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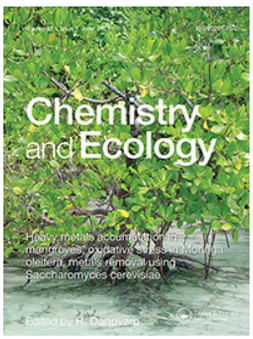

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Spatial distribution of heavy metals in the Ga-Selati River of the Olifants River System, South Africa

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ABSTRACT

The Ga-Selati River is subjected to different forms of pollution from mining, industrial and agricultural activities, and human settlements. The objectives of the study were to assess heavy metal pollution and to determine possible sources of pollutants in the river. Water and sediment samples were collected and analysed for the following selected metals: arsenic (As), chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn) using sequential Inductively Coupled Plasma-optical emission spectrometry (ICP-OES). The enrichment factor (EF) and geo-accumulation index (I_{geo}) were used to determine the level of metal pollution in the sediment. The results indicated that Cr and Ni were the most accumulated elements in the sediments, and the midstream sites (S4 and S5) showed a much higher pollution level than the upstream and downstream sites. The main sources of pollutants were mining, wastewater/sewage and agricultural discharges. This may pose a serious threat to the river and health risk to the nearby rural communities, which rely on the river, especially for drinking water. Proper management strategies to reduce pollution is therefore necessary.

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Heavy metals; pollution; nutrients; geo-accumulation; sediment; water quality

1. Introduction

Globally, many rivers are being degraded due to pollution from mining, industrial and agricultural run-off, and increasing human settlements [1–3]. The pollutants from these human activities include heavy metals. Heavy metals are among the most serious pollutants facing freshwater systems due to their high toxicity, persistence and tendency to bioaccumulate [4]. High levels of heavy metals have a significant impact not only on the environment but also on human health [5]. Heavy metals have natural (e.g. weathering and erosion) and anthropogenic origin [6–8].

When heavy metals are released into rivers, they are distributed between the dissolved phase and the river sediments [9]. Sediments play an important role in determining the pollution patterns of aquatic systems and serve as a sink for heavy metal pollutants, and may serve as a potential source of secondary metal pollution, which may also reflect their contamination level [10,11]. Thus, the accumulation of heavy metals in the sediment poses a long-term threat to the aquatic environments [12] and may affect

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aquatic organisms through bioassimilation and bioaccumulation [13–16]. When heavy metals enter aquatic organisms, they bioaccumulate and become available to higher trophic level organisms, such as birds and humans, and may pose a potential risk to their health [17,18]. High levels of heavy metals in biota may also contribute to the decline in their populations [19]. Assessment of heavy metals in the sediment provides a useful information and potential mobility and bioavailability of the metals for proper management policies [4,20].

In South Africa, there has been an increase in heavy metal pollution in freshwater ecosystems due to the effects of rapid urbanisation and industrialisation [21, 22]. The Ga-Selati River supplies water for various human activities, such as mining, agriculture, industries and domestic usage in its catchment. As a result of these activities, the river receives both point- and non-point-sources (diffuse) which can potentially cause heavy metal pollution in the river. A number of sediment quality indicators have been developed, such as enrichment factor (EF) [23] and geo-accumulation index (I_{geo}) [24,25], which determine whether the heavy metals in sediments are from natural phenomena or anthropogenic activities. The objectives of the study were to (i) investigate spatial distribution and concentrations of heavy metals, chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn), and a metalloid, arsenic (As) in the sediments of Ga-Selati River and (ii) identify the possible sources using heavy metals indices. We hypothesised that the distribution of heavy metals varied among the sites and the midstream and downstream sites with higher human impacts would be more polluted than the upstream sites. The results would provide basic information for the assessment of heavy metals in the river and management of sediment pollution.

2. Materials and methods

2.1. Study site

The Ga-Selati River is located in Limpopo Province, South Africa. It takes its source in the Drakensberg Mountains in the Legalametse Nature Reserve, and merges with the larger Olifants River at the boundary of the Kruger National Park, near the Phalaborwa mine [26]. Rainfall in the area ranges from 1500 mm/yr, in the upper catchment to less than 500 mm/yr in the lower catchment, most of the rainfall occurs in summer. At the upper catchment, the topmost ridges are primarily grassland. On the steep escarpment slopes, there are patches of Afro-montane forest, while the lower plains, comprise an arid or relatively humid savannah [27].

Nine (9) sampling sites were selected along the Ga-Selati River (Figure 1), S1 (Dindinie) was located near Legalametse Nature Reserve and commercial farms (24°8′30.81″ S 30°18′11.63″ E). S2 (Harmonie) was located just above Harmonie Dam and surrounded by commercial farms (24°3′28.55″ S 30°29′41.96″ E). S3 (Grovelotte) near Selati Game Reserve (24°0′19.64″ S 30°40′29.25″ E). S4 (Ngulube) was near a lodge (23°55′17.13"S 30°51′13.39"E). S5 (Namakgale) was close to the Namakgale Township (23°58′36.61″ S 30°59′03.95″ E). S6 (Mica) near Phalaborwa town (23°58′38.34″ S 31°04′26.54 ″E). S7 (Bosveld) near Bosveld fertiliser factory (23°59′06.89″ S 31°04′44.15″ E). S8 was near phosphate mine and processing plant (24°00′39.08″ S 31° 05′01.39″ E), and S9 (Lepelle) near the FOSKOR mine and industrial complex (24°02′16.93"S 31° 07′59.64"E).

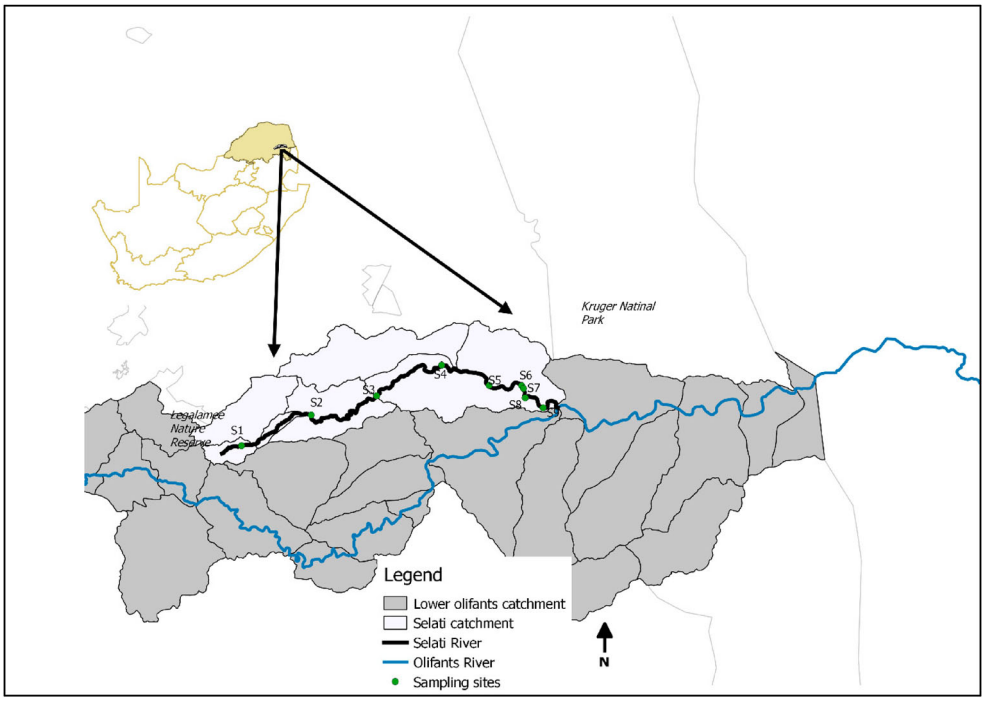

Figure 1. Map of the Ga-Selati River of the Olifants River System showing the sampling sites.

There are mining, agricultural and industrial activities and human settlements along the Ga-Selati River. The sampling sites were selected to represent the land use activities along the river.

2.2. Water and sediment sampling

Samples were collected in July (winter) and November (spring), 2017 and February (summer), April (autumn), 2018. During each survey, water temperature (°C), pH, dissolved oxygen concentration (DO), electric conductivity (EC), total dissolved solids (TDS) and salinity (ppt) were measured *in situ* at each site using a handheld multi-parameter probe (YSI Model 554 Data logger). Water samples were collected in 500 mL 10% nitric acid pre-treated polypropylene bottles and stored at 4°C prior to analyses. Turbidity and nutrients, such as ammonia (NH_3,) nitrite ($NO_{2)}$, nitrate (NO_3) and phosphate (PO_4) were determined using a spectrophotometer (Merk Pharo 100 Spectroquant™). The metals in the water samples were analysed in batches with blanks using inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer, Optima 2100DV).

Surface sediment samples were collected at a depth of about 5–10 cm using a spatula. At each site, five sub-samples were mixed together, forming a composite sample [28]. The samples were placed in 10% nitric acid pre-treated polyethylene ziplock bags, transported to the laboratory and were frozen (−20°C) prior to chemical analysis [29]. Sediment samples were analysed for elements at an accredited (ISO 17025) chemical laboratory WATERLAB (PTY) LTD in Pretoria, South Africa. The samples were put in acid-washed

polypropylene pre-weighed vials and dried at 60°C for 24 h. The samples were then sieved through a 2-mm nylon sieve to remove any stones and coarse debris. Then 0.1 g of each sediment sample was digested with 8 mL of 68% nitric acid (HNO3) and 3 mL of 40% hydrochloric acid (HCl). It was then filtered through a membrane filter and the concentrations of As, Cr, Fe, Mn, Ni and Zn were analysed using inductively coupled plasma–optical emission spectrometry (ICP-OES) (Perkin Elmer, Optima 2100 DV). Concentrations of the metals in the sediments were calculated and expressed as mg/kg dry weight. Analytical accuracy was determined using certified standards (De Bruyn Spectroscopic Solutions 500 MUL20-50STD2) and recoveries were within 10% of certified values.

2.3. Statistical analysis

The mean and standard deviation of the physicochemical variables, metals and nutrients were determined. Two-way analysis of variance (ANOVA) was done to determine differences for mean metal concentrations among sites and seasons, using Statistica (Version 10).

Enrichment factor (EF) method was used to assess the presence and level of pollution in the sediment [30,31]. EF is calculated as:

$$\mathrm{EF} = [C_x/(\mathrm{Fe})]/[(\text{Baseline } C_x)/(\text{Baseline Fe})],$$

where C_x is the metal concentration [32,33]. The average shale values of metals by Turekian and Wedepohl [34] was used as background values for heavy metals. The concentration of Fe was used as a reference value for the study. To account for natural heavy metal concentrations, EF is normalised to sediment using Al or Fe content. In this study, Fe was selected while determining EF-values. Several authors have successfully used iron (Fe) to normalise heavy metal contaminants [35,36]. Values of EF were used to assess the pollution of bottom sediment samples into the following classes: ($\mathrm{EF} < 2$) deficiency to minimal enrichment; ($2 < \mathrm{EF} < 5$) moderate enrichment; ($5 < \mathrm{EF} < 20$) significant enrichment; ($20 < \mathrm{EF} < 40$) very high enrichment; and ($\mathrm{EF} > 40$) extremely high enriched [30].

2.4. Geo-accumulation index (I_{geo})

The index of geo-accumulation (I_{geo}) was used to measure the sediment contaminations. It considers both the natural geological process and the impact of human activities on heavy metal pollution [37].

The value of the geo-accumulation index is calculated by the following equation:

$$I_{\mathrm{geo}} = \log_2\left(\frac{C_x}{1.5\mathrm{B}_n}\right),$$

where C_x is the concentration of the examined metal in the sediment, B_n is the geochemical background value of a given metal in the shale [34] and the factor 1.5 is used to account for the possible variations in the background values. There are seven classes of geo accumulation index [37]. The classes range from Class 0 (unpolluted) to Class 6 (extremely polluted); 0 ($I_{\mathrm{geo}} \leq 0$) uncontaminated, class 1 ($0 < I_{\mathrm{geo}} < 1$) uncontaminated to

moderately contaminated, class 2 ($1 < I_{geo} < 2$) moderately contaminated, class 3 ($2 < I_{geo} < 3$) moderately to heavily contaminated, class 4 ($3 < I_{geo} < 4$) highly contaminated, class 5 ($4 < I_{geo} < 5$) heavily to extremely contaminated, class 6 ($I_{geo} \geq 5$) extremely contaminated [30].

3. Results and discussion

3.1. Physicochemical properties

The recorded pH values at all the sampling sites were slightly alkaline. The values ranged from 7.99 at S1 to 9.32 at S5. No significant difference was observed among the sites ($p > .05$). The high pH recorded in the water could be due to the discharge of alkaline effluent from human activities in the catchment [38]. The mean temperature ranged from 20.1°C at S1 to 26.0°C at S3. The mean DO ranged from 9.9 mg/l at S1 to 7.6 mg/l at S3. The low DO concentration at S3 could be attributed to either the high temperatures recorded at the site or the presence of water impoundment just above the site. Water impoundment can affect physical and chemical factors, such as stream substrate, DO, water temperature and metals [39,40]. The mean electrical conductivity (EC) ranged from 170 µS cm^{-1} at S1 to 1484 µS cm^{-1} at S9. The concentration gradient of EC from upstream to downstream might have been the result of the effluents from the catchment [41]. The mean total dissolved solids (TDS) ranged from 82.0 mg/l at S1 to 693 mg/l at S9. The TDS levels recorded throughout the study were below the recommended guideline value of 1000 mg/l for the protection of aquatic life and for domestic water supply [42]. The mean turbidity ranged from 1 NTU at S1 to 13 NTU at S9. Turbidity values were higher at midstream (i.e. S4, S5 and S6) than the upstream and downstream sites. This could be due to effluents from the human activities especially wastewater discharges from the human settlements. The mean salinity ranged from 0.08 ppt at S1 to 0.69 ppt at S9. Generally, TDS, EC and salinity showed concentration gradient from upstream to downstream (Table 1), and likely due to runoff from the catchment. There were significant differences in TDS, EC and salinity among the sites ($p < .05$).

3.2. Nutrients

The mean ammonia levels in the samples ranged from 0.03 mg/l at S3 to 0.34 mg/l at S6. Mean nitrate levels ranged from 0.47 mg/l at S1 to 3.44 mg/l at S4. The nitrate levels measured in all the sampling sites were below the Canadian Council of Ministers of the Environment (CCME) [43] value of 13 mg/l for the protection of aquatic life and the United States Environmental Protection Agency (USEPA) [44] limit of 10 mg/l. The mean levels of nitrite were extremely low at all the sites with the highest value of 0.20 mg/l at S6. Mean ortho-phosphate (PO_4^{3-}) ranged from 0.21 mg/l at S4 to 2.47 mg/l at S5. Nutrient levels were lower at the upstream sites, S1 and S2 compared to the other sites. The highest concentrations of nitrate and phosphorous were recorded in the midstream sites, S4 and S5 respectively (Figure 3). Sewage could be the source of the high phosphate level at S5, as the site is close to the Namakgale Township. High concentration of phosphate usually occurs in waters that receive sewage, leaching or runoff from cultivated land [45].

Table 1. Mean physicochemical variables (SD) of the nine sampling sites in the Ga-Selati River.

	S1	S2	S3	S4	S5	S6	S7	S8	S9
pH*	7.9––8.8	8.2–8.7	8.5–9.0	8.5–8.9	8.6–9.3	8.4–8.6	8.3–8.6	8.2–8.6	8.6 ± 9.1
EC (µS/cm)	170 ± 27	254 ± 119	348 ± 135	362 ± 69	847 ± 236	1017 ± 330	1074 ± 334	1129 ± 379	1484 ± 450
TDS (mg/l)	82.0 ± 12	118 ± 57	155 ± 49	169 ± 26	387 ± 213	472 ± 139	503 ± 140	514 ± 157	693 ± 177
DO (mg/l)	9.9 ± 1.9	9.0 ± 1.1	7.6 ± 0.58	8.3 ± 1.9	8.1 ± 1.8	8.6 ± 2.1	9.0 ± 2.4	8.5 ± 2.7	7.8 ± 1.8
Temperature (°C)	20.1 ± 2.9	25.5 ± 7.4	26.0 ± 8.3	22.9 ± 5.6	24.5 ± 7.1	23.3 ± 6.9	22.8 ± 6.0	22.6 ± 6.1	23.3 ± 7.7
Turbidity (NTU)	1.0 ± 0.8	7.0 ± 3.1	7.0 ± 1.5	7.0 ± 1.3	9.0 ± 0.6	13.0 ± 6.5	11.0 ± 5.2	7.0 ± 5.1	6.0 ± 3.6
Salinity (ppt)	0.08 ± 0.02	0.11 ± 0.06	0.11 ± 0.1	0.17 ± 0.03	0.38 ± 0.22	0.46 ± 0.15	0.5 ± 0.15	0.5 ± 0.17	0.69 ± 0.18
Nitrite (mg/l)	0.03 ± 0.06	0.03 ± 0.03	0.05 ± 0.06	0.02 ± 0.01	0.03 ± 0.04	0.2 ± 0.14	0.11 ± 0.04	0.05 ± 0.02	0.05 ± 0.04
Nitrate (mg/l)	0.47 ± 0.31	0.55 ± 0.12	1.4 ± 0.6	3.44 ± 2.8	1.71 ± 2.3	1.51 ± 0.8	1.76 ± 0.8	1.68 ± 0.4	2.65 ± 1.1
Ammonia (mg/l)	0.05 ± 0.05	0.04 ± 0.01	0.03 ± 0.02	0.06 ± 0.04	0.05 ± 0.03	0.34 ± 0.11	0.18 ± 0.10	0.14 ± 0.04	0.08 ± 0.03
Phosphate (mg/l)	0.42 ± 0.03	0.45 ± 0.04	0.51 ± 0.3	0.21 ± 0.2	2.47 ± 0.9	0.86 ± 0.33	1.05 ± 0.7	1.15 ± 0.8	0.88 ± 0.7

Notes: pH: the values are the range; SD: standard deviation.

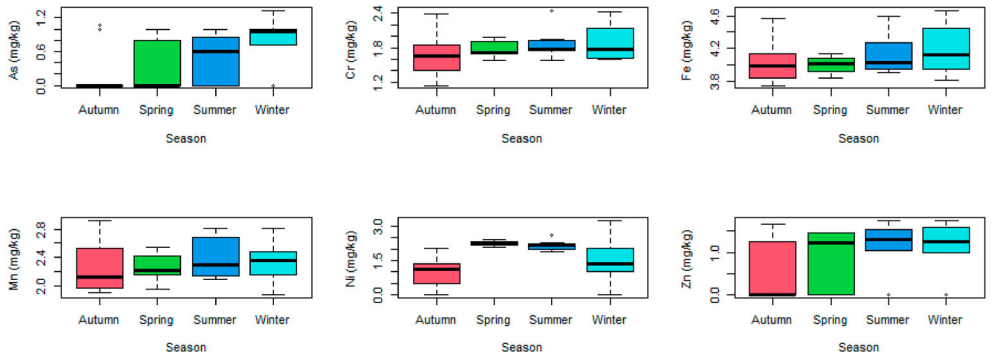

Figure 3. Box and Whisker plots for the seasonal distribution of heavy metal concentrations in the sediments of the Ga-Selati River.

3.3. Heavy metals in water

Most of the metals in the water were below the detection level (Table 2). There were no significant variations in metal concentrations among the sites ($p > .05$). The highest mean Fe concentration was 0.3 ± 0.01 mg/l at S1. For Mn, the highest mean concentration of 0.14 ± 0.09 mg/l was found at S2 and the highest Zn concentration of 0.04 ± 0.02 mg/l was at S2 and S4. The Fe concentration recorded at S1 and Zn concentration recorded at all the sites were above the water quality guidelines recommended by South African Department of Water Affairs and Forestry (DWAF) [46]. The relatively high levels of Zn at S2 and S4 in the water column could be due to agricultural activities in the area, mainly attributed to the presence of unused remains of zinc sulphate in fertilisers [47,48].

3.4. Heavy metals in sediment

The spatial distribution of heavy metals (As, Cr, Fe, Mn, Ni and Zn) are presented in Figure 2, The highest mean concentrations of all the metals were found at S4. The concentrations of Cr, Fe and Mn were significantly different among the sites, but there were no significant differences for As, Ni and Zn among the sites (Table 3). The significant seasonal difference

Table 2. Mean metal concentrations (mg/l) in the water at the different sites of Ga-Selati River of the Olifants River System (mean and SD).

Site	B	Fe	Mn	Zn
S1	0.01 ± 0.00	0.30 ± 0.10	0.01 ± 0.02	0.02 ± 0.01
S2	0.02 ± 0.02	0.21 ± 0.19	0.14 ± 0.09	0.04 ± 0.01
S3	0.02 ± 0.01	0.05 ± 0.03	0.01 ± 0.00	0.03 ± 0.00
S4	0.03 ± 0.02	0.15 ± 0.11	0.03 ± 0.02	0.04 ± 0.02
S5	0.06 ± 0.04	0.11 ± 0.13	0.02 ± 0.01	0.03 ± 0.02
S6	0.08 ± 0.02	0.20 ± 0.11	0.06 ± 0.02	0.03 ± 0.02
S7	0.08 ± 0.01	0.17 ± 0.10	0.06 ± 0.03	0.01 ± 0.01
S8	0.07 ± 0.02	0.10 ± 0.10	0.04 ± 0.02	0.02 ± 0.01
S9	0.08 ± 0.02	0.10 ± 0.05	0.04 ± 0.03	0.03 ± 0.02
Guidelines	1.2[2], 1.5[3]	0.3[3]	0.18*[1]; <1.3	0.002*[1], 0.03[3]

Notes: * – Water Hardness dependent. References: 1 – DWAF (1996) – South African Water Quality Guidelines: Volume 7: Aquatic Ecosystems; 2 – BC-EPD (2006) – British Columbia Environmental Protection Division: Water Quality Guidelines; 3 – CCME (2012) – Canadian Council of Ministers of the Environment: Water Quality Guidelines: Aquatic Life.

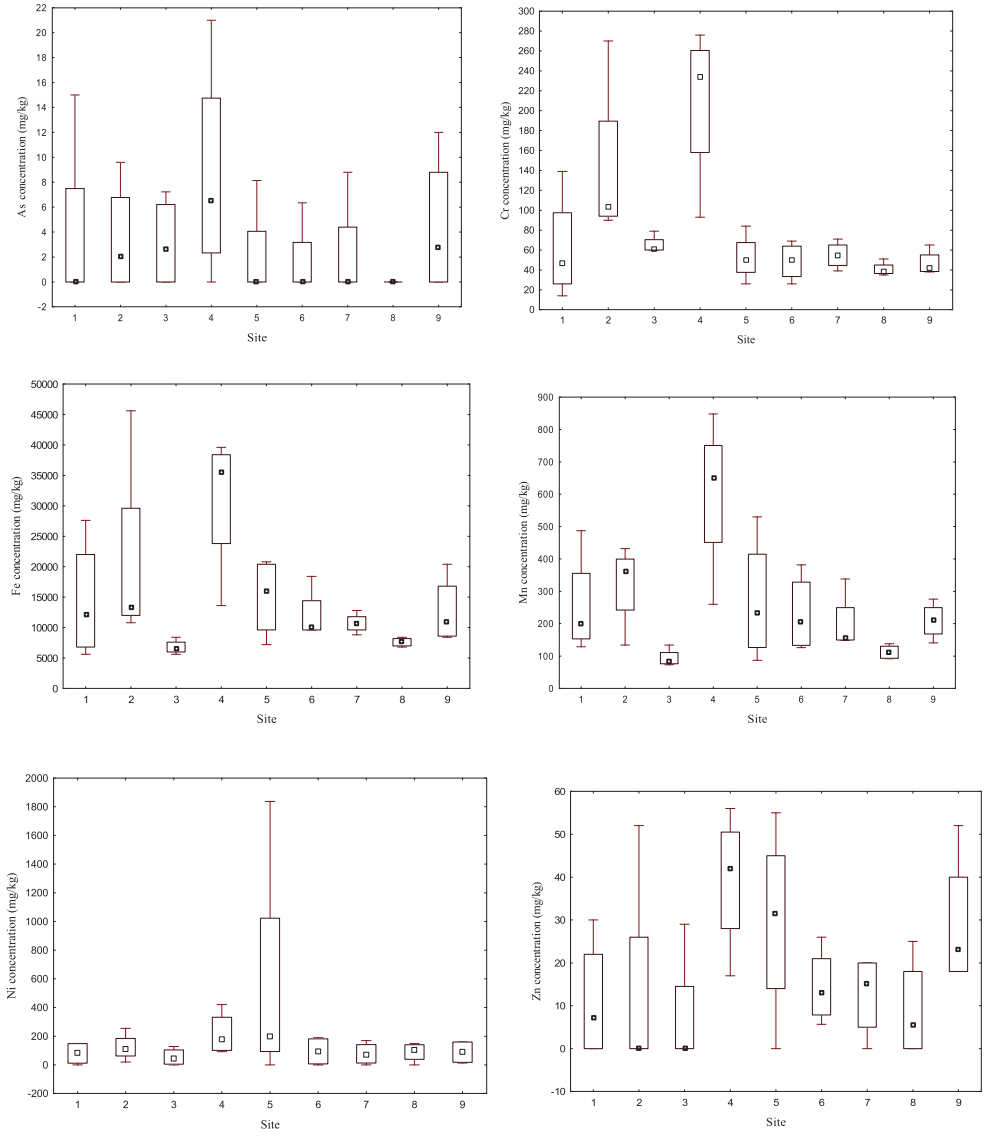

Figure 2. Box and Whisker plots for the spatial distribution of heavy metal concentrations in the sediments of the Ga-Selati River.

Table 3. Two-way analysis of variance (2-way ANOVA) of the metals in the sediments identifying differences among sites and seasons. Bold values indicate $p < .05$.

	Site		Season		Site × season	
Variable	*F*	*p*	*F*	*p*	*F*	*p*
As	0.760	.640	2.203	.106	0.081	.813
Cr	5.795	**.0003**	1.791	.175	0.076	.784
Fe	4.160	**.003**	2.040	.135	0.407	.527
Mn	4.604	**.001**	0.906	.452	0.178	.675
Ni	1.061	.422	8.254	**.0006**	0.484	.491
Zn	1.905	.106	1.289	.300	0.295	.590

was observed for Ni, but not the other metals (Table 3). The mean concentration of Cr exceeded the average shale value at S4 (209 mg/kg) and S2 (142 mg/kg). The mean Ni concentrations exceeded the average shale value (68 mg/kg) at all the sites except S3, S8 and S9. The mean concentrations of As exceeded the CCME guideline value of 5.9 mg/kg at S1, S4 and S9. The mean concentrations of Cr also exceeded the CCME guideline value of 37.3 mg/kg at all sites (Table 4).

The elements that are of concern in the river are As, Cr and Ni. The higher As contamination at S1 and S4 might be coming from fertilisers and pesticides used in commercial farms [49,50], while the contamination at S9 was attributed to the mining near the site. Arsenic compound (As_2O_3) can be produced from processing of ores containing mostly Cu, Pb, Zn, Ag and Au. Large-scale open-pit copper mining and a diverse range of minerals and metals including uranium, nickel, gold, silver, platinum and palladium are mined in the Ga-Selati river catchment [51]. Arsenic is also present in ashes from coal combustion. Arsenic is associated with skin damage, increased risk of cancer and problems with the circulatory system [52]. Chromium and its salts are used in pigments and paints, fungicides, and chrome alloy and chromium metal production [42]. In this study, the main sources of Cr in the sediment could be from agricultural, mining and industrial activities. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. In humans, Cr can cause allergic dermatitis [52].

For Ni, the higher concentration at S4 and S5 could be from agricultural runoff. Some chemical fertilisers and pesticides are known to contain Ni [53]. In addition, the source of higher Ni concentration at the downstream sites might be from urban activities and Phalaborwa Industrial complex effluents [54], and combustion of fossil fuels [55]. Nickel occurs only at very low levels in the environment and is essential in small doses, but it can be toxic when the maximum tolerable level is exceeded. The Ni contamination in the river is of great concern as it can cause health problems, such as cardiovascular diseases, chest pain, dizziness, dry cough, headache, kidney diseases and nausea in humans [18].

There was also considerable seasonal variability in metal concentrations. The highest concentration of all the metals except Ni were observed during winter (Figure 3). The highest Cr concentration was recorded at S3 during autumn. Arsenic and Zn constituted a very small percentage in all the seasons (Figure 4). There were no significant seasonal differences in metal concentrations for Cr, Fe, Mn, Ni and Zn ($p > .05$). However, there was a significant seasonal variation in the concentration of As ($p < .03$). Higher concentrations As, Cr, Fe and Mn found during winter might be due to the low water flow in

Table 4. Comparative analysis of heavy metal concentration (mg kg^{-1}) of Ga-Selati River sediment with average shale values and CCME reference values.

Metals	Present study	Average shale values[a]	CCME
As	5.0–15.0	13	5.9
Cr	41.0–209	90	37.3
Fe	7469–31,100	47,200	–
Mn	94–601	850	–
Ni	72–395	68	–
Zn	14–52	95	123

[a]Ref. [34].

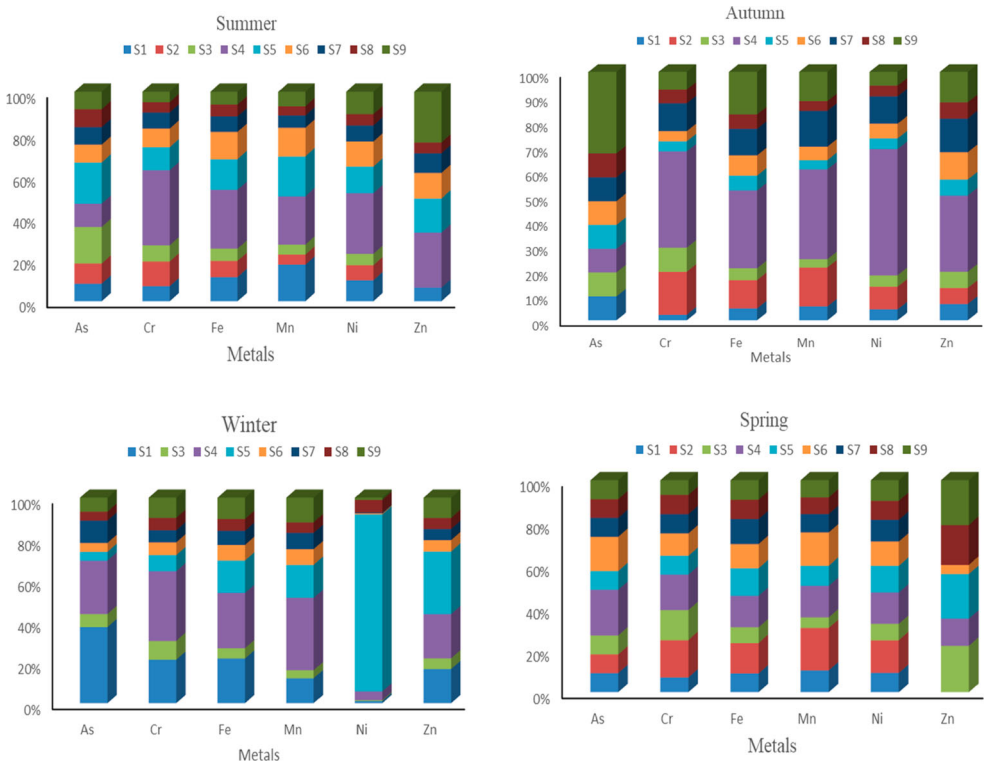

Figure 4. Seasonal distribution of metals in the sediment of Ga-Selati River at the different sites.

winter which resulted in the precipitation of these metals in the sediments than the other seasons [56].

3.5. Enrichment factor and geo-accumulation index

The enrichment factor (EF) was applied to assess the possible sources of the metals. The results of the EF is shown in Table 5; As (0.86–7.44), Cr (1.86–4.02), Mn (0.61–1.55), Ni (4.22–11.18) and Zn (0.76–1.94). The EF value of As was greater than 2 at S3, Cr was between 2 and 5 at S1, S2, S6, S7 and S8, and greater than 5 at S3. In the case of Ni, the EF values were between 2 and 5 at S1, S2, S4, S8 and S9, whereas, the EF values were greater than 5 at S3, S6 and S7, and greater than 20 at S5. The EF values of Mn and Zn were all below 2. The relatively higher EF values of Cr and Ni may be due to

Table 5. Enrichment factor for heavy metal in sediments in the Ga-Selati River.

Metal	S1	S2	S3	S4	S5	S6	S7	S8	S9
As	1.61	0.74	2.59	1.10	1.13	1.27	1.64	1.67	1.76
Cr	2.25	3.57	5.03	3.53	1.84	2.13	2.68	2.81	1.93
Fe	1	1	1	1	1	1	1	1	1
Mn	0.98	0.86	0.76	1.07	1.00	1.07	1.04	0.91	0.91
Ni	3.95	4.10	5.78	4.84	25.85	5.56	5.12	4.82	4.82
Zn	0.46	0.36	0.88	0.63	1.06	0.60	0.58	1.13	1.13

Table 6. Geo –accumulation index for heavy metal in sediment of Ga-Selati River. Highlighted values indicate contamination.

I_{geo}	As	Cr	Fe	Mn	Ni	Zn
S1	−1.608	−1.123	−2.300	−2.323	0.580	−2.698
S2	−1.966	−4.265	−1.716	−2.000	0.273	−1.454
S3	−1.478	−1.056	−3.381	−3.837	−0.494	−2.293
S4	−0.826	0.630	−1.185	−1.089	1.091	−3.988
S5	−1.286	−1.347	−2.238	−2.253	2.458	−1.865
S6	−1.699	−1.462	−2.565	−2.474	−0.086	−3.351
S7	−1.286	−1.297	−2.727	−2.644	−0.055	−3.071
S8	−0.971	−1.718	−3.224	−3.474	0.230	−2.988
S9	−1.114	−1.523	−2.482	−2.643	−0.220	−3.880

human activities occurring in the catchment [57]. However, the relatively low EF values of Mn and Zn is an indication that they originate mainly from natural sources [40].

Geoaccumulation index; calculated I_{geo} values based on the average shale are presented in Table 6. The I_{geo} value for As, Fe, Mn and Zn fall in class '0', indicating background concentration in all the sites. Whereas, I_{geo} value of Cr falls in class 1 at S4, indicating uncontaminated to moderately contaminated. Nickel falls in class 2 and class 3 at S4 and S5, respectively, indicating moderately to heavily contaminated sediments. The contamination of Cr and Ni at S4 and S5 is attributed to wastewater/sewage discharge from the lodge and township near S4 and S5, respectively [58]. The high I_{geo} values for Ni at S4 and S5 show that these sites receive a considerable amount of Ni contamination [59].

4. Conclusion

In the water, the upstream sites generally had lower nutrients and heavy metal levels as compared to the midstream and downstream sites. The concentrations of As, Cr and Ni exceeded the average shale values in certain parts of the river. The results of the enrichment factor and geo-accumulation index (I_{geo}) showed that Cr and Ni were the main metal pollutants in the sediments of Ga-Selati River. Mining activities, agricultural runoff, lithology, and other anthropogenic inputs are probable sources of As, Cr and Ni pollution in the river. The high concentrations of heavy metals may pose an ecological risk to the river and may affect the communities, especially those that depend directly on the river for drinking water and food (fish). It is therefore important to monitor the river and implement remedial measures to protect the river.

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