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Urbanizing with or without nature: pollution effects of human activities on water quality of major rivers that drain the Kumasi Metropolis of Ghana

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Abstract The effects of urbanization such as population upsurge, increased industrialization, urban agriculture, and rural–urban migration of persons exert pressure on the limited water resources in most cities. This study investigated the impact of human activities on the water and sediment quality of the three main rivers (Wiwi, Subin, and Suntre) in Kumasi, the second-largest city in Ghana. The physicochemical parameters and the concentrations of contaminants, including heavy metals, polycyclic aromatic hydrocarbons, pesticide residues, and microbial loads in the rivers, were linked to the specific human activities at the riverbanks. While all the 37 pesticide residues investigated in river sediments had concentrations below the detection limits (0.005 mg/kg for organochlorines, 0.010 mg/kg for organophosphates, and 0.010 mg/kg for synthetic pyrethroids), the study showed that the sediments are polluted with petrogenic and pyrogenic polycyclic aromatic hydrocarbons. River Subin, the most polluted among the three rivers, recorded benzo[*e*]pyrene concentrations up to 47,169 µg/kg. The geoaccumulation index and concentration factors show that the rivers are highly contaminated with metals such as cadmium, chromium, mercury, and arsenic and are related to human activities. The microbial quality of the rivers was poor, recording specific microbial loads of 6.8, 4.1, and 1.5×10^7 counts/100 mL respectively for Wiwi, Subin, and the Suntre Rivers. The three water bodies are therefore not suitable for recreational and irrigational purposes.

Keywords Water pollution · Contamination · Industrialization · Urbanization · Environmental impact · Rural–urban migration

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Introduction

Water is a basic need for all life forms on the earth and is an essential component in human activities in agricultural, domestic, industrial, and recreational settings. Without access to fresh water, all the sustainable development goals planned for poverty reduction and securing the general well-being of populations (UNEP, 2020) would not be attained. However, in developing countries, not much consideration has been given to adequately secure this priceless natural resource (Mishra et al., 2019). Surface water bodies are sometimes used as receptacles for waste dumping in many cities in developing countries (Boadi & Kuitunen, 2002; Mbugua, 2017). Consequently, some surface water resources have been rendered unsuitable for human consumption due to the accumulation of large volumes of dirt, debris, and toxicants such as heavy metals, pesticide residues, and polycyclic aromatic hydrocarbons that emanate from human activities (Edokpayi et al., 2017). As the population in cities increases, the problem of urban water pollution will increase as more people compete for the limited freshwater resources. The rate of population growth and urbanization are alarmingly high in some cities.

Africa has the highest global growth rate of 3.5% (Saghir & Santoro, 2018). The annual population growth rate in Ghana's capital city, Accra, is 4.3% (Rain et al., 2011), while that of Kumasi (the second-largest city) is 5.6%, which is more than twice the average national growth of 2.5% (Amoateng et al., 2018). The rapid population growth in the Kumasi Metropolis has drastically increased the demands on land for development, putting intense pressure on the ever-limiting land resources around water bodies leading to contaminations of the main water bodies. The riparian areas of the rivers have been under extreme human activities in recent years, adversely affecting the quality and quantity of water that drain the city (Boadi et al., 2018; Keraita et al., 2003).

Studies have been conducted on heavy metal pollution in some water bodies (Akoto et al., 2020; Opoku et al., 2020), street dusts (Rweyemamu et al., 2020), and polycyclic aromatic hydrocarbons in soils and water in the industrial hub of Suamein the Kumasi Metropolis (Bandowe & Nkansah, 2016). Also, Monney (2013) found a drastic deterioration in the water quality as River Aboabo flows through the densely populated areas of Aboabo, Moshie Zongo, and Anloga in the Metropolis. However, none of these studies assessed the relationship between land use and the type of pollutants they emit into the water bodies.

Therefore, the goal of this study was to assess the impact of human activities on the quality parameters of the three main rivers that drain the Kumasi Metropolis of Ghana. Specifically, the physicochemical qualities, heavy metals and polycyclic aromatic hydrocarbons concentrations, microbial loads, and pesticide residues found in the water and sediments of the Wiwi, Subin, and Suntre Rivers were correlated to the human activities that take place at their banks. This study will help improve knowledge on the relationships between human activities at the banks of the rivers and the pollution they produce.

Relevance of the study

The attainment of the Sustainable Development Goals (SDGs), particularly SDG 6, 11, and 14 in many cities in the global south, has been undermined by rapid and unguarded urbanization. Water bodies are adversely affected by rapid urbanization in cities. In this regard, the attainment of the loveable and sustainable cities, as envisioned in the SDGs, is dependent on our ability to manage human activities and preserve surface water bodies properly. This study is relevant to Ghana's natural resource management and environmentally sustainable solutions targeting the county's developing agenda of promoting a green economy. The study will also serve as a template to other cities in the global south that have characteristics similar to Kumasi, Ghana, and reinforce the need for environmental improvement in the region.

Methods

Study area

The Kumasi Metropolis — located approximately 250 km NW of Accra, the capital of Ghana — is found between latitude 6°35′–6°40′ North and longitude 1°30′–1°35′ West. The Metropolis has an approximate land area of 214.3 km^2 which is occupied by some 1,730,249 inhabitants, representing 36.2% of the total population of the Ashanti Region (GSS, 2010). The population density in the Metropolis is 8075 people per square kilometre. The three rivers studied are the main water bodies that drain the Metropolis. Water and sediment samples were taken from locations (Fig. 1) along the rivers banks where human activities are pronounced from May to August 2019. Among the sampling points were light human activities areas (Wi1, Wi3, Wi6, Sb8, and St4), and heavy human activity areas (Wi7, Wi11, St1, St2, St3, Sb1, Sb2, Sb3, and Sb4).

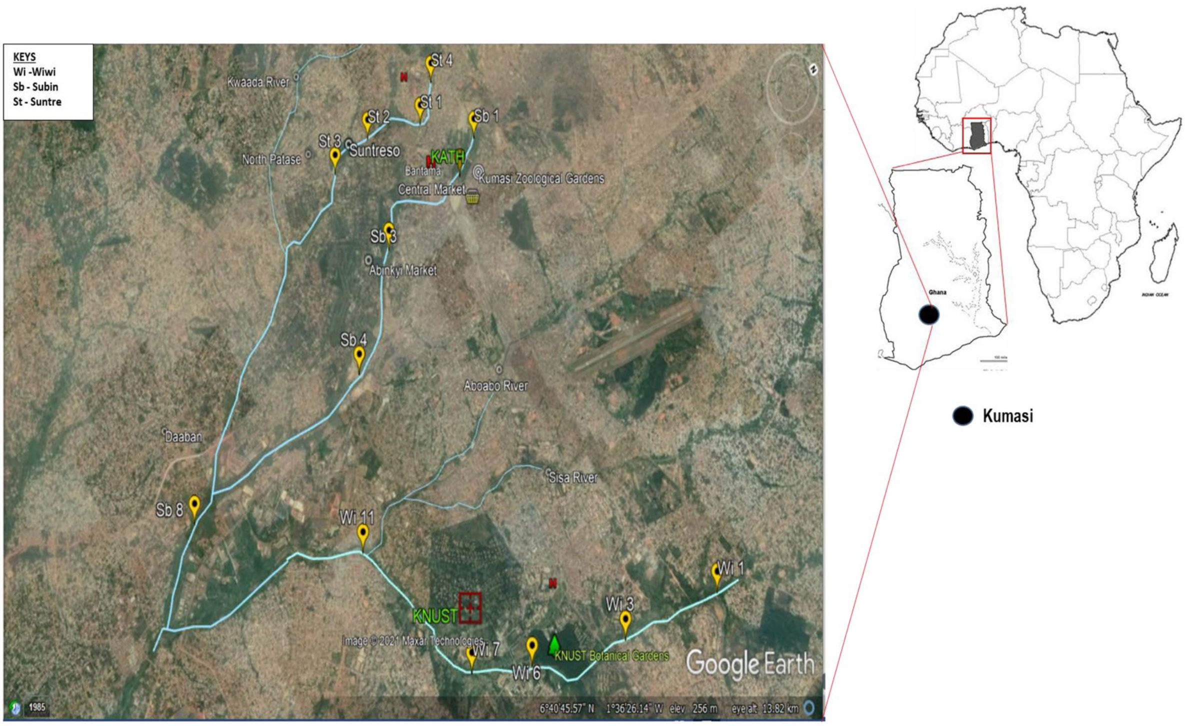

Fig. 1 Location map showing sampling points along Wiwi, Subin, and Suntre rivers that drain the urban settlement in Kumasi metropolis, Ghana

Water and sediment sampling

For the Wiwi, two samples were taken from upstream points (Wi1 and Wi3), one midstream (Wi6), and two other samples were collected downstream (Wi7 and Wi11), spanning from Wiwiso (Wi) through Gyinyaase Junction (Wi11) where the Sisa and the Aboabo Rivers join the Wiwi River. Sampling on the Subin River covered points from its source at the Bantama Racecourse (Sb1), through to Daaban (Sb8). Samples were also taken at the midsection of the river at the Abinkyi Market (Sb3). The other samples were picked from Asokwa (Sb4) and Daaban (Sb8), where the Suntre and the Kwaada Rivers join the Subin. Five other sampling points were selected from the source at North Suntreso (St4) and two others from between the Bantama (St2) and North Suntreso (St1) parts of the river. The last of them (St3) was taken from the Suntre River in the North Patase section.

Surface water (0–10-cm depth) was collected into pre-cleaned 1 L polyethene bottles. The sediment samples were collected using the grab approach (Hageman et al., 2019) and filled into hermetically closed borosilicate glass bottles. Physical parameters (pH, conductivity, temperature, total dissolved solids, and salinity) were measured in situ using multi-meter probes (Model: Horiba U-51 and Model: HACH 2100 P). In the laboratory, water samples were stored in a refrigerator at −4 °C. Sediments were air-dried in a fumehood and oven-heated at 105 °C constant weight, then pulverized and sieved through a 0.5-mm metric test sieve before their storage.

Physicochemical parameters

The turbidity of the river water samples was measured using a standardized nephelometer (Hanna Instrument, Wagtech International), based on a standard method (Jain et al., 2020). Biochemical oxygen demand was measured as the milligrams of oxygen consumed per day during a 5-day incubation of water samples at 25 °C (Ma et al., 2020). Chemical oxygen demand was determined using the standard dichromate titration method (Ma, 2017). Colour was determined by comparison to a reference colour disc (Magubane et al., 2019) in a Lovibond apparatus (EC 2000 Pt–Co, USA).

Trace metal analyses

Metals in the sediments were initially screened using the Niton XL3t GOLD + X-ray fluorescence spectrometer (Rweyemamu et al., 2020) after calibration and standardization using NIST 2709a certified reference material. The average recoveries from triplicate runs of the reference material were satisfactory, range from 88 ± 9% for arsenic to 99 ± 8% for zinc. The reproducibility of the analysis was checked through the analysis of five duplicate samples yields a percentage difference of ≤ 6%, indicating a satisfactory agreement of readings. Other quality checks included analysis of procedure, reagents, and control blanks, as well as triplicate analysis of samples. One-quarter (25%) of all the samples, representing various settings, were analysed using a calibrated Agilent 7800 inductively coupled plasma-mass spectrometer (ICP-MS) as a confirmatory test for the XRF analyses. For this, about 1 g aliquots of sediment and water samples were digested in aqua regia (1HCl:3HNO) at 150 °C for an hour on a heating block. These were further analysed with the ICP-MS using the US-EPA Method 6020B (Darko et al., 2017). The percentage recoveries (92–80%) and the reproducibility (8–16%) obtained from a triplicate analysis of NIST 2710 certified reference material were satisfactory.

Metal pollution analysis

The occurrence and the anthropogenic contributions to the elevated concentrations of the metals defined by the geo-accumulation and concentration factor were defined by Eqs. (1) and (2):

$$\text{Geoaccumulation index, Igeo} = \log_2[(C_s/1.5C_r)] \tag{1}$$

$$\text{Concentration factor, CF} = C_s/C_r \tag{2}$$

where C_s is the level of heavy metal measured in the sediment and C_r is the geochemical background concentration serving as a reference indicator. The factor, 1.5, is matrix correction used to minimize the possible effects of variations in the environment. Background values of 0.3 mg/kg for As, 0.01 mg/kg for Cd, 1.29 mg/kg for Co, 4.67 mg/kg for Cr, 12.6 mg/kg for Cu, 0.005 mg/kg for Hg, 4.28 mg/kg for Ni, 7.91 mg/kg Pb, and 7.49 mg/kg for Zn from the KNUST Botanical Gardens (Akoto et al., 2020; Opoku et al., 2020) were used.

Pesticide residue extraction, clean up, and analysis

Pesticide residue analysis was carried out by the Pesticide Residues Analysis Laboratories of the Ghana Standards Authority, Accra (ISO Certificate #: D-PL-15208–01-00). Reference standards for 27 pesticides (lindane, alpha-endosulfan, beta-HCH, delta-HCH, aldrin, heptachlor, gamma-chlordane, dieldrin, endrin, beta-endosulfan, p,p´-DDT, p,p´-DDD, p,p´-DDE, endosulfan sulphate, methoxychlor, methamidophos, phorate, fonofos, diazinon, dimethoate, pirimiphos-methyl, chlorpyrifos, malathion, fenitrothion, parathion, chlorfenvinphos, profenofos, allethrin, bifenthrin, fenpropathrin, lambda-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, deltamethrin) were obtained from Ehrenstorfer GmbH (Augsburg, Germany).

About 10 g of the prepared sediment samples were extracted into 10 mL aliquots of acetonitrile through ultra-sonication for about 2 min, followed by shaking for 30 min at 300 motions/min and then a 30-min standing to allow phase separation. The supernatants obtained were dried using 2 g anhydrous magnesium sulphate and concentrated to about 1 mL on a rotary evaporator operating at 38 °C. The extracts were cleaned up using 10 mL polypropylene cartridges packed with activated silica gel (heated at 130 °C for 10 h). A 10-mL portion of acetonitrile was used to elute the column, and the eluate concentrated to near dryness using the rotary evaporator. The residue was re-dissolved in 1 mL ethyl acetate for gas chromatography (Ahammed Shabeer et al., 2018).

Organochlorine and synthetic pyrethroids residual pesticide were determined using a Varian CP-3800 gas chromatograph (Varian Inc. USA) coupled with CombiPAL autosampler and Ni-63 electron capture detector. Separation of analytes was achieved on a capillary column (Merk, 29,806-U, SLB®-35 ms Capillary GC Column L × I.D. 30 m × 0.25 mm, df 0.50 µm) + (30 m + 10 m EZ guard column × 0.25 mm internal diameter, 0.25 µm film thickness of VF-5 ms) at injector and detector temperatures of 270 °C and 300 °C, respectively. The oven temperature was programmed at 70 °C for 2 min, ramped at 25 °C/min to 180 °C, and finally ramped at 5 °C/min to 300 °C giving a total runtime of 31.4 min. The carrier gas was nitrogen, flowing at 1 mL/min, and the detector makeup gas at 29 mL/min. Aliquots (1 µL) of the purified pesticide extract was injected by the splitless mode into the gas chromatograph (Fosu-Mensah et al., 2016).

Organophosphorus residues were analysed on the same GC but using a pulse flame photometric detector. The conditions for the GC analyses were capillary column coated with VF-1701 ms (30 m×0.25 mm internal diameter, 0.25 µm film thickness). The injector and detector temperature were set at 270 °C and 280 °C, respectively. The oven temperature was programmed as follows: 70 °C for 2 min, ramp at 25 °C min^{-1} to 200 °C, held for 1 min, and finally ramped at 20 °C min^{-1} to 250 °C and maintained for 3.3 min. Nitrogen was used as carrier gas at a flow rate of 2.0 mL min^{-1} and detector makeup gases (17.0, 14.0, and 10.0 mL min^{-1}) for air-1 hydrogen and air-2, respectively. The injection volume was 2.0 µL. The total run time for a sample was 14 min (Fosu-Mensah et al., 2016; García Ríos et al., 2020).

The concentrations of the pesticide residues identified using the retention times of the external standard were found using peak area integration on prepared calibration curves. The limits of detection and quantification were found based on 3 and 10 times the noise/signal ratios of serially diluted samples fortified with certified reference material (ERM-BC403). The method's detection limit was 0.005 mg/kg for organochlorines, 0.010 mg/kg for organophosphates, and 0.010 mg/kg for synthetic pyrethroids. Recovery of the internal standards ranged between 70 and 120% for all pesticides analysed.

Analysis of polycyclic aromatic hydrocarbons

A standard mix of polycyclic aromatic hydrocarbons containing 100 µg/mL each of anthracene, benzo[a]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, fluoranthene, and pyrene; 200 µg/mL each of benzo [*g,h,i*] perylene; and fluorene and 1000 µg/mL each of 1-methylnaphthalene, 2-methylnaphthalene, naphthalene, and acenaphthene was obtained from Sigma Aldrich, Japan. Calibration standards ranging from 5 to 125 ng/g was prepared from the standard mix. About 1 g aliquots of sediments were mixed with 10 mL of HPLC grade acetonitrile in a 50-mL centrifuge tube for a minute, followed by an Agilent Bond Elut QuEChERS AOAC extraction salt packet containing 6 g of anhydrous $MgSO_4$ and 1.5 g of anhydrous NaOAc. The sample tubes were re-vortexed for 1 min and then centrifuged at 4000 rpm for 5 min (Morin-Crini et al., 2020).

Solid-phase extraction clean up

About a 6.0-mL portion of the upper acetonitrile layer was aliquoted into a 15-mL Bond Elut QuEChERS AOAC Dispersive SPE tube, which contained 400 mg of primary, secondary amine exchange material, 40 mg of C-18 EC, and 1200 mg of anhydrous $MgSO_4$. The tube was vortexed for 1 min and then centrifuged at 4000 rpm for 5 min. A 4-mL aliquot of the extract was filtered through a 0.45-µm polyvinylidene fluoride syringe filter; then, 100 µL of the extract was injected into the HPLC system (Ankar-Brewoo et al., 2020). A Cecil-Adept binary pump HPLC coupled with Shimadzu 10AxL fluorescence detector (Ex: 254 nm, Em: 390) with Phenomenex hyperclone BDS C18 column (150×4.60 mm, 5 µm). The mobile phase composition was Solution A (acetonitrile) and Solution B (deionized water) at 0.8 mL/min. Gradient elution was used with the following combination, 0–5 min: 60% A, 40% B; 5–15 min: 90% A, 10% B; 20 min: 100% A, 0% B; and 28–30 min: 60% A, 40% B. Polycyclic aromatic hydrocarbons in samples were identified using the retentions times of the standards and quantified using a prepared calibration curve. Analyses of samples were carried out in triplicates. The limit of detection for all polycyclic aromatic hydrocarbons ranged from 0.10 to 6.46 ppb. Diagnostic ratios (Deelaman et al., 2020; Gao et al., 2019) were applied to predict the characteristics and the sources of polychlorinated hydrocarbon pollution in water and sediments.

Bacteriological analysis

Isolation and counting of total coliforms, faecal coliforms, *Escherichia coli*, and enterococci were carried out using the most probable number method, using 100 mL aliquots of the water samples (Akrong et al., 2019; Januário et al., 2019). Protocols for contamination control were strictly followed to assure data quality. Washing and cleaning procedures were thoroughly carried out, and all the glassware was autoclaved at 121 °C at 15 pounds per pressure inch for 15 min. Replicates were run to ensure the integrity of the results. Blank samples were also run to ensure there were no inherent biases in the methods used.

Prediction of associations between human activities and contamination

To find the association between the contaminants and the specific human activities that take place at the riverbanks, a non-parametric Mann–Whitney *U*-test (Marozzi, 2013) was used to compare differences in concentrations of analytes. Differences were considered significant at $p < 0.05$. All data management, visualization, and statistical analyses were performed on R version 3.5.2. Principal components analysis (PCA) was conducted using the PAST (Paleontological Statistics Software Package for Education and Data Analysis) software (Paleontological Electronica, Denmark) to identify associations between the different datasets and to find underlying patterns. The correlation option was chosen for this test (Amponsah et al., 2020).

Results and discussions

Human activities and land-uses

A catalogue of human activities that go on along the first 100 m off the banks of the rivers, together with their GPS coordinates, types of samples collected, and sensory analyses of the view on sites, are all recorded in Table S1 (Supplementary data). Dumping of household trash into the river bodies was a key human activity observed. Uncontrolled open burning of waste and trash dumping into the riparian areas (Fig. 2) were commonly observed along the river banks. All three rivers were littered with single-use plastics. Plastic pipes were also seen connected directly from some household sewage systems into the rivers. Other observations include the use of the riverbanks as farmlands, residences, creeks, vehicle

Fig. 2 A picture showing some human activities observed at the riparian areas of the water bodies that flow through the Kumasi metropolis in Ghana. The riparian areas along the Suntre River (**A** and **B**) has auto-fitting shops and car washing bays sited. The riverbank of Wiwi at Wiwiso (**C**) shows animal dung by free-range animals. The Subin River (**D**) close to the Abinkyi Market shows some indiscriminate trash disposals in and along the river course

washing bays, and auto-mechanic workshops. There were also the disposal points for junk metal parts, glasses, and plastics along the rivers.

Water quality analyses

Physical and chemical properties of the rivers in Kumasi

The temperature recorded across the three rivers was stable due to the stable ambient air temperature (Table 1). The water temperature showed no statistically significant difference ($p > 0.05$) in areas of heavy and light human activities at the riverbanks. The pH value recorded was within the WHO allowable value of 6.5–8.5 (WHO, 2011) and showed no statistically significant differences ($p > 0.05$) in heavy and light human activity areas.

Turbidity

Turbidity ranged from 0.575 to 10.30 NTU for the Wiwi River, 4.30 to 16.75 NTU for the Subin River, and 2.36 to 19.50 NTU for the Suntre River (Table 1). The Subin River recorded the highest turbidity (16.75 NTU). The water samples were filled with black colloids resulting from the dissolution of organic matter (Setareh et al., 2021) released into the water from the markets sited along the river at both banks. Also, suspended matter and microorganisms might cause turbidity. The mean turbidity for the three rivers (Wiwi 7.84 NTU, Subin 10.30 NTU, and Suntre 7.26 NTU) was above the set upper allowable limit of 5 NTU (WHO, 2011). The release of untreated waste effluents into the rivers and suspended matter may have contributed to the high turbidity recorded.

The Subin River receives untreated waste from various places in the Metropolis, including the Kejetia Mall Complex, the Kumasi Zoological Gardens, the Komfo Anokye Teaching Hospital, the Kumasi Central Market, and the entire Adum and Asafo townships. The waste generated from these places combined with siltation arising from the unpaved areas that direct their surface runoff into the river may have contributed to the high turbidity in the river. The turbidity distributions of the three rivers in the light and heavy human activity areas differed significantly (Mann–Whitney $U = 17.5$, $p < 0.05$, 2-tailed).

Colour

The Suntre River is colourless from its source at North Suntreso (St4). However, the river runs black just about 200 m away at Abrepo Junction (point located between St1 and St4) where it is joined by a drain. The Subin River is black at the source (Sb1), midstream (Sb3), and downstream (Sb4), where it flows through concrete storm channels in the central business district of the Metropolis. It, however, turns brownish-grey at the Daaban area (Sb8), where it joins the Kwaada and Suntre Rivers. The colour of all the water samples was outside the WHO permissible limit of 5 Hazens (WHO, 2011). Colour in surface water results from the leaching of organic materials and is, primarily, the result of dissolved and colloidal substances present (Garbowski, 2019). Overall, the colour of the rivers indicates a health threat to those who use the water (Völker & Kistemann, 2011). However, the water colour at the light and heavy human activity areas was not significantly different ($p = 0.282$).

Total dissolved solids, electrical conductivity, and salinity

Except for the electrical conductivity in the Subin River, most of the other physical parameters, including total dissolved solids and salinity (Fig. 3), were higher than the acceptable standards of the World Health Organization (WHO, 2011). The total

Table 1 The mean and corresponding standard deviations of the physical properties (temperature, pH, turbidity, colour) of Wiwi, Subin, and Suntre rivers in Kumasi, Ghana

Water sample	Temperature (°C)	pH	Turbidity (NTU)	Colour (Hazen)
Wiwi	28.12 ± 0.08	6.65 ± 0.81	7.72 ± 4.49	34 ± 8.94
Subin	26.6 ± 0.35	6.93 ± 0.49	10.29 ± 5.84	640 ± 260.80
Suntre	26.05 ± 0.13	7.08 ± 0.25	8.79 ± 7.51	650 ± 191.50

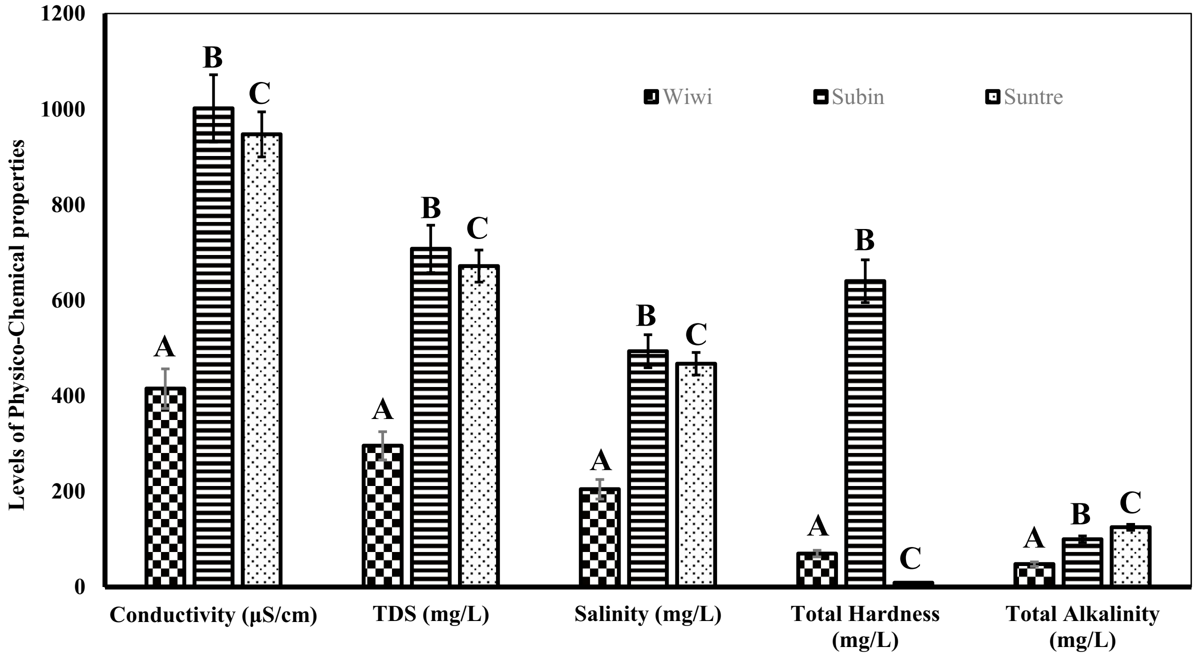

Fig. 3 The mean and standard deviation of the physical properties of the three main rivers; Wiwi (**A**), Subin (**B**), and Suntre (**C**), in Kumasi, Ghana, showing high levels of conductivity, dissolved solids, and colour

dissolved solids found in the Subin River exceeded the recommended level of 500 mg/L for aquatic life to thrive (US EPA, 1988). Generally, all the rivers had high salinity and total dissolved solids, which showed no statistically significant differences ($p > 0.05$) in heavy and light human activity areas. The satellite markets and refuse dumps sited at the banks of the rivers could be the cause of the high conductivity and total dissolved solids (Akanchise et al., 2020) in the Subin and Suntre Rivers. Conductivity was highest in the Subin River. However, electrical conductivity showed no statistically significant differences ($p > 0.05$) across the three rivers in heavy and light human activity areas.

Total alkalinity and hardness

In the Wiwi River, total alkalinity and hardness values ranged from 40 to 80 mg/L and 25 to 250 mg/L, respectively (Fig. 4). Total alkalinity and hardness at the Subin River were 40–180 mg/L and 25–100 mg/L, respectively. In the Subin River, alkalinity and water hardness were comparatively low where the Daaban River and Subin River meet (Sample point Sb8). This could be a result of the dilution effect of the Daaban River.

Nutrients: nitrates and phosphates

The three rivers recorded nitrate concentrations above the WHO limit of 5.0 mg/L (WHO, 2017). The high nitrate concentrations indicate the three rivers are highly polluted (Fig. 4). The mean phosphate concentrations were 0.67 ± 0.33, 0.45 ± 0.11, and 0.47 ± 0.27 mg/L for Wiwi, Subin, and the Suntre Rivers, respectively (Fig. 4). The phosphate concentrations were relatively high compared to the natural background of 0.02 mg/L (WHO, 2017). Except for three points on the Suntre River, all other sites recorded values higher than the WHO limit of not greater than 0.3 mg/L (WHO, 2017). The high concentrations of phosphates may be due to seepages from decomposed organic trash from dumpsites (Onyekwelu & Aghamelu, 2019), domestic wastewater and agricultural runoffs deposited into the water bodies (Saadat et al., 2018), and the application of phosphorus-containing agrochemicals by vegetable farmers along the Wiwi River from Wiwiso (Wi1) through to Gyinyaase (Wi11). High phosphate

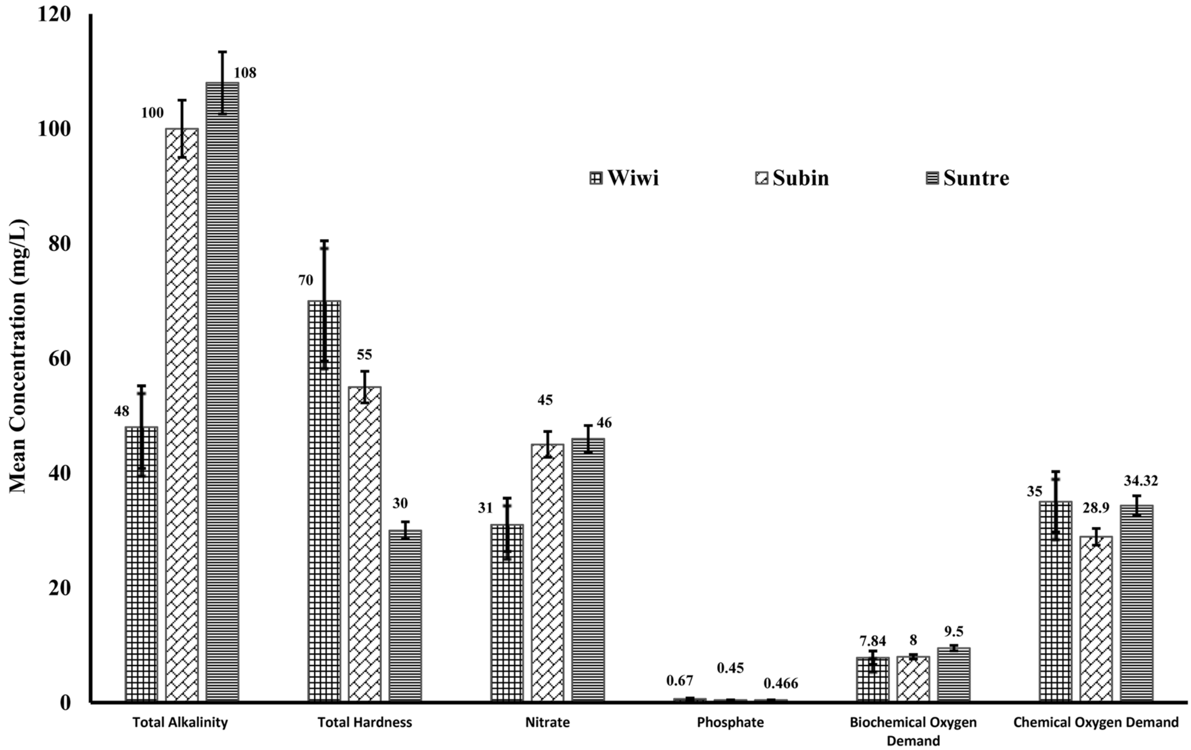

Fig. 4 Mean levels and standard deviations of the chemical properties of the Wiwi, Subin, and Wiwi Rivers found in the Kumasi Metropolis

concentration is responsible for the eutrophication of a water body as phosphorus is a limiting nutrient for algae growth (WHO, 2017). It would then lead to the proliferation of phytoplankton and their decomposition over time, leading to a high chemical oxygen demand.

Biochemical and chemical oxygen demands

Oxygen demands for chemical or biochemical processes are indicators of the quantities of decomposing organic matter present in the water body (Findlay, 2021). The mean biological oxygen demand in the Wiwi, Subin, and Suntre rivers was 7.84 ± 1.64, 8.00 ± 1.90, and 9.50 ± 2.39 mg/L, respectively. The mean chemical oxygen demand for the Wiwi, Subin, and Suntre Rivers were 35 ± 4.72, 28.9 ± 6.79, and 34.32 ± 4.08 mg/L, respectively. But the acceptable limits are 2 mg/L and 20 mg/L, respectively (WHO, 2011). The natural background levels of biochemical oxygen demand for freshwater range from 1.0 to 3.0 mg/L (WHO, 2017). This implies that all the water bodies are polluted based on their biochemical and chemical oxygen demands. This could be due to the rivers' proximity to dumpsites, which could contribute to the loading of organic matter into the water bodies. The implication of high biochemical oxygen demand in the rivers is that the oxygen present in the water will be used to decompose materials, and thus, is unavailable for aquatic life.

The principal component analysis for physicochemical parameters is given in Fig. 5. All the three rivers have a similar description of their physicochemical parameters by the first and second axes (Fig. 5a), which together explain 66% (Fig. 5b) of the total variation in the datasets. According to the loadings plot (Fig. 5c), conductivity, TDS, salinity, and colour trend positively together in the first component, meaning that these parameters have a similar occurrence in the rivers. To the first component, Subin and Suntre contribute the most. To the second component, Wiwi and Subin contribute the most, and to the third component, Wiwi and Suntre contribute most to the formation of that axis. For all the three

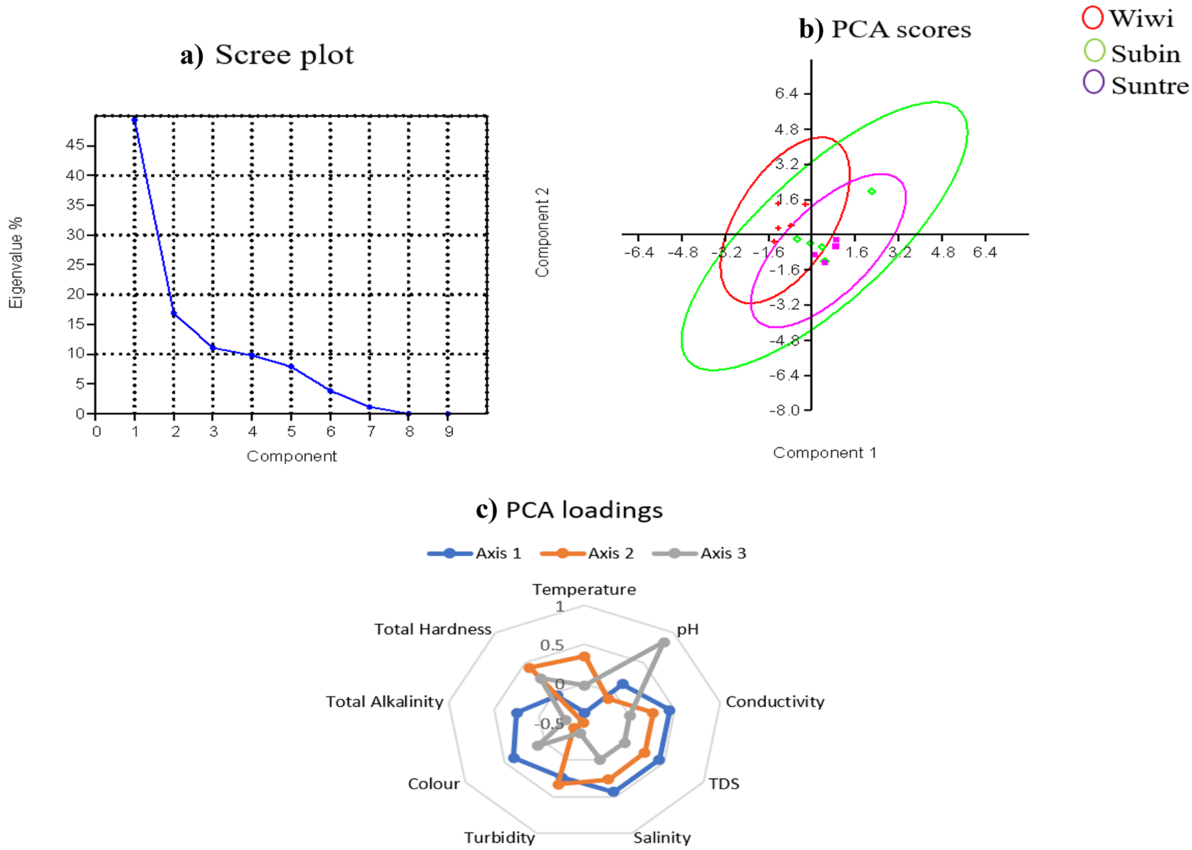

Fig. 5 Scree plot, scores, and loadings of principal component analyses of physicochemical parameters in rivers Wiwi, Subin, and Suntre in the Kumasi metropolis

components, conductivity, TDS, and salinity trend together with the same strength. Similarly, the turbidity and total alkalinity trend together with the same strength. In the first component, temperature trends negatively with all other parameters, meaning that as temperature increases in the river, the other parameters decrease.

Sediment quality analysis

Pesticide residues

None of the water bodies showed detectable levels of the 37 pesticide residues (including 13 organophosphorus pesticides, 15 organochlorines, and 9 synthetic pyrethroids) investigated in the sediments. However, that is not a confirmation of the absence of any pesticides as the residues may just be below the detection limits of the equipment used (< 0.005 mg/kg for organochlorines, < 0.010 mg/kg for organophosphates, and < 0.010 mg/kg for synthetic pyrethroids).

Polycyclic aromatic hydrocarbons

Eighteen polycyclic aromatic hydrocarbons (PAH) were investigated in the sediments of Wiwi, Subin, and the Suntre rivers (Fig. 6). The mean levels of the polycyclic aromatic hydrocarbons in the Wiwi, Subin, and Suntre Rivers in Kumasi ranged from non-detections (acenaphthalene in all three rivers) to 9482.89 µg/kg (Benzo[*e*]pyrene) in Subin. Naphthalene and its derivatives (acenaphthene, acenaphthylene, and fluorene) were the predominant PAH in the sediments. The mean concentrations of naphthalene (172.22 µg/kg), acenaphthene (12.53 µg/kg), acenaphthylene (67.53 µg/kg), and fluorene (18.43 µg/kg) in the sediments of all three rivers exceeded the recommended exposure limits. At these

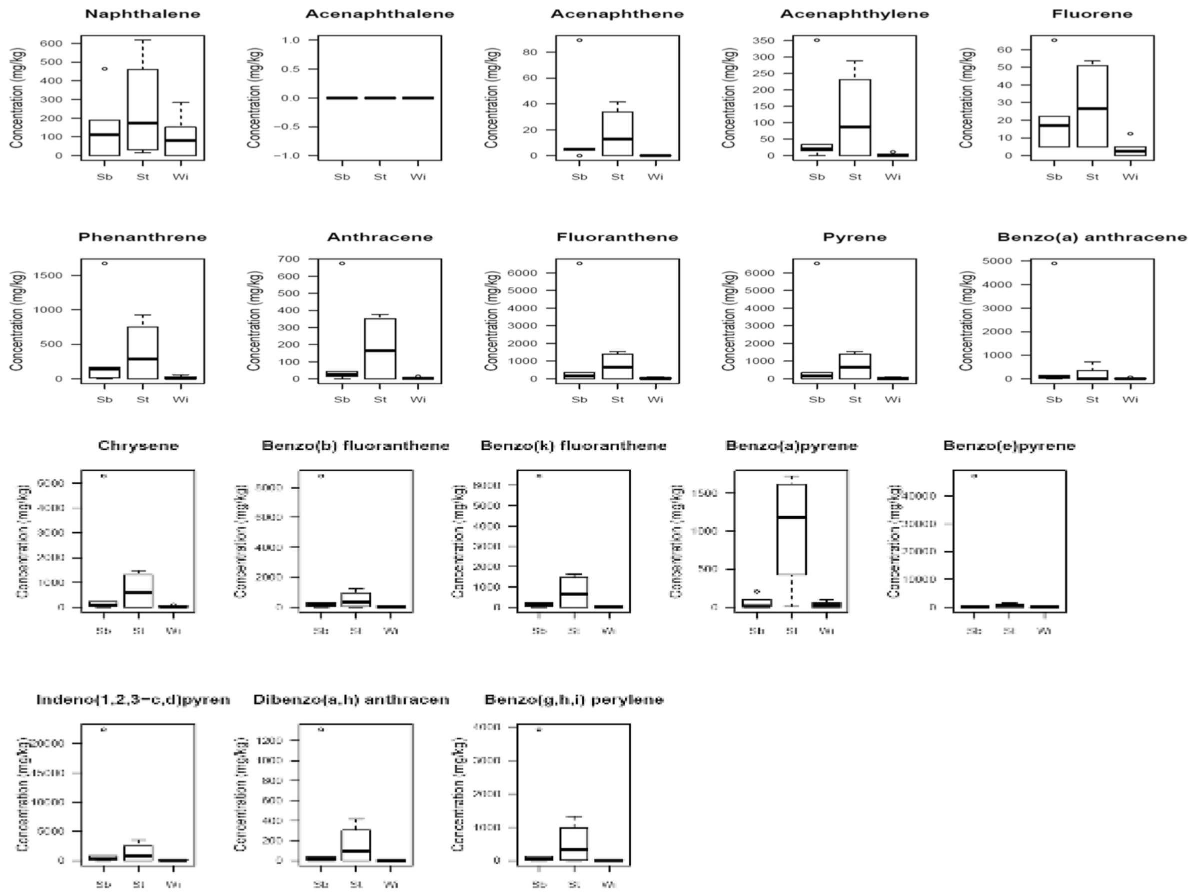

Fig. 6 Concentrations of the polycyclic aromatic hydrocarbons found in the sediments of Rivers Wiwi, Subin, and Suntre in the Kumasi metropolis in Ghana

concentrations, benthic organisms could suffer in health leading to their deaths (McGrath et al., 2019). Though residents in Kumasi do not directly consume these waters, they are used for domestic chores in the surrounding communities such as Asago, just 9 km from the central business district (Kumasi et al., 2011). Children swim in the rivers while others fish in the Wiwi River (Wi6 and Wi7) and in the Daaban sections (Sb8) where the Subin, Suntre, and the Kwaada Rivers join. The Wiwi River serves as irrigation water for vegetable farmers along the river from the upstream (Wi1 and Wi3) through to the downstream (Wi6, Wi7, and Wi11). The people who consume food products from this polluted water body are very likely to be exposed to the contaminants.

Probable carcinogenic and mutagenic toxicities of polycyclic aromatic hydrocarbons in the rivers in Kumasi

Seven carcinogenic PAH including benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[a]pyrene, dibenzo[*a,h*]anthracene, and indeno[*1,2,3-c,d*]pyrene accounted for a major portion of all the 18 PAH measured in the sediments (Fig. 6). The highest level of carcinogenic PAH in the sediments was recorded in Subin and Suntre. This suggests industrial effluents are discharged into the rivers. Also, leachates from various approved and illegal (convenient) dumpsites found around may contribute significantly to the pollution of the rivers.

The diagnostic ratios show that the rivers are polluted by PAH compounds of both petrogenic and pyrogenic sources. A point on the Wiwi River recorded 100% petrogenic contaminations, whereas two points on River Subin recorded 100% pyrogenic PAH contamination. Results from the Wiwi River showed that only two points (Wi3 and Wi11) where there are heavy vehicular activities) had petrogenic PAH pollution. The possible human activities that may have contributed to the pollution are outlined (Supplementary Table S1). However, the frequencies of the sources of PAH pollutants found were not consistent with the specific human activities carried along the rivers, thus, ruling them out as the point sources for the pollutions. Therefore, the pollution could result from atmospheric depositions from non-point sources (Jia et al., 2019). The polycyclic aromatic hydrocarbons could have travelled by air from distant sources and later became mobile in runoffs (Gaurav et al., 2021).

Pollution indices of the rivers' sediments

The heavy metal concentrations in the sediments of the three rivers (Wiwi, Subin, and Suntre) are presented in Fig. 7.

Except for mercury, the highest concentrations of all the metals were found in the Suntre River. All the points on Subin and Wiwi rivers recorded chromium concentrations higher than 100 mg/L. All the rivers recorded chromium and cobalt concentrations greater than 50 mg/L at all points. Sediments from the Wiwi River consistently measured more than 60 mg/kg of chromium throughout its course. For example, a point close to the Abinkyi Market (Sb3) on the Subin River recorded lead concentrations of

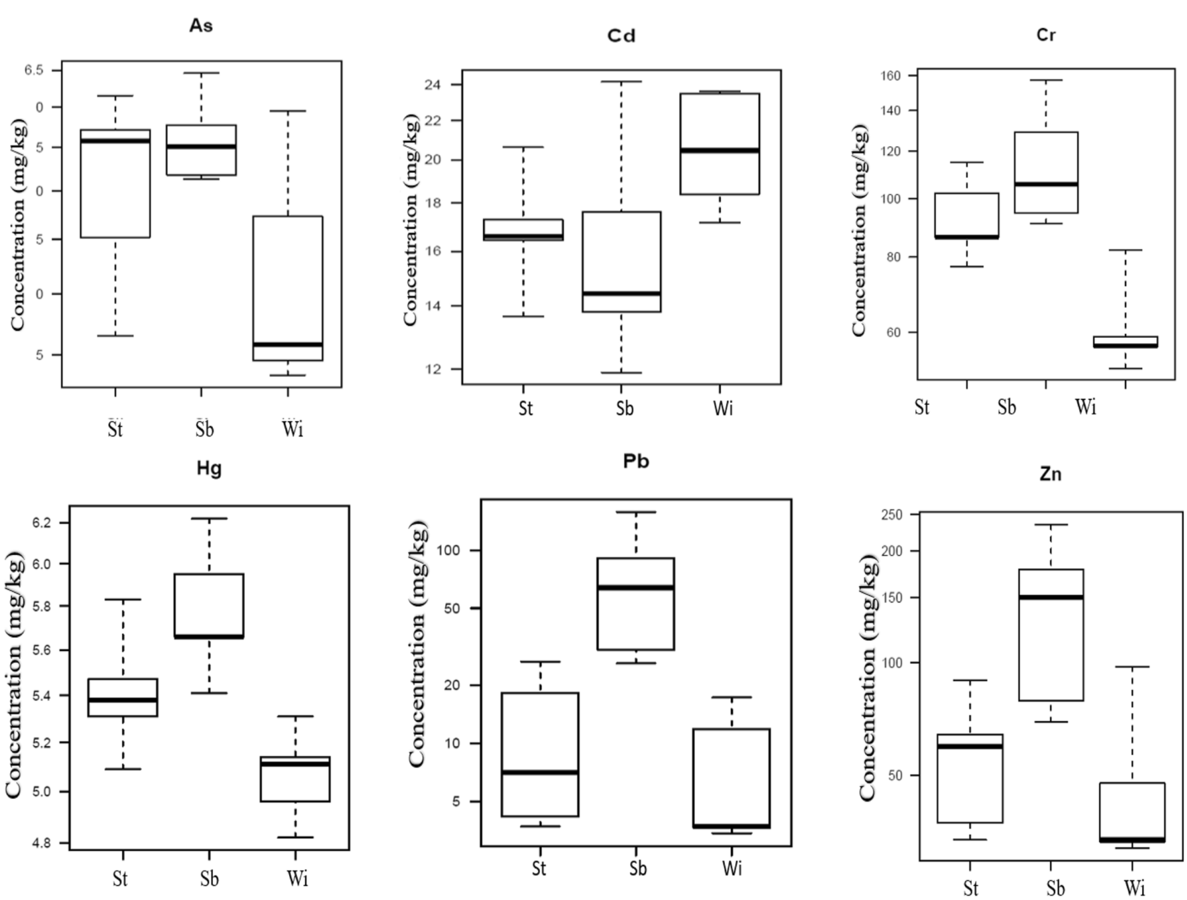

Fig. 7 Boxplot of heavy metals concentrations found in rivers Wiwi, Subin, and Suntre in the Kumasi metropolis of Ghana

157.73 mg/kg. The average concentration of Pb in the Subin River was 46 mg/kg. River sediments could be the major sources of Pb contamination (Islam et al., 2018). It is a ubiquitous pollutant that could find its way into water bodies through the discharge of industrial effluents (Islam et al., 2018). However, none of such companies was located along the three rivers in this study. Heavy metal concentrations at sites in the vicinity of heavy human activities did not differ significantly ($p > 0.05$) from those in the area of light human activities.

Geoaccumulation indices of metals in the river sediments

The rivers are polluted with various toxic metals (Table 2). The Subin River was the most polluted with heavy metals. Toxic metal concentrations exceeding the background levels indicate pollution due to human activities (Li et al., 2020). The concentrations of the heavy metals found in the river are about 10 times the background levels. The Igeo values were 10.26 (Cd), and 9.4 (Hg) in the sediment samples of the Wiwi River. The Igeo showed that all the points on the Wiwi River were contaminated with Cd, Hg, Co, and Cr. The Igeo for the Subin River sediment samples indicated high to extremely high contamination with heavy metals (As, Cd, Co, Cr, Hg, and Zn) at the river's source at the Racecourse (Sb1). The Igeo values for Subin River sediments indicated high to extremely high levels of contamination of heavy metals (As, Cd, Co, Cr, Hg, and Zn) at the river's source at Bantama (Sb1), Kumasi Zoological Gardens (Sb2), and Abinkyi Market (Sb3).

Concentration factors of metals in the river sediments

Concentration factors (Table 2) were employed to determine the extent of human contributions to the contaminations of metals river sediments in Kumasi. Among the studied metals, Cu in the sediments of Wiwi was not from anthropogenic sources (Varol, 2011). Pb in the Wiwi sediments was not high enough to pollute the river downstream (Wi11). The Igeo values indicate that the present levels of Cu and Pb at Subin's source (Sb1) do not strongly contribute to pollution. However, just about 500 m from the source, at Sb2, the sediments samples were moderately contaminated with Pb. The Suntre River sediment samples were polluted with Cd and Hg at all the river sections (St1, St2, and St4). A similar observation about Cd and Hg was made of the sediments from the Wiwi and Subin. Human activities were found to be the leading cause of pollution in all cases.

The main human activity that could connect the heavy metals polluting the rivers in Kumasi is the

Table 2 The geoaccumulation and concentration factors of metals found in the Wiwi, Subin, and Suntre rivers of Kumasi, Ghana

	Geoaccumulation index[a]			Concentration factor[b]		
	Wiwi	Subin	Suntre	Wiwi	Subin	Suntre
As	3.32	3.68	3.41	15.37	19.55	16.43
Cd	10.41	10.02	9.92	2065	1663	1471
Co	4.68	5.73	5.10	38.56	85.75	51.74
Cr	2.48	4.00	3.65	12.94	24.15	18.87
Cu	0.28	0.47	0.01	0.76	2.08	1.29
Ni	1.09	1.54	1.47	3.86	4.39	4.15
Pb	0.00	1.08	1.09	0.67	5.82	4.15
Hg	9.38	9.61	9.52	1004	1181	1100
Zn	1.66	2.94	2.70	4.80	13.54	9.88

[a]For the geoaccumulation indices, the results of metal contamination were categorized into six purity classes as Igeo < 0, class 0 (uncontaminated sediments); 0 < Igeo < 1: class I (uncontaminated to moderately contaminated sediments); 1 < Igeo < 2: class II (moderately contaminated sediments); 2 < Igeo < 3:class III (moderately to highly contaminated sediments); 3 < Igeo < 4: class IV (highly contaminated sediments); 4 < Igeo < 5: class V (highly to extremely contaminated sediments); Igeo > 5: class VI (extremely contaminated sediments) as presented in Table 4.13 (Duncan et al., 2018; El-Sayed et al., 2015)

[b]The contamination categorizations were in an increasing order rated from 1 to 6, with 0 = none, 1 = none to medium, 2 = moderate, 3 = moderate to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong (Varol, 2011)

practice of urban agriculture (Kubier et al., 2020). This study could not link phosphate fertilizer usage to the farming activities that go on along the Wiwi River. Moreover, the Subin and the Suntre had no agricultural activities, yet the same metals polluted them. Elevated concentrations of other trace metals, such as Pb, which can also occur as impurities in phosphate fertilizers, were identified as pollutants from human activities.

Principal component analysis of metals in the river sediments

The results of the principal component analysis of the heavy metals are given in Fig. 8. The scores plot (Fig. 8a) shows the scores for the first two components. Rivers Subin and Wiwi had most of their variance explained by the second component. In contrast, Suntre is slightly more aligned to the first component, indicating that this river is the most polluted. The loadings in the first two components are shown in the loadings plot (Fig. 8b). The variables with the greatest influence in the loadings for PC1 are Co, Cr, Cu, Hg, Ni, Pb, and Zn. These variables are directed almost entirely along PC1, indicating a common occurrence of these metals at the same place at the same time. The PC2 is influenced more strongly by As and Cd. All the metals, except cadmium and antimony, tend to occur at high concentrations at the same time in the rivers, as evidenced by high loadings to the first axis. This could be as a result of the human activities carried out in and around the rivers. The scree plot (Fig. 8c) shows that the first and second components are the most important for this analysis because they have eigenvalues ≥ 1. The first component (or axis) explains

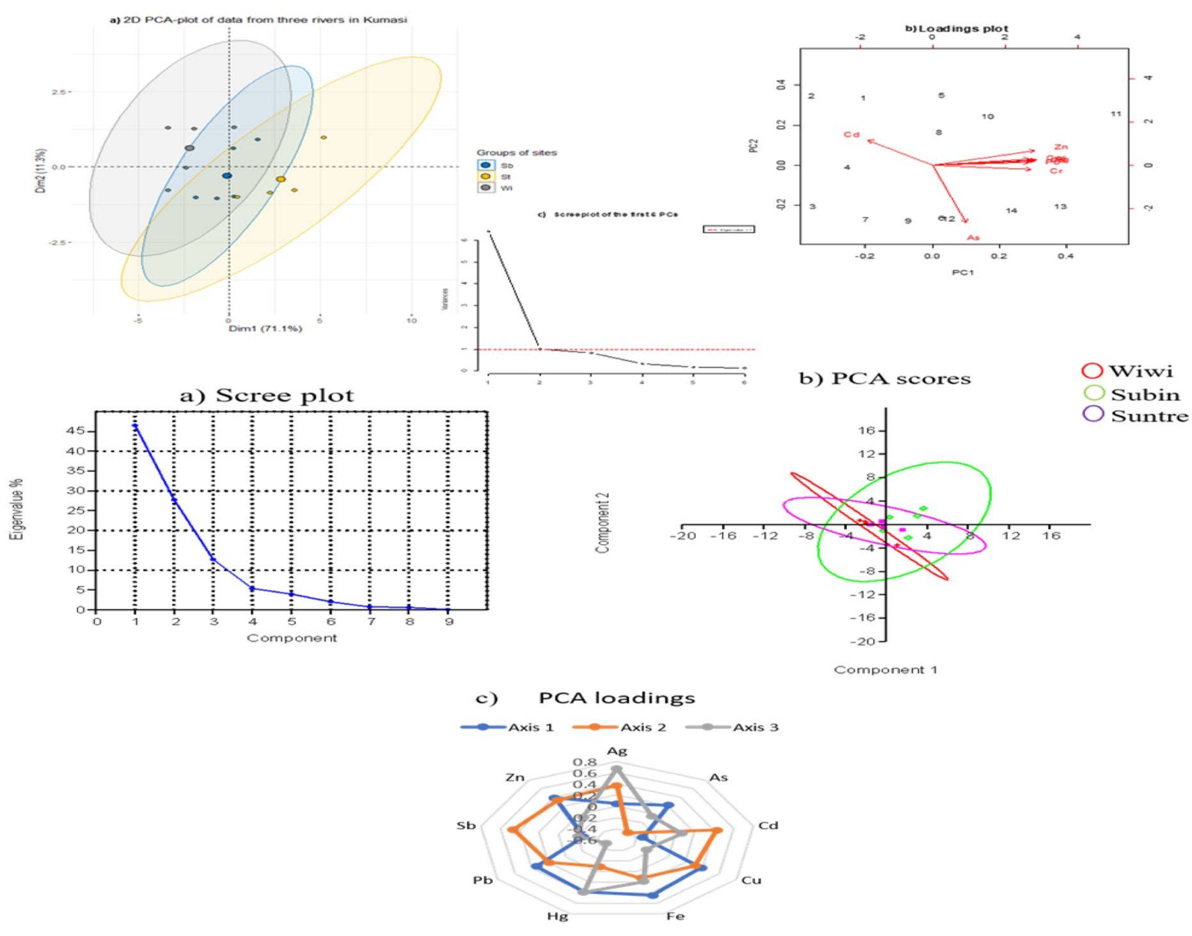

Fig. 8 Scree plot, scores, and loadings of principal component analysis of heavy metals in rivers Wiwi, Subin, and Suntre

71% of the total variation within the datasets, and the second explains 11%.

Microbiological qualities of water from the rivers in Kumasi

The results of the microbiological quality of water samples from the Wiwi, Subin, and the Suntre Rivers are shown in Fig. 9. The mean of the total coliforms, faecal coliforms, *Escherichia coli*, and faecal enterococci counts in the water samples were 1.932×10^{14}, 4.1×10^{9}, 3.1×10^{6}, and 79.88×10^{2} CFU/100 mL, respectively, all of which surpassed the allowable limits of 400 total coliforms/100 mL and 10 faecal coliforms (E. coli)/100 mL (GEPA, 1994). The enormously high counts of the microbial load in the three rivers show they are extremely polluted with faecal matter. The sources of the three rivers defy the odds in the microbial loads. The source of the Wiwi River, for example, had 2.35×10^{13} CFU/100 mL for total coliforms, 4.15×10^{10} CFU/100 mL for faecal coliforms, 2.35×10^{8} CFU/100 mL *E. coli*, and 1.2066×10^{4} CFU/100 mL faecal enterococci. However, the counts quickly increased more than tenfold as the water passed through a nearby settlement area. The human activities recorded at the time may have resulted in this level of pollution. Domestic effluents are allowed into the river without going through any form of water treatment. The garbage from homes dumped at the riverbanks and the practice of open defaecation were common phenomena at all sampling sites, with exceptions to St4 and Wi11.

The Wiwi River is mainly used as irrigation water for the countless stretch of vegetable farms sited along the river from Wiwiso (Wi1) through to Gyinyaase (Wi11). Subin and Suntre also registered very high counts of total coliforms (2.35×10^{15} counts/100 mL). The water bodies are influenced by several human activities such as hospitals, markets, and schools that discharge their wastes directly into them.

Under this investigation, the rivers in Kumasi scored zero passes in quality when the EU Guideline Directive of less than 100 faecal coliforms per 100 mL and 100 enterococci per 100 mL of water was used. The same conclusion could be made based on the Imperative Directive of <2000 faecal coliforms per 100 mL. These water bodies are not suitable for irrigational and recreational purposes. The *E. coli* counts in sites with heavy human activities were statistically higher than sites with light human activities (Mann–Whitney $U=40.5$,

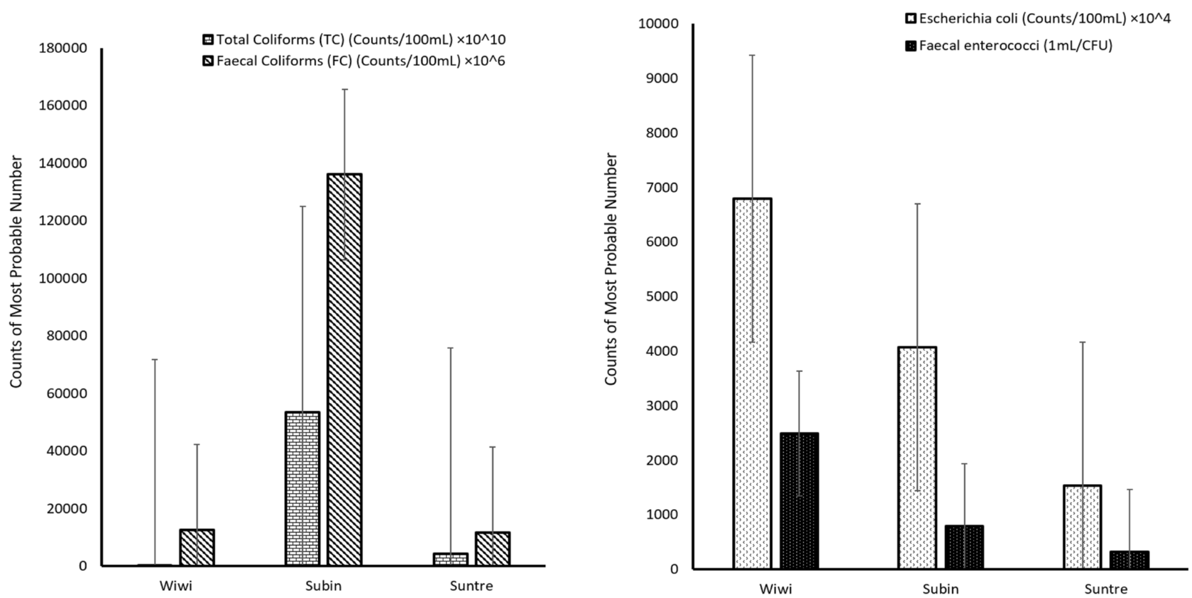

Fig. 9 Summary of the microbiological quality of water from the Wiwi, Subin, and the Suntre rivers in the Kumasi metropolis showing **A** faecal coliform counts and *Escherichia coli* counts and **B** faecal counts and faecal enterococci count

$p = 0.029$). Other microbial measures showed no significant differences between heavy and light activities sites.

Conclusions

All the three rivers (Subin, Wiwi, and Suntre) in the Kumasi metropolis are polluted due to human activities found along the banks (within the first 100 m). The water bodies are highly contaminated with microorganisms and toxic chemical species such as heavy metals and polycyclic aromatic hydrocarbons. Biological and chemical oxygen demands of the rivers are very high, and the waters appear coloured. Pollution of the rivers is highest upstream and may affect lives in the watercourse. The physicochemical characteristics of the rivers do not render them conducive for irrigation in urban agriculture or recreational activities. It is recommended that the surface waters in Kumasi be adequately managed by restricting the land use at riverbanks and maintaining buffer areas as pressure points during flooding. The water from these rivers should not be used for irrigational or recreational purposes.

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Declarations

Conflict of interest The authors declare no competing interests.

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