6}Cfu/ml. The possible reason for the high E. coli at the river source (Race course upstream) may be due to surface runoff of faeces from humans through open defecation and also the presence of larger flocks of birds around the River Subin. Comparing our microbial load results to acceptable limit suggest that the River Subin is highly contaminated. The high total and faecal coliform levels observed make the river unsuitable for swimming, boating and fishing [31,48]. The general sanitary qualities of the river are unacceptable, as indicated by the total and faecal coliform counts. Waters with zero total and faecal coliform counts are considered safe for domestic use, which would not pose any human health risk. We observed that faecal coliform load ranged from 1.48×10^{7} to 9.16×10^{8} Cfu/100 ml and Faecal Enterococci load ranged from 4.56×10^{2} to 1.68×10^{3} Cfu/100 ml which were above the acceptable level of less than 100 Cfu/100 ml for faecal coliform and Faecal Enterococci in water [34]. We also observed that *E. coli* load ranged from 2.34×10^{6} to 9.29×10^{6} Cfu/ml, which was above the acceptable limits of 0 Cfu/ml [35,50]. Presence of E. coli and coliform in surface water indicates the possibility of contamination by other pathogenic microbes, which makes the water unsafe [6]. In a previous study to assess the microbial quality of surface water sampled from Isiolo county in Kenya reported a mean load of 39.2 Cfu/ml for *E. coli*, 3421 Cfu/ mL for *Clostriduim pafringens* and 740 Cfu/mL for *Staphylococcus aureus* [35]. Leslie [25] reported that faecal coliforms count for water sampled from surface water were above 300×10^{4}/100 ml. The total coliform had a strong positive correlation with

Table 3
Mean concentration (mg/kg) of heavy metals in the sediments of River Subin ($n = 3$).

Metal	Race course downstream	Race course upstream	Wood village	Asokwa
Ag	56.57	24.04	44.02	45.14
As	2.67	2.61	1.61	3.66
Cd	59.56	34.58	63.12	49.89
Co	58.34	47.16	26.03	64.54
Cr	111.28	137.44	45.9	159.9
Cu	37.1	76.3	19.15	93.91
Fe	27,764.91	24,947.19	6944.59	39,041.79
Hg	4.25	3.32	3.30	4.05
Mn	464.83	454.91	91.02	589.56
Ni	14.23	10.96	11.11	13.51
Pb	28.19	50.62	4.34	116.93
Zn	52.08	186.86	44.77	438.82

faecal Enterococci ($r^2 = 0.83$). We observed a moderate positive correlation between temperature and total coliform and a weak correlation between temperature and *E. coli*. Microorganism are known to have strong relation with turbidity [11,15]. In the current study, we observed positive correlation between turbidity and faecal enterococci but not with total coliform, *E. coli* and faecal coliforms. Contrary to our observation, previous work reported a positive correlation between coliform and turbidity. pH affects both biological and chemical processes in water. We observed a positive correlation between pH and *E. coli* but not with faecal coliforms, faecal enterococci and total coliform.

Heavy metals concentration and pollution assessment

The levels of heavy metals in the sediment of river Subin taken from four sites along the river are presented in Table 3. The concentration range of Ag from 24.04 mg/kg (Race course upstream) to 56.57 mg/kg (Race course downstream). The concentration is much higher compared to 0.10 mg/kg limit [46]. Levels of Cd ranged from 34.58 mg/kg (Race course upstream) to 63.12 mg/kg (Wood village), The levels of Cd were found to be higher than the permissible value of 0.99 mg/kg [46]. Co concentration ranged between 26.03 mg/kg (Wood Village) and 64.54 mg/kg (Asokwa), which is far above the results of Topeoglue et al. [44] and Balkis et al. [10]. Cr concentration varied between 45.9 mg/kg (Wood village) to 159.9 mg/kg (Asokwa). The concentration of Cu ranged from 19.15 mg/kg (Wood village) to 93.91 mg/kg (Asokwa). Levels of Fe present in the river sediments sampled from Race course downstream, Race course upstream, Wood village and Asokwa recorded a mean concentration of 27,764.91, 24,947.19, 6944.59 and 39,041.79 mg/kg, respectively. In the earth crust, Fe is most bountiful element and it makes big percentage of the crustal composition. Its abundance in the Earth's crust is associated with its nuclear stability [26]. Therefore, anthropogenic and natural sources may affect the level. Concentration of Hg was within the range of 3.30 (Wood village) to 4.25 mg/kg (Race Course downstream). Another metal of importance to the study is Mn and ranges from 91.02 mg/k (Wood village) to 589.56 mg/kg (Asokwa). This is much higher than the WHO [48] limit of 0.5, an indication that concentration is affected by anthropogenic sources, Pb ranged from 4.34 mg/kg (Wood village) to 116.91 mg/kg (Asokwa) and Zn levels ranged from (44.77) mg/kg (Wood village) to 438.82 mg/kg (Asokwa). The maximum mean concentrations of Hg, Cr, Cu, Zn, Pb and Cd were above the upper continental crust standard of 0.05, 92, 28, 67, 17, 0.09 mg/kg, respectively, for river water sediment [38]. This suggests that anthropogenic sources mostly influenced the concentrations. The levels of As in the River Subin sediments were within the range of 1.61 mg/kg (Wood village) to 3.66 mg/kg (Asokwa), Ni ranged from 10.96 mg/kg (Race course upstream) to 14.23 mg/kg (Race course downstream). As and Ni level was below the upper continental crust standard of 4, 8 and 47 mg/kg, respectively, for river water sediment [38]. The low level suggest that it may come from natural sources.

Multivariate statistical analysis

Correlation coefficients analysis between heavy metals. Pearson correlation is a straightforward statistical method for determining the strength of an association between two variables [4]. A correlation coefficient of > 0.7 indicates a strong relationship between two variables, while a value of zero indicates no relationship [18]. Moreover, correlation coefficients of 0.4 to 0.7 indicate a moderate relationship and > 0.4 indicate a poor relationship between two variables [27]. Correlation analysis aids in comprehending the interdependence of several water quality metrics. It was commonly used to establish a link between physical and chemical properties. Pearson correlation analysis was conducted amongst heavy, as listed in Table 4. Fe correlated significantly positively with As ($r^2 = 0.988$) and Co ($r^2 = 0.976$) at $p < 0.05$. Also, Mn significantly correlates well with Co ($r^2 = 0.966$, $p < 0.01$), Cr ($r^2 = 0.970$, $p < 0.01$) and Fe ($r^2 = 0.982$, $p < 0.01$). Pb correlated significantly with Zn ($r^2 = 0.983$) at $p < 0.01$, while Ni strongly correlates with Hg ($r^2 = 0.999$, $p < 0.01$). Strong correlations suggest a common source amongst these metals [13,14].

Principal component analysis. Principal component analysis (PCA) is a widely used statistical technique that summarises many variables to a few important scores (components) was applied to identify possible sources of pollutants and their associations by applying varimax rotation with Kaiser normalisation. By extracting the eigenvalues and eigenvectors from the

Table 4
Pearson correlation matrix of 12 heavy metals in the sediment of the River Subin.

	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Ag	1											
As	0.062	1										
Cd	0.849	−0.401	1									
Co	0.250	0.937	−0.286	1								
Cr	−0.227	0.938	−0.680	0.882	1							
Cu	−0.427	0.872	−0.747	0.698	0.937	1						
Fe	0.092	0.988*	−0.410	0.976*	0.948	0.833	1					
Hg	0.756	0.645	0.298	0.819	0.453	0.193	0.699	1				
Mn	−0.008	0.948	−0.523	0.966*	0.970*	0.831	0.982*	0.645	1			
Ni	0.790	0.612	0.350	0.788	0.407	0.149	0.664	0.999**	0.604	1		
Pb	−0.107	0.942	−0.445	0.766	0.873	0.927	0.882	0.412	0.814	0.382	1	
Zn	−0.194	0.863	−0.445	0.633	0.793	0.912	0.779	0.264	0.698	0.237	0.983*	1

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

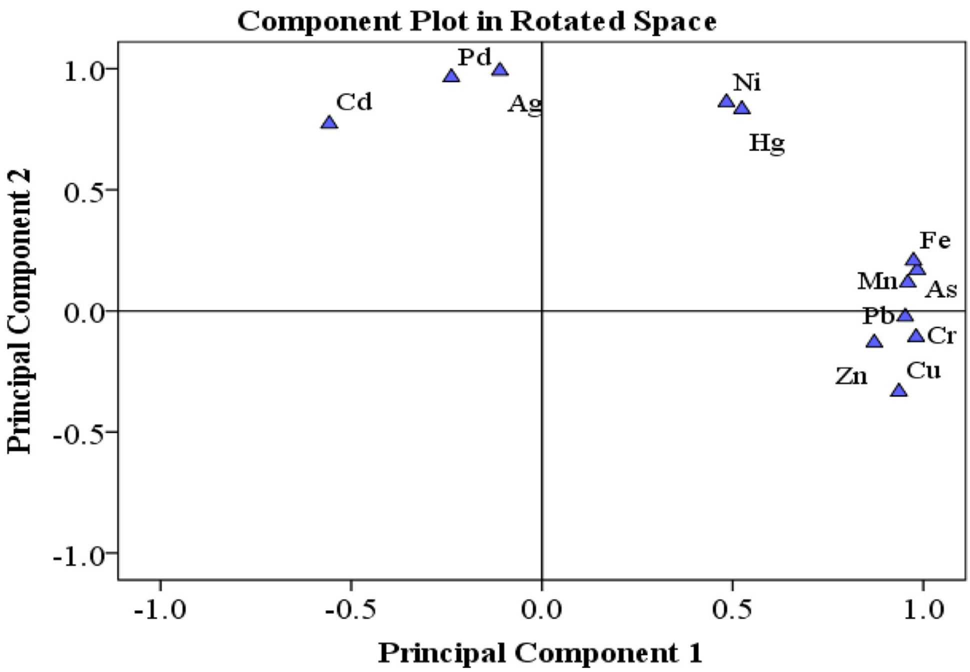

Fig. 2. Principal component profile of heavy metals in the sediment of different sampling sites.

correlation matrix, the major parameters that influenced groundwater quality as well as the percentage of variation were estimated. Two principal components that explained 94.688% of total variance from the data set were obtained at eigen value > 1. A biplot of the PCA loadings is shown in Fig. 2, and the relationships amongst the heavy metals were observed. The first component explains 65.112% of the total variance and loads heavily on As, Co, Cr, Cu, Fe, Mn, Pb and Zn. The eight elements in the first component emanate from municipal wastewater [28], as well as, natural sources and natural organic matter that was decomposing, dissolving and permeating into waterways during rainy season [39]. Cd had a moderate negative loading, implying a different contamination source from the other elements in component one. The second component, dominated by Ag, Hg and Ni, accounts for 29.576% of the total variance. Natural sources predominantly contributed to principal component 2. Overall, PCA demonstrated significant natural sources and anthropogenic contributions of the heavy metals in groundwater (Table 5).

In this current study, 32 elements were identified to be present in the sediments of River Subin. 12 heavy metals (Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn and Co) of concern were assessed against contamination factor, contamination degree and pollution load index (Table 6). CF for Ag was found to be > 6 an indication of sediment been highly polluted with this element. Photographic, electrical and usage of silver nano-particle materials are known to be the major anthropogenic sources of the metal and are released into aquatic ecosystem through wastewater discharge [30,40,47,51]. The CF of As was found to be < 1, indicating that the river sediments are not polluted by this element. The CF index of Cd follows class 4,

Table 5
Rotated component matrix of two-component model.

Parameters	Component PC1	PC2
Ag	−0.209	0.969
As	0.962	0.260
Cd	−0.635	0.692
Co	0.863	0.470
Cr	0.988	0.000
Cu	0.964	−0.246
Fe	0.949	0.308
Hg	0.440	0.891
Mn	0.945	0.228
Ni	0.397	0.913
Pb	0.937	0.044
Zn	0.876	−0.076
Eigenvalue	2.231	1.174
% of Variance	65.112	29.576
Cumulative%	65.112	94.688

High loadings are indicated in bold.

Table 6
Some heavy metal contamination factor (CF), contamination degree (CD) and pollution load index (PLI) values of sediments from River Subin.

	Contamination factor (CF)			
Heavy Metal	Race course downstream	Race course upstream	Wood village	Asokwa
Ag	805.28	343.43	628.85	644.85
As	0.20	0.20	0.12	0.28
Cd	198.53	115.26	210.4	166.3
Cr	1.24	1.53	0.51	1.77
Cu	0.82	1.69	0.42	2.08
Fe	5.88	0.53	0.15	0.83
Hg	10.62	8.3	8.25	10.13
Mn	0.54	0.53	0.11	0.69
Ni	0.21	0.16	0.16	0.19
Pb	1.40	2.53	0.22	5.84
Zn	2.43	1.96	0.47	4.61
Co	3.07	2.48	1.37	3.39
Contamination degree (CD)	1030.22	478.6	851.05	840.96
Pollution load index (PLI)	18,607.77	3677.33	39.08	40,018.04

which suggests a high level of contamination. The CF index for Cd for the various sampling sites suggests that the river stretch at Wood village is more polluted with this element compared to the other sampling sites. Possibly, the reason for high Cd levels of the river sediment at Wood village could be due to the numerous industrial activities around compared to the other sites. Cadmium occurs in agricultural soils where phosphate fertiliser is applied, paints, colours, glass finish, galvanised pipes and nickel–cadmium batteries [36,42]. Cd is known to be bio-accumulative, very mobile and persistent in river bodies and is toxic to invertebrates and fishes [33,42]. The average concentration of Cr in the sediments of the River Subin was recorded as 111.28 mg/kg at Race course downstream, 137.44 mg/kg at Race course upstream, 45.9 mg/kg at Wood village and 159.9 mg/kg at Asokwa. The level of Cr in the sediments of the river was above the permissible value of 43.4 mg/kg [46]. The contamination factor index revealed that sediments collected at Asokwa had the higher level (1.77) of Cr while sediments from the river at Wood village had the lowest (0.51). However, CF index for Cr in the sediments of the River Subin suggested a class 2 with moderate level of contamination. The possible sources of Cr include municipal effluents, laundry chemicals, paints, leather, road runoff due to tire wear, corrosion of bushings, brake wires, radiators textile and tanneries, which contaminate both the water and sediment of the river when it enters into the river. A mix of these sources is dotted along the banks of the river. Higher levels of Cu in water are very dangerous to fishes, invertebrates and aquatic plants. We observed an average range of 19.15 to 93.91 mg/kg for the concentration of Cu in the sediment of River Subin, which was above the USEPA permissible limits of 31.6 mg/kg. The CF of Cu was high at Asokwa (2.08) and low at Wood village (0.42). The CF for the metal was in class 2, indicating a moderate level of pollution. The concentration of Fe in the sediment of River Subin ranged from 6.9×10^3 to 2.7×10^4 mg/kg, which was below the shale background level of 47,200 [45]. The CF of Fe was high at Race course downstream (5.88) and low at Wood village (0.15). The CF index for Fe (0.15–5.88) in the sediments of River Subin suggested a class 3 with considerable CF. Fe could be coming from the bedrock

Table 7
Geo-accumulation index (*I*geo) of the River Subin sediments.

Sampling site	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Co
Race course downstream	9.1	−2.87	7.07	−0.28	−0.87	−1.35	2.83	−1.46	−2.85	−0.09	−1.45	1.03
Race course upstream	7.86	−2.87	6.28	0.03	0.18	−1.51	2.47	−1.49	−3.22	0.75	0.39	0.72
Wood village	8.74	−3.61	7.15	−1.56	−1.82	−3.36	2.46	−3.82	−3.20	−2.79	−1.67	−0.13
Asokwa	8.78	−2.42	6.81	0.24	0.47	−0.86	2.76	−1.11	−2.92	1.96	−0.29	1.18
Min	7.86	−3.61	6.28	−0.28	−1.82	−3.36	2.46	−3.82	−3.22	−2.79	−1.67	−0.13
Max	9.1	−2.42	7.15	0.24	0.47	−0.86	2.83	−1.11	−2.85	1.96	0.39	1.18
*I*geo class	6	0	6	1	1	0	3	0	0	2	1	2

underlying the river or the numerous ferrous-metallic smelting activities and vehicular repair garages dotted along the river stretch. The concentration of Hg in the sediment of River Subin ranges from 3.30 to 4.25 mg/kg, which was above the shale background level of 0.4 [45]. The CF of Hg was high at Race course downstream (10.62) and low at Wood village (8.25). The CF for Hg was in class 4, indicating very high pollution level. Hg causes severe toxic effects in higher animals upon acute or chronic exposure [20]. The industrial activities of metal scrap processing may account for the high level of Hg in the river sediment. The contamination factor index suggested that, Mn and Ni were in class 1, indicating that this metal did not pollute the river sediments. CF for Pb at Race course downstream and Race course upstream fell under class 2 with moderate level of pollution. CF for Pb at Wood village indicated no pollution while CF for Pb at Asokwa fell under class 3 with considerable level of pollution. Contamination factor for Co and Zn fell under class 3 with considerable level of sediment pollution by these elements. Data from Contamination degree ($CD > 24$) and pollution load index ($PLI > 1$) suggest a progressive deterioration of pollutant at the various site.

Geoaccumulation index (Table 7) revealed that the four sites of the River Subin were extremely contaminated with Ag and Cd. But As, Fe, Mn and Ni fell under class 0 with *I*geo < 0, indicating the four sampling sites were not polluted by these elements. *I*geo of Cr, Cu and Zn for the sampling site fell under class 1, suggesting an uncontaminated to moderately level of contamination. The *I*geo of Pb and Co were under class 2 with moderate levels of contamination.

Conclusion

The present study assessed the physicochemical, heavy metals and microbial load of water sampled from the River Subin, which flows through the metropolis of Kumasi- Ghana and serves as drinking water for communities downstream. The results in this study indicate that the water is polluted and not suitable for portable uses such as human consumption and domestic uses. The microbial load suggests that the river was highly polluted by total coliform, faecal coliform, enterococci, and E. coli. Also, the results for *I*geo, CF, CD and PLI indexes suggest high levels of Ag, Cd, Cr, Cu, Fe, Hg, Co, and Zn contamination in the sediments of River Subin. Using the various pollution indicators, this work has shown the extent of pollution of the River Subin and thus, urgent management strategies are needed to mitigate further deterioration of the river. Authorities need to put control mechanisms to address sanitation and waste disposal problems in the Kumasi Metropolis to prevent the river from further pollution and push for restoration of the river.

Declaration of Competing Interest

The authors declare that they have no competing interests

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