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Sewage Effluent Causes Metal Pollution of a Sub-tropical River System in Zimbabwe

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Abstract
Metal pollutants are persistent in the environment and of concern to human health. The aim of the study was to assess the distribution of metals (Cr, Fe, Pb, Mg and Cu) in Sebakwe River. Water and sediment samples were collected from upstream reference sites (4 and 5) and influenced downstream sites (1, 2 and 3) of the sewage effluent discharge point. Pb concentrations in water were significantly higher ($p < 0.05$) in sites 1 and 2 downstream of the sewage discharge point. In the sediments, the sites downstream of the effluent discharge point had significantly higher concentrations of Cu ($p < 0.05$) and Cr ($p < 0.05$). A comparison of metal concentration in water with World Health Organization and Standards Association of Zimbabwe standards revealed that the levels of Pb in water were above the recommended limits, posing a health risk to Pb poisoning for people living along Sebakwe River.

Keywords Metal pollution · Sediments · Water · Sewage effluent

The pollution of aquatic resources is of global concern as it causes deterioration of aquatic health and lead to human health problems (Geijzendorffer et al. 2019). Metals are among the pollutants of major concern when introduced into the aquatic environment due to their persistence (Ravindra and Mor 2019). The dissolved metals can be lowered in concentration by adsorption onto particulate organic matter which sink to the sediment (Jenne 2018). A result is elevated levels of metals in the bottom sediment (Dube et al. 2019; Utete et al. 2018). Resuspension of bottom sediments through bioturbation results in the release of metals back into water column, hence the sediments act as both source and sink of metals (Cheng et al. 2019).

Pollutants in the aquatic environment originate from point or non-point sources (Schaffner et al. 2009). Industrial processes and artisanal gold mining are a major source of metals into the aquatic environment (Mataba et al. 2016; Teta et al. 2017). In addition, urban surface runoff and sewage effluent discharges are also contaminated with metal elements (Patel et al. 2018). When the metals are discharged in the aquatic environment, they may represent potential risk, not only to the aquatic biota but to human health (Verhaert et al. 2019). The metals may accumulate in tissues of aquatic biota making their toxicities of significance along entire food chains, including humans (Verhaert et al. 2019).

Sebakwe River serves as a major source of domestic and irrigation water for human communities along the river. The expansion of urban, agricultural and industrial activities has produced vast amounts of wastes potentially contaminated with metals (Utete et al. 2018). Managing this metal waste is a challenge especially in developing countries. For example, sewage treatment plants in most developing countries are not designed to remove metals from the effluent. Along the Sebakwe River is a sewage treatment plant that discharges treated effluent into the river.

Therefore, the general aim of this study was to assess the spatial distribution of metal concentrations in Sebakwe River in relation to sewage effluent discharge. Specifically, we compared metal concentration in the water and sediments in sites upstream against downstream of the sewage effluent discharge point. We also compared the metal concentration in water with World Health Organization (WHO) and Standards Association of Zimbabwe (SAZ). We hypothesized that sewage effluent discharge introduce metal pollution in the Sebakwe River.

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Materials and Methods

Sebakwe River is located in the Manyame Catchment and passes through Kwekwe in the Midlands Province of Zimbabwe of Zimbabwe. Kwekwe City and its peri-urban environment are part of the Manyame Catchment area. Sebakwe River is a recipient of domestic and industrial waste effluent from the City of Kwekwe. The rural communities around Sebakwe River abstract water from the river for domestic and irrigation purposes.

Water and sediment samples were collected once in December 2018 and once in January 2019. This period represent the rain season. Five sampling sites were located along Sebakwe River to capture downstream and upstream point source of sewage effluent discharge (Fig. 1). Sites 1–3 were located downstream while sites 4 and 5 were located upstream of the discharge point and were used as reference sites. The Kwekwe City sewer reticulation works is comprised of waste stabilization ponds and two Biological Nutrient Removal (BNR) activated sludge plants. The volume of sewage influent and effluent has increased over time evidenced by increase in the population of Kwekwe City from 75.425 (1992) to 100 900 (2012).

Water samples were collected in duplicate from each site at 5 cm below the water surface. The water samples were placed in sterile polythene bottles, acidified with 10% nitric acid (pH 2) to keep metal ions in the dissolved state, as well as to prevent microbial activities (American Public Health Association 1998). Sediment samples were collected at the same sites with water samples. About 500 g of sediment samples were collected from a depth of 20 cm using a hand sediment core with 2.5 inch diameter. At each site, the sediments were collected from a radius of 5 m to produce a composite sample.

The water samples were filtered through a millipore filtration assembly, using 0.45 mm membrane filter. The filtrate was acidified with concentrated HNO_3 to a pH of < 2. A volume of 50 mL sample was mixed with 5 mL of concentrated HNO_3 (Merk, Germany). The mixture was heated at 130℃ on hot plate till the volume came to about 25–30 mL and light color. After cooling, the digested sample was filtered through Whatman no. 41 filter paper and the volume was made to 100 mL with deionized water. A blank solution was similarly prepared following the same protocol.

The sediment was sieved and ground to fine particles (< 200 µm). An acid based digestion procedure was used for the digestion of sediments and water samples (Greenberg et al. 1980; Utete et al. 2018). One gram of the sediment sample was placed in 250 mL flask and mixed with 10 mL of 50% HNO_3 (55%, Merk, Germany) for digestion. The mixture was heated to 95℃ without boiling. After cooling the sample, it was refluxed with repeated additions of 65% HNO_3 until no brown fumes were given off. The solution was then allowed to evaporate until the volume was reduced to 5 mL. After cooling, 10 mL of 30% H_2O_2 was added slowly to the digested sample and the mixture was refluxed with 10 mL of 37% HCl at 95℃ for 15 min. The digested sediment was then passed through Whatman no. 41 filter paper, washed with a 0.1 M HNO_3 solution then made to 100 mL volume using deionized water.

For quality assurance and control (QA/QC), blank samples were processed simultaneously after every ten samples and analyzed using the same procedure. All blanks were

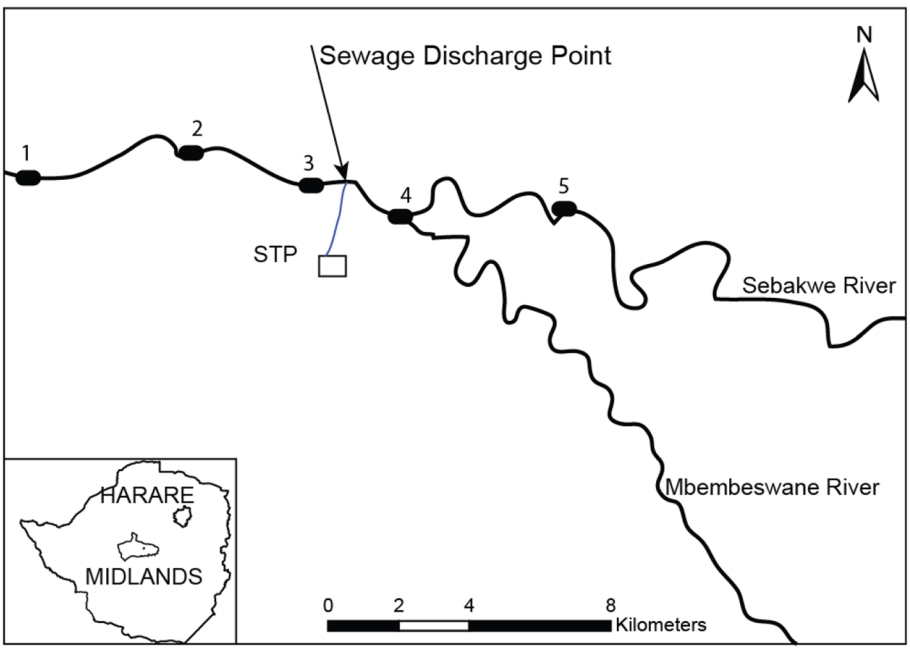

Fig. 1 Location of sampling sites (1–5) along Sebakwe River. Sites 1–3 are downstream while 4 and 5 are upstream of the discharge point of the Sewage Treatment Plant (STP)

below the instrumental detection limit. The heavy metals (Cr, Fe, Pb, and Cu) were analyzed with an air-acetylene flame atomic absorption spectrometer (AAS) Perkin-Elmer Model Analyst 400. The detection limits of the AAS for the analyzed metals were 0.01 mg L^{-1} for Fe, Pb, Cr, and 0.005 mg L^{-1} for Cu.

One way analysis of variance (ANOVA) was used to test for significant differences in metal concentrations in water and sediments among the sites. A Shapiro test ($p > 0.05$) was used to check if the residuals approximated a normal distribution. Turkey (HSD) post hoc test was performed to determine which sites significantly differed from each other in metal concentration.

To evaluate the sediment quality, the geo-accumulation (I-geo) and pollution load index (PLI) of the five metals were calculated (Muller 1969; Tomlinson et al. 1980). The geo-accumulation index (Igeo) is defined by the following equation:

$$\text{Igeo} = \log_2(\text{Cn}/1.5 \times \text{B}n)$$

where, Cn is concentration of metal n and Bn is background or preindustrial concentration of the metal (n), here given by the average values of metal concentration before the effluent discharge. Constant factor K is a background matrix correction factor, because of lithospheric effects, which is usually defined as 1.5 (Muller 1969). I-geo is classified into six classes following Muller (1969). The PLI is defined as the n^{th} root of the multiplications of the contamination factor of metals (CF) (Tomlinson et al. 1980)

$$\text{CF} = \text{C metal}/\text{C background}$$

$$\text{PLI} = (\text{CF1} \times \text{CF2} \times \text{CF3} \times \ldots\ldots\ldots \text{CF}n)^{1/n}$$

where CF = contamination factor, n = number of metals, C metal = metal concentration in polluted sediments C background = background value of that metal. Values of PLI > 1 indicate that metal pollution exists and PLI < 1, imply there is no metal pollution (Tomlinson et al. 1980). To assess the human health risk, the metal concentrations in water were compared with WHO (2016) and SAZ (1997) guidelines for drinking water quality.

Results and Discussion

The concentrations of metals in water along Sebakwe River occurred in the order Pb > Mg > Fe > Cu > Cr and varied with ranges of: Pb (0.06–0.14) mg L^{-1}, Mg (0.03–0.10) mg L^{-1}, Fe (0.01–0.07) mg L^{-1}, Cu (0.02–0.16) mg L^{-1}, and Cr (0.01–0.08) mg L^{-1} (Table 1). Overall, there was a highly significant difference in Pb (ANOVA: $F = 33.49$, $p < 0.01$) among the sites. A post hoc pairwise test revealed that downstream sites 1 and 2 after the point source discharge of sewage effluent had significantly higher Pb concentration (0.13 ± 0.02) mg L^{-1} and (0.125 ± 0.04) mg L^{-1}, respectively, compared to the upstream sites. There was no significant difference in Mg (ANOVA: $F = 3.05$, $p = 0.1$), Fe (ANOVA: $F = 4.33$, $p = 0.05$), Cu (ANOVA: $F = 3.1$,

Table 1 Metal concentration in water (Mean ± SD) compared to WHO and SAZ standards water quality guidelines for drinking water in mg L^{-1}

	Site	Mg	Fe	Cu	Cr	Pb
Water	1	0.08 ± 0.01	0.04 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.13 ± 0.04
	2	0.07 ± 0.01	0.05	0.04 ± 0.01	0.04 ± 0.01	0.125 ± 0.02
	3	0.08 ± 0.02	0.07 ± 0.01	0.12 ± 0.03	0.06 ± 0.01	0.1 ± 0.01
	4	0.05 ± 0.02	0.05 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.06 ± 0.02
	5	BDL	0.01 ± 0.01	0.05 ± 0.01	0.01 ± 0.01	0.04 ± 0.01
Sediment	1	1.23×10^{-5}	1.5×10^{-5}	8.75×10^{-5}	5.25×10^{-5}	2.75 10^{-5}
	2	8.25×10^{-4}	2.3×10^{-4}	4.75×10^{-5}	6×10^{-5}	5.25×10^{-5}
	3	1.825×10^{-4}	1.6×10^{-5}	2×10^{-5}	8.25×10^{-5}	8.25×10^{-5}
	4	1.9×10^{-4}	5.5×10^{-5}	4.75×10^{-5}	4.5×10^{-5}	3.5×10^{-5}
	5	1.125×10^{-4}	2.23×10^{-4}	2.75×10^{-5}	2×10^{-5}	1.5×10^{-5}
	WHO[a]	0.5	0.3	1	0.1	c
	SAZ[b]	1	0.3	0.1	c	0.05

The detection limits of the analyzed metals were 0.01 mg L^{-1} for Fe, Pb, Cr, and 0.005 mg L^{-1} for Cu

BDL below detection limit

[a]WHO – World Health Organization (2016) – Guidelines for drinking water quality

[b]SAZ – Standards Association of Zimbabwe (1997) – ZWS Specifications for drinking water supplies (ZWS 960:1997)

[c]Values are not given in the SAZ and WHO standards

$p = 0.09$) and Cr (ANOVA: $F = 1.63$, $p = 0.22$) concentrations among the five sites.

The metal concentration in sediments along Sebakwe River was in the ranges: Mg (7×10^{-5}–2.3×10^{-4}) mg g^{-1}, Fe (4×10^{-5}–5×10^{-4}) mg g^{-1}, Cu (1×10^{-5}–1×10^{-4}) mg g^{-1}, Cr (1×10^{-5}–1.3×10–4) mg g^{-1} and Pb (1×10^{-5}–1×10^{-4}) mg g^{-1}. Overall, there was a significant difference in Cr (ANOVA: $F = 7.33$, $p = 0.01$) and Cu (ANOVA: $F = 7.9$, $p = 0.01$) concentrations among the sites. A post hoc pairwise test showed that site 1 downstream of the point source sewage discharge had significantly higher concentration of Cu ($9 \times 10^{-5} \pm 1 \times 10^{-5}$) mg L^{-1} compared to upstream sites 4 ($4.75 \times 10^{-5} \pm 2 \times 10^{-5}$) mg g^{-1} and 5 ($2.75 \times 10^{-5} \pm 1 \times 10^{-5}$) mg g^{-1}. Similarly, Cr at downstream site 3 ($5.25 \times 10^{-5} \pm 4 \times 10^{-5}$) mg g^{-1} was significantly higher than at site 5 ($2 \times 10^{-5} \pm 1 \times 10^{-5}$) mg g^{-1} upstream. There was no significant difference in Pb (ANOVA: $F = 2.57$, $p = 0.13$), Mg (ANOVA: $F = 1.10$, $p = 0.31$) and Fe (ANOVA: $F = 2.8$, $p = 0.11$) concentration in the sediments among the sites. The metals in the sediments occurred in the order Pb > Mg > Fe > Cu > Cr.

The PLI across all sites in Sebakwe River was greater than 1, showing accumulation of the metals (Table 2). The PLI values for upstream reference sites (4–5) were less than downstream impacted sites (1–3). The surface sediments upstream of the sewage treatment plant were unpolluted by the metals investigated in this study (I-geo < 1). Site 3 immediately after the sewage discharge point was slightly and moderately polluted with Cr (I-geo = 0.76) and Pb (I-geo = 1.13), respectively. Similarly, sites 1, 2 and 3 downstream of the effluent discharge point were slightly polluted with Cu, Fe and Pb, respectively (Table 2).

The results of metal concentrations in Sebakwe River indicate that Mg, Fe, Cu and Cr are below the permissible SAZ and WHO limits (Table 1). The concentrations of Pb are above the SAZ and WHO permissible limits at all sites.

The study investigated the extent of metal pollution in water and sediments of Sebakwe River. As hypothesized, sewage effluent discharge contributed metal pollution in Sebakwe River. Our results showed that sites upstream of the sewage effluent discharge point were not heavily polluted with metals. The high levels of Cu and Cr in water at site 3 immediately after the STP can be attributed to domestic and sewage industrial effluent from the treatment plant. The results from this study confirm findings from similar studies in the region where high levels of metals were observed in rivers due to sewage effluent (Dube et al. 2019; Teta et al. 2017). High levels of Pb were recorded at site 2, located under the bridge along the highway characterized by high volumes of traffic. Other studies have shown that the combustion of petrol is a major source of atmospheric lead, which can be deposited into the surface water (Chrastný et al. 2018; Hwang et al. 2016). The metals in low concentration upstream of the sewage effluent discharge point may have originated from non-point surface runoff originating from Ferro-chrome Company, and lead acid manufacturing and repair industries in the area. Previous studies have shown that the ferro-chrome company contribute particulate metal polluted dust to the atmosphere and surrounding areas (Pumure et al. 2003). In addition, Sebakwe River flows across the great dyke of Zimbabwe that is rich in mineral deposits such as Fe which may contribute to metal pollution of the aquatic ecosystems in the region. The metals in the city's sewage effluent system are expected to be removed during primary settling and activated sludge process. However, the efficiency of metal removal by these processes is dependent on plant operating parameters, physical or chemical factors and biological factors that always vary with regions (Lester 1983).

The sediment downstream of the sewage effluent point source were slightly to moderately contaminated with metals. However, the sediment metal levels in this study were lower compared to those of polluted rivers and dams in the region (Nhiwatiwa et al. 2011; Utete et al. 2018). The sites after the sewage effluent discharge point along Sebakwe River are experiencing progressive deterioration (PLI > 1) due to anthropogenic inputs of metals hence the need to be monitored. The results from this study form a baseline for future monitoring of metal pollutants in Sebakwe River.

A continued exposure of surface water and sediments to metal pollution has a potential negative impact on the aquatic ecosystem because metals are persistent in the environment and may be bio-accumulated or bio-magnified in the food chain (Jayakumar and Muralidharan 2019). For example, sediments are an integral component of aquatic environment providing habitat, feeding, spawning and rearing areas for many organisms (de Castro-Catala et al. 2016). Several studies have shown that heavy metals bio-accumulate in the

Table 2 The geo-accumulation and pollution load of metals in Sebakwe River

Site	Mg	Fe	Cu	Cr	Pb	PLI
1	−0.88912	−0.47612	0.63743	0.106915	−0.44746	1.295846
2	−1.45943	0.140549	−0.24393	0.29956	0.485427	1.349103
3	−0.314	−0.38301	−1.49185	0.758992	1.137504	1.443019
4	−0.2559	−1.92358	−0.24393	−0.11548	−0.09954	1.04238
5	−1.01197	0.098113	−1.03242	−1.2854	−1.32193	0.799318

aquatic food chain and their impact varies (Verhaert et al. 2019) resulting in a shift in the species composition, and genetic diversity of the ecosystem (Hamilton et al. 2016; Zhang et al. 2019). Similar studies have reported an accumulation of heavy metals in the tissues of fish living in polluted water (Verhaert et al. 2019).

Pb levels are above the WHO (2016) and SAZ (1997) permissible limits. Some human communities along Sebakwe River use the water from Sebakwe River for domestic purposes. Acute exposure of humans to Pb induces brain damage and central nervous system while chronic exposure may cause adverse effects on the blood, central nervous system, blood pressure, kidneys, and vitamin D metabolism (Lentini et al. 2019). This makes the Pb contaminated water unsuitable for human consumption (WHO 2016). Lead exposure can have serious consequences for the health of children because they absorb 4–5 times as much ingested lead as adults from a given source (Ahamed and Siddiqui 2007). Children who survive severe lead poisoning may be left with mental retardation and behavioral disorders (Lidsky and Schneider 2003). At lower levels of exposure, lead can affect children's brain development resulting in reduced intelligence quotient (IQ), behavioural changes and increased antisocial behaviour (Olness 2003). A limitation in this study was on the types of metals that could be analyzed due to the availability or resources. Future studies in Sebakwe region should consider monitoring a wide range of metal pollutants from human subjects. Other studies where humans are exposed to metals and other organic pollutants have detected Pb from blood and breast milk samples (Pajewska-Szmyt et al. 2019).

Overaly, heavy metal pollution in Zimbabwe and other developing countries is of environmental and health concern. Several studies in Zimbabwe have shown that water bodies are heavily polluted with metals from sewage effluent (Teta et al. 2017; Utete et al. 2018). There is a need by relevant authorities to enforce legislation governing effluent disposal. Furthermore, a continuous and systematic monitoring of effluent quality to prevent further deterioration of water bodies in the region is needed. As the economies of developing countries grow and resources become available, it is recommended to adopt international advanced metal treatment technologies.

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