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Evaluation of temporary seasonal variation of heavy metals and their potential ecological risk in Nzhelele River, South Africa

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Abstract: Surface water is often used as alternative source of drinking water in many regions of the world where the potable water supply is erratic or not present. The concentration of heavy metals was assessed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The impact of temporary seasonal variation on the contamination level was also assessed. Contamination factor (CF) and Hakanson's potential ecological risk (E_r and RI) indices were used to evaluate the toxicity levels of the metals in the sediments of the river. Higher concentrations of Fe, Mn, Pb, Cu and Zn were determined in the dry season in the river water whereas in the sediments higher levels were recorded for Al, Fe, Cd, Cr, Cu and Zn in the wet season. The average CF values for all the metals showed a low contamination level in the sediment, except for Cu and Cd which had moderate and considerable contamination levels, respectively. Similarly, Cu showed a moderate ecological risk level ($E_r = 62.90$) only in March 2014, for other months Cu and the other metals investigated had E_r values < 40 which implies low ecological risk. The mean relative abundance of heavy metals in the sediments follows the trend $Al > Fe > Mn > Cu > Zn > Cr > Pb > Cd$.

Keywords: Contamination factor, risk analysis, sediment contamination, seasonal variation, trace metals, human health, water quality

1 Introduction

Contamination of freshwater courses and their sediments by heavy metals is a global problem which has attracted policy makers and researchers because of the toxicity associated with them as well as their bioaccumulation potential [1]. This has led to the formulation of several sediment quality guidelines (SQGs) which have been useful in identifying pollutants of concern [1,2]. Based on information gathered from the SQGs, adequate monitoring frameworks have been designed. Cevik et al. [3] reported that SQGs are useful for the assessment of the health of sediment ecosystems as well as the protection of benthic organisms in freshwater ecosystems. Apart from various SQGs, some other indices have been formulated to test the contamination level and ecological risk of single and total heavy metals in sediments for example the geo-accumulation index (I_{geo}), enrichment factor (EF), Newrow integrated pollution index (P_n), contamination factor (CF) and ecological risk index (RI) [4–9]. Background levels of heavy metals in sediments of various countries are often required to calculate the relative toxicity of heavy metals in sediments but due to lack of such data in some countries, average heavy metals levels in sedimentary rock, continental crust, world shale, among others are often employed [1,6,10]. In this study, we used the contamination factor and ecological risk index developed by Hakanson which is based on the assumption that the sensitivity of the aquatic system depends on its productivity [1,5]. He used a toxic-response factor for a given heavy metal [1].

The concentration of heavy metals, exposure route, duration of exposure, age, genetic, chemical species as well as the nutritional status of the exposed individuals are part of various factors that influence the potential toxicity of heavy metals to humans [11]. Heavy metals are

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known to be toxic, persistent and have bio-accumulation tendencies in environmental media [12–14]. Once released, they can stay for exceptionally long period of time, resisting degradation and undergoing various chemical processes in water. They are easily converted into more toxic forms by microorganisms and converted into organic forms, some of which can be harmful to humans and aquatic ecosystems [12,15–17]. Monitoring of sediments is important because they serve as both carriers and sinks for pollutants, and reflect the history and anthropogenic inputs of the pollutants into the aquatic ecosystem [1,3,18]. Metals adsorbed onto sediments can easily be released under suitable conditions (such as change in temperature, pH, dissolved oxygen as well as the solubility of the chemical species) into the water column therefore acting as a source of secondary pollution [19,20]. The National Research Council of America [21] and Knox et al. [22] reported that trace metal contaminated sediments can cause direct and indirect risks as these metals are easily absorbed and become bio-accumulated in sea foods which may lead to possible human exposure.

Heavy metal contamination of rivers and sediments have been linked to several human activities that occur both far and close to the natural resource such as settlements, farms, game reserves, car wash, mining industries, storm water runoff, and wastewater treatment facilities [23]. de Melo Gurgel et al. [24] and Chaves et al. [23] reported that anthropogenic activities performed very close to rivers poses threat to the aquatic ecosystems and humans as contaminated water becomes a channel through which several diseases are spread to people living around the water resource. High levels of heavy metals have been reported in different species of aquatic organisms such as macrophytes, phytoplanktons, zooplanktons, prawns and fish in concentration beyond the permissible limits and this serves as a pathway to humans [25,26]. Other studies have implicated high concentration of heavy metals in the aquatic ecosystems to have adverse effects on benthic organisms, which include retarded growth, change in reproduction cycles and death in some species of fish [1,27–29]. High heavy metal levels in freshwater makes them unsuitable for human consumption, livestock watering and irrigation. Studies on the evaluation of the potential risk of heavy metals in South African river systems is limited and this study is the first to evaluate the potential ecological risk associated with heavy metals in Nzhelele River sediments. The objective of this study is to (i) assess heavy metals contamination of Nzhelele River which is often used by people for various purposes, (ii) investigate the effects of seasonal variations on the level of metals determined and (iii) to evaluate the possible ecological risk of the metals levels found.

1.1 Study area

Nzhelele River is located between latitudes 22°53'15.8" S and 22°54'5" S and longitudes 30°11'10.2" E and 30°11'23.5" E in the Limpopo Province of South Africa (Figure 1) [30]. Major land uses include formal and informal settlements, subsistence agriculture and the Siloam waste stabilization ponds (WSPs) which release effluents into the river. The study area is semi-arid with a shortage of potable water supplies. Residents depend largely on the abstraction of water from the Nzhelele River to meet their water needs without any form of treatment. Nzhelele River's catchment area is 2, 436 square kilometers and it is a major water watercourse in the Limpopo Province of South Africa [31]. Rainfall is highly seasonal with 95% occurring between October and April [30]. The region is characterized by a warm wet season which is associated with high temperatures up to 40°C usually between October and March (with peak precipitation in January and February) and cold dry season (April–September) [32].

2 Materials and Methods

2.1 Sampling

Thirty-six water and thirty-three sediment samples were collected randomly from different sampling sites along Nzhelele River from January to June 2014. The sampling bottles (polyethylene) were washed using anionic detergents and then rinsed with tap water followed by distilled water. Concentrated nitric acid (5%) was added to samples collected for total metal determination. Physico-chemical parameters like pH and electrical conductivity (EC) were measured *insitu* using 340i pH and EC multimeter (WTW, Weilheim, Germany) [33]. Turbidity of the river water was also measured using TB 200 turbidimeter (Orbeco Hellige, Sarasota, FL, USA) [33]. The samples and control were transported, preserved, digested and analyzed bearing in mind issues of quality control and assurance as recorded in Edokpayi et al. [34].

2.2 Analysis of Heavy Metals

The analysis of the digested samples was performed with an inductively coupled plasma optical emission spectrometer (ICP-OES) ICAP 6500, Thermo Scientific, Johannesburg, South Africa. The condition setting for the ICP-OES is presented in supplementary data 1. Calibration standards

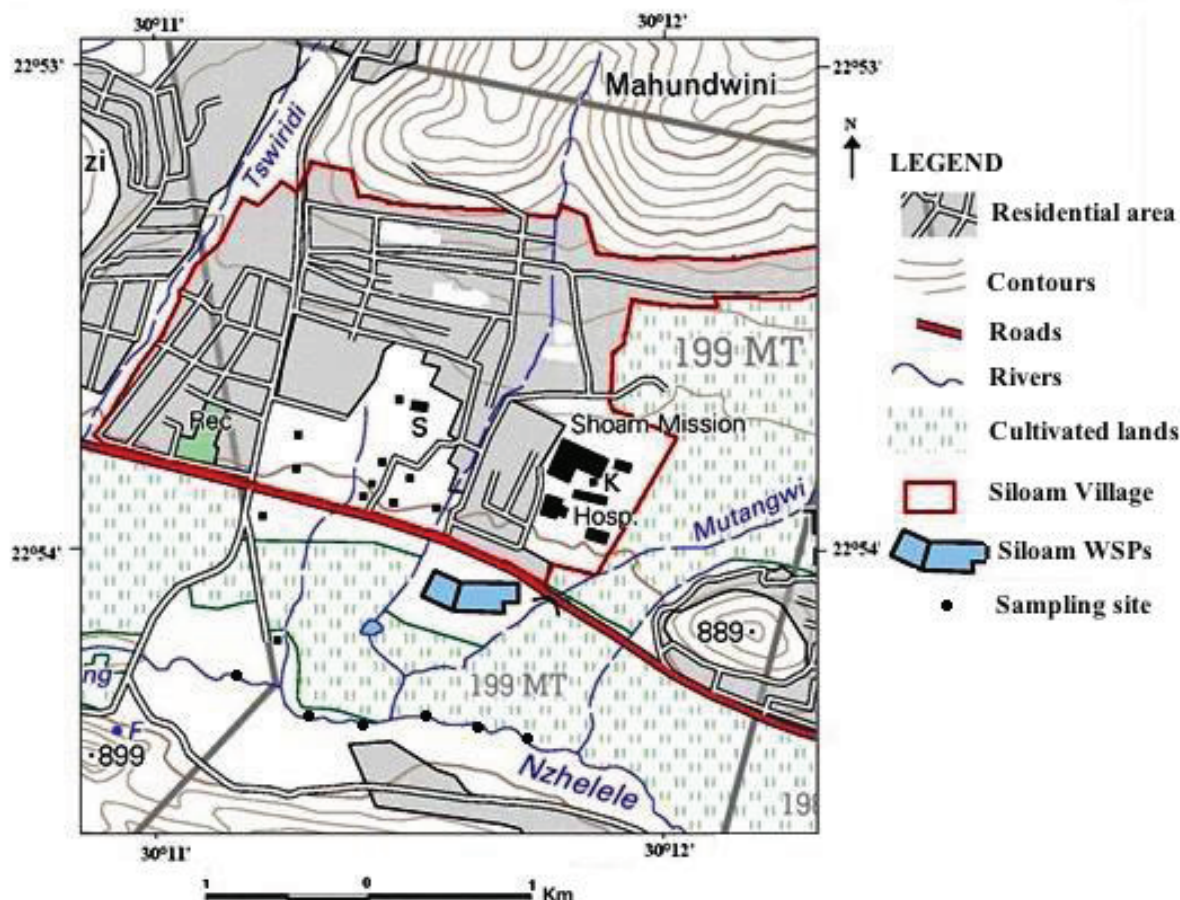


Figure 1: Map of the study area [30].

were prepared from a multi-element stock solution of 100 mg/L. The detection of the method limit was determined for each element by adhering to the procedures of the United States Environmental Protection Agency (US EPA) [35] method 200.7. Spike recovery method was used to validate the analytical method and instrument used for the analysis [34]. Statistical analysis was performed using the IBM SPSS statistics package 20.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and Discussion

Acceptable recoveries in the range of 90-110% and 85-120% for water and sediment samples, respectively were obtained from the spike recovery test. The method detection limit for metals in the water and sediment samples varied between 1 µg/L for Pb to 25 µg/L for Al [32].

3.1 Physico-chemical parameters

The average pH values of Nzhelele River over the study period were found to be in the range of 7.21-7.76 (Supplementary data 2), which complied with the Department of Water Affairs and Forestry (DWAF) and that of the World Health Organization (WHO) guideline value of 6-9 for domestic water use [28,36]. An average pH value of 7.62 was obtained in the wet season which was slightly higher than 7.47 in the dry season. This level did not differ significantly ($p>0.05$) for both the wet and the dry season. This implies that seasonal variations do not lead to considerable changes in pH. Weak and non-significant correlations were computed for pH values in the wet and the dry seasons. Turbidity is usually associated with reduced penetration of light rays into the river which can adversely affect benthic organisms [19]. The average turbidity values obtained decreased consistently from 678 NTU (January) to 1.4 NTU (June 2014) (Supplementary data 2). The higher values obtained in the wet season (January-March) is due to higher rainfall than in the dry season (April-June). The

mean values obtained during the sampling period for both seasons were higher than the DWAF and WHO standards of ≤ 1 NTU for domestic water. A positive and significant correlation was computed for turbidity levels for both seasons ($r = 0.723$, $p < 0.01$). Seasonal variations in turbidity levels in various rivers in South Africa have been reported in the literature [37,38].

The average EC values were in the range of 8-14 mS/m (Supplementary data 2), with the values for the wet and dry seasons differing significantly ($p < 0.05$), indicating that seasonal variations have the potential to cause change in the conductivity. EC values in both seasons showed a weak correlation with each other which was not significant ($r = 0.210$, $p > 0.05$). The lower values of EC observed in the wet season could be dilution of dissolved salts due to rainfall [39]. As rainfall decreases, the level of EC increases due to the concentration of the ions due to evaporation in the river. Similar findings were reported in the literature [40,41]. However, Anhwange et al. [42] and Shabalala et al. [43] recorded higher values of EC in the wet season which was attributed to runoff of ionic materials from soils into the rivers during rainfall. The values obtained in this study for both seasons were within the recommended guidelines of DWAF (70 mS/m) [28] and WHO (600 mS/m) [36] for domestic water use.

3.2 Trace metals concentrations

The monthly average concentrations of Al ranged from 1.172-29.094 mg/L (Table 1) in the water samples and 2331-4707 mg/kg in the sediments of Nzhelele River (Figure 2). The levels obtained in the water samples exceeded the DWAF threshold value (0.15 mg/L) for domestic water use. Highest Al concentration was obtained in January (29.094 mg/L) in which rainfall was at its peak. The reason for this could be attributed to high surface runoffs from agricultural land and soil rich in Al during incidences of rainfall [34]. The concentration of Al in the aqueous environment is pH dependent. Al is usually soluble and toxic to aquatic species at acidic pH. It is also soluble at alkaline pH but non-toxic [44]. The World Health Organization (WHO) do not have a guideline value for Al as it is considered to be of no risk to humans at low concentrations but a health based value of 0.9 mg/L was adopted by WHO [36]. High Al concentration in domestic water have been correlated to Alzheimer's disease and renal failure [44]. The average levels of Al obtained in this study exceeded this guideline value which implies that the consumption of this Al rich water could have adverse effects on human health.

Currently, there is no sediment quality guidelines (SQGs) in South Africa for metal concentration in freshwater sediments [45] and therefore the SQGs of the Canadian Council of Ministers of the Environment (CCME) for sediments in freshwater was employed in this study [2]. Currently no guideline value has been assigned to Al. The Al concentrations in the river waters differed significantly to their levels in the sediments ($p < 0.01$) (Supplementary data 3), indicating that Al concentrations in the sediments is different from their levels in the water of Nzhelele River as expected. The levels of Al determined can be linked to its relative abundance in earth and high levels of Al have been previously recorded in South Africa river systems [12,15,20]. Also, the use of Al-containing materials within the river catchment area could also be responsible for the high levels as there is no effective solid waste collection and disposal system in the villages surrounding the river. Therefore, during rainfall the storm water generated can easily carry Al-containing materials to the river and this possibly explains its higher concentration determined in the wet season.

The average concentration of Fe was in the range of 1.028-4.991 mg/L (Table 1), which exceeded the DWAF threshold value of 0.1 mg/L for all the sampling period. In the sediments, the mean Fe concentration varied between 1175-5252 mg/kg (Figure 2). There is no CCME SQG value for Fe but the levels determined were high. Mn is often considered as one of the least toxic metals and its level fluctuated between 0.052-0.545 mg/L during the period of sampling, which exceeded the DWAF [28] threshold limits for domestic (0.05 mg/L) and irrigation (0.02 mg/L) water uses. The mean lowest and highest concentrations of Mn in the sediments of Nzhelele were 120 mg/kg (June) and 516 mg/kg (April) respectively. There is no CCME guideline for Mn in freshwater sediment. The concentrations of Mn in the water of Nzhelele River varied significantly ($p < 0.05$) with their concentrations in the sediments (Supplementary data 4).

The average concentrations of Cd ranged between 4.0×10^{-4} and 2×10^{-3} mg/L and complied with the 0.003 mg/L guideline of WHO [36] and the DWAF [28] threshold value of (0.005 mg/L) and therefore the levels of Cd determined in this study would not constitute a human health concern. In the sediments, the average concentrations of Cd varied from 0.006 - 4.056 mg/kg (Figure 2). CCME [2] guideline value for Cd in sediment is 0.6 mg/kg and was exceeded in Nzhelele Rivers from January-March. The other sampling months had values below 0.6 mg/kg (Figure 2). Wastewater effluents and run-offs from agricultural lands and landfills are the major anthropogenic sources of Cd in aquatic ecosystem [46]. Cd in the river water did not vary significantly ($p > 0.05$) with their levels in the sediments.

Table 1: Average level of trace metal in Nzhelele River water.

Trace metal concentration (mg/L)	Sampling Months					
	January	February	March	April	May	June
Al	29.094±9.26	3.089±1.12	1.172±0.41	3.550±1.12	3.704±2.42	1.834±1.06
Cd	0.001±0.001	0.001±0.002	0.002±0.001	0.0004±0.01	0.001±0.002	0.001±0.001
Cr	0.396±0.08	0.363±0.05	0.285±0.82	0.045±0.01	0.386±0.05	0.082±0.16
Cu	0.066±0.01	0.027±0.01	0.028±0.01	0.025±0.01	0.048±0.03	0.043±0.03
Fe	4.991±2.47	1.180±0.18	1.028±0.24	1.777±0.44	3.001±1.12	1.172±0.84
Mn	0.145±0.08	0.052±0.01	0.214±0.05	0.545±0.23	0.516±0.09	0.281±0.17
Pb	0.010±0.001	0.001±0.001	0.002±0.00	0.011±0.01	0.013±0.01	0.010±0.001
Zn	0.115±0.02	0.042±0.01	0.046±0.01	0.065±0.02	0.131±0.07	0.057±0.02

The mean Pb concentrations in the river waters were in the range 0.001–0.013 mg/L (Table 1). The concentration of Pb determined did not comply with DWAF [28] set value of 2×10^{-4} mg/L for the protection of aquatic ecosystems. However, the concentrations of Pb in the river water exceeded the benchmark value of 0.01 mg/L in April (0.019 mg/L) and May (0.013 mg/L) but complied for the rest of the months. In the sediments, Pb average concentrations varied between 0.248 mg/kg and 2.71 mg/kg (Figure 2) and was below the CCME [2] tolerable limit of 32.2 mg/kg for Pb in freshwater sediments. There was, however, a significant difference ($p < 0.01$) in the concentration of Pb in the river waters and sediments (Supplementary data 3).

The average Cr concentrations in the river water ranged from 0.045–0.396 mg/L (Table 1) and exceeded the DWAF and WHO guideline value of 0.05 mg/L for domestic water use except for the month of April (0.045 mg/L) [28,36]. The average concentrations of Cr in the sediments ranged between 7.804 mg/kg and 51.288 mg/kg (Figure 8). The CCME [2] guideline value for Cr in freshwater sediments (37.3 mg/kg) was exceeded in January and April although the values found in February (32.193 mg/kg) and March (31.061 mg/kg) were also close to the threshold value. However, the difference in the means of Cr determined in the water and sediments sample was statistically significant ($p < 0.05$) (Supplementary data 4).

Average Cu concentrations in the water samples varied between 0.0257 mg/L and 0.066 mg/L and did not exceed the benchmark values of 2 mg/L [36] and 1 mg/L [28] for domestic water use. In the sediments, the levels of Cu ranged between 2.182–566 mg/kg (Figure 2). The mean concentration of Cu in the sediments of the river complied with the guideline value of 37.5 mg/kg assigned by CCME [2] for Cu in freshwater sediments in all the sampling months except in March (566 mg/kg). Similarly, significant differences exist in the mean of Cu concentration in water and sediments ($p < 0.05$).

Zn average concentration in the river water ranged from 0.042–0.131 mg/L (Table 1), below the 3 mg/L assigned by DWAF [28] for domestic water use. The mean concentration of Zn in the sediments ranged between 2.605 and 202 mg/kg (Figure 2), which complied with the CCME [2] threshold value of 123 mg/kg for the protection of aquatic ecosystems except for March (202 mg/kg). The concentrations of Zn in the water and sediments varied significantly ($p < 0.05$).

3.3 Influence of temporary seasonal variation of heavy metals in Nzhelele River

Higher concentrations of Al in the water of the river were found in the wet season (10.565 mg/L) compared to the dry season (2.963 mg/L) (Table 2a). The mean difference of Al in the water varied significantly ($p < 0.05$) for both seasons. Similarly, the mean concentration of Al in the sediments was higher in the wet season (4312 mg/kg) compared to the dry season (3147 mg/kg) but the mean difference did not vary significantly ($p > 0.05$) (Table 2b). Higher concentrations of Fe were determined in the river water in the dry season (5.804 mg/L) than in the wet season (2.304 mg/L), this difference was statistically significant ($p > 0.05$). In the sediment, the average levels of Fe in the wet (3206 mg/kg) and in the dry (2862 mg/kg) season did not vary significantly ($p > 0.05$). In the river water, a higher concentration of Mn was determined in the dry season (0.755 mg/L) than in the wet season (0.129 mg/L) but this level in both seasons did not vary significantly ($p > 0.05$). Similarly, in the sediment Mn recorded a higher concentration during the dry season (306 mg/kg) than in the wet season (199 mg/kg) but this difference was not statistically significant ($p > 0.05$). High concentration of Cd in sediment was only observed during the wet season

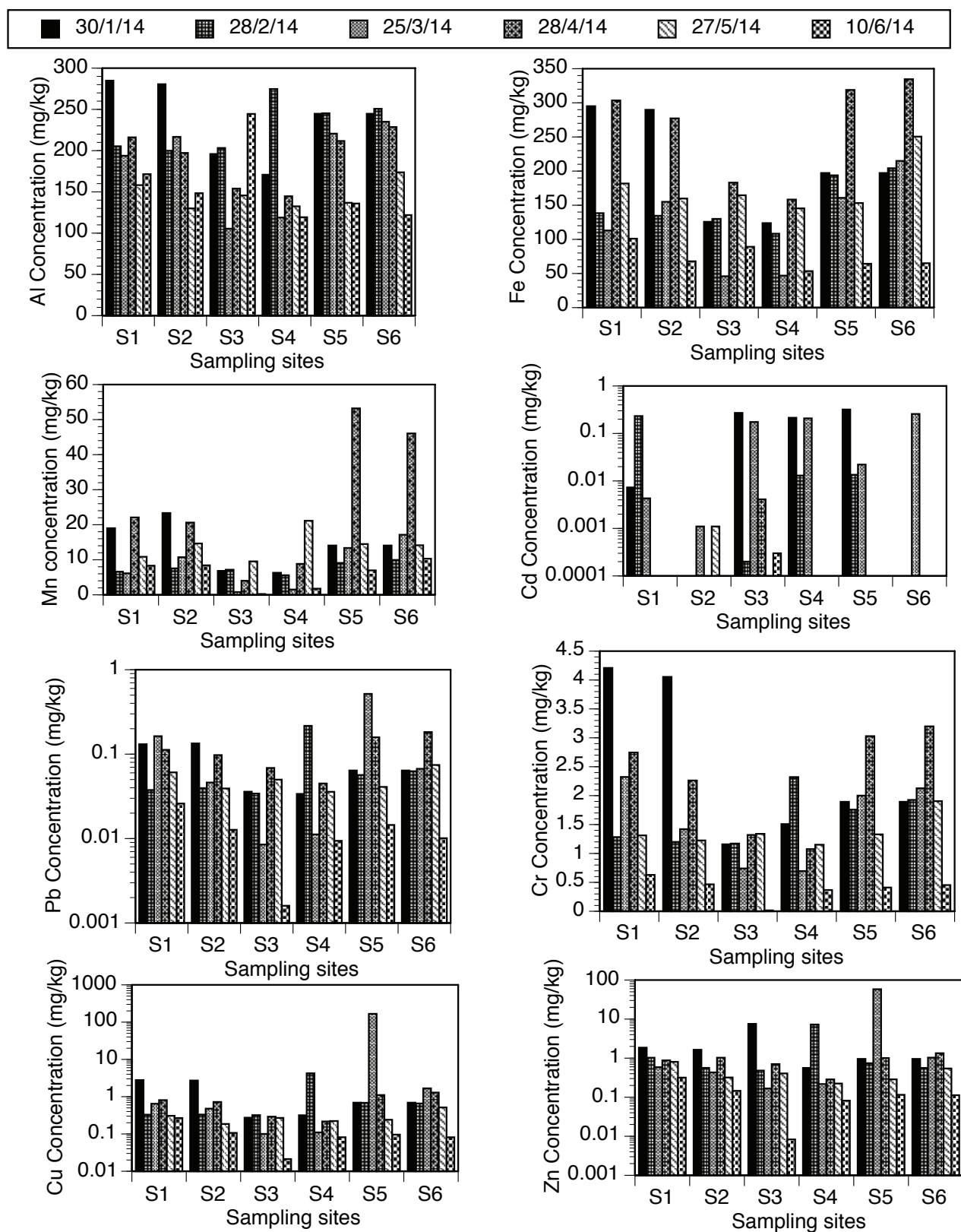


Figure 2: Heavy metal concentration (mg/kg) in Nzhelele sediments from January-June 2014, S1-S6 represent various sampling sites.

(2.52 mg/kg) and could be attributed to high precipitation which subsequently led to higher run-off of Cd containing materials from agricultural and semi industrial lands into the rivers [21].

The levels of Cd in the river sediments for the wet and the dry seasons varied significantly ($p < 0.01$). In the river water, the same concentration of Cd (0.001 mg/L) was determined in both seasons. Average Pb concentration in the river water was higher in the dry season (0.165 mg/L) than in the wet season (0.053 mg/L) and their mean difference varied significantly ($p < 0.05$). No significant variation was calculated for the average levels of Pb in the river sediments between the wet (1.847 mg/kg) and dry seasons (1.122 mg/kg) ($p > 0.05$). Higher levels of Cr were determined in the wet season (0.344 mg/L) than in the dry season (0.187 mg/L) and this difference in means was statistically significant ($p < 0.01$). The concentration of Cr in the sediments was higher in the wet season (38.18 mg/kg) than the dry season (26.22 mg/kg) but this mean difference was statistically insignificant ($p > 0.05$). Seasonal variation determined in the levels of Cu in the water for both the wet (0.385 mg/L) and the dry (0.403 mg/L) seasons was not significantly different ($p > 0.05$). Higher levels of Cu in the sediments was recorded in the wet season (20.35 mg/kg). Seasonal variation in Cu levels of the sediments was significant ($p < 0.05$) for the wet and the dry seasons. In the wet season, Zn concentration was lower (0.062 mg/L) than that of the dry season (0.086 mg/L), this could be due to dilution effects in the wet season and evaporation effects in the dry season. The difference in the means for both seasons in the river water did not vary significantly ($p > 0.05$). Higher levels of Zn were recorded in the sediments during the wet season (31.81 mg/kg) than in the dry season (7.285 mg/kg) but the mean difference was not significant ($p > 0.05$).

Metal levels in rivers are largely influenced in the wet season by storm water run-off from the surroundings on the river catchment and this usually leads to an increase in heavy metal concentration. High dilution of heavy metals due to increased water volume and flow is another factor that can influence the concentration of metals in a river during the wet season. In the dry season, there is a concentration of heavy metals due to reduced water volume and flow and increased evaporation from water bodies [34]. This can consequently lead to increased levels of heavy metals in the river. In this study, higher levels of heavy metals were determined in the Nzhelele River in the dry season (Cu, Fe, Mn, Pb and Zn) than in the wet season (Al, and Cr). Similar concentrations of 0.001 mg/L were determined for Cd. Islam et al. [47] reported that

metal concentration is expected to be low during the wet season due to the dilution effect on heavy metals but some site-specific activities and source of metal contamination could lead to an exception to this general trend. Different trends of seasonal effects on heavy metal levels in water and sediments have been reported [47-50].

3.4 Potential ecological risk of trace metals in Nzhelele River sediments

The risk associated with the levels of trace metals determined in the sediments was computed using the potential ecological index (RI) reported by Hakanson [5] which defined RI as

$$RI = \sum_{i=1}^n E_r^i \quad (1)$$

Where E_r^i refers to the potential ecological risk coefficient of a single element and it is defined as

$$E_r^i = T_r^i \times C_f^i \quad (2)$$

Where T_r^i is the toxic response factor for a given trace metal. The T_r^i values have been assigned for Cd, Pb, Cr, Cu, Mn and Zn as 30, 5, 2, 5, 1 and 1 respectively [5,10,58]. C_f^i represents the contamination factor which is used to measure the level of contamination of sediments by trace metals. C_f^i is defined as

$$C_f^i = \frac{C_i}{C_o} \quad (3)$$

C_i refers to each metal concentration in the sediments; and C_o is the background value of trace metals in sediments. There are no background values for trace metals in sediments in South Africa [43] and therefore the shale average concentrations of trace metals in global sediments reported by Turekian and Wedepohl [10] were used. $C_i < 1$ infers a low contamination of metals in the sediments, $1 \leq C_i \leq 3$ infers a moderate contamination of sediments and $3 \leq C_i \leq 6$ represents considerable trace metal contamination of sediments and $C_i > 6$ represent very high contamination of sediments [1,5,51]. From the results presented in Table 3, CF values for all the elements in each of the sampling months were less than 1, except for Cu and Zn in March and Cd in January-March. The average CF values for all the metals showed a low contamination level in the sediment, except for Cu and Cd which had a moderate and considerable contamination level, respectively. Most of the metals (Al, Cd, Cr, Cu, Pb and Zn) showed a higher

Table 2a: Mean concentrations of trace metal levels (mg/L) in the wet and the dry season of the water of Nzhelele River and the difference in their means at $p = 0.05$.

Metals	Wet	Dry	p-value
Al	10.57	2.96	0.03
Cd	0.001	0.001	0.078
Cr	0.344	0.187	0.008
Cu	0.385	0.403	0.789
Fe	2.304	5.804	0.382
Mn	0.129	0.755	0.063
Pb	0.053	0.165	0.016
Zn	0.065	0.086	0.223

Table 2b: Mean concentrations of trace metal levels (mg/kg) in the wet and the dry season of Nzhelele River sediments and the difference in their means at $p = 0.05$.

Metals	Wet	Dry	p-value
Al	4312	3147	0.064
Cd	4.16	0.082	0.00
Cr	38.18	26.22	0.169
Cu	20.35	7.286	0.025
Fe	3206	2862	0.771
Mn	199	306	0.324
Pb	1.847	1.122	0.470
Zn	31.81	9.411	0.103

contamination level in the wet season. The CF values for Mn were higher in the dry season while Fe had the same CF value for both seasons.

The E_r and RI values are associated with a scale of pollution levels of sediments; $E_r < 40$ has low ecological risk; $40 < E_r \leq 80$, moderate ecological risk; $80 < E_r \leq 160$, appreciable ecological risk; $160 < E_r \leq 320$, high ecological risk; and >320 , serious ecological risk [1,5,51-52]. The values of E_r for all the metals were < 40 implying low ecological risk except for Cu in March and Cd between January-March (Table 4). There was an appreciable risk for Cd in February, high ecological risk in March and a seriously ecological risk in January. Copper had a moderate ecological risk in March. The mean values of E_r calculated for each of the metals throughout the sampling period showed low ecological risk for all the metals except for Cd which showed an appreciable ecological risk. For most of the metals, higher values of E_r were computed during the wet season than in the dry season.

The RI method covers a variety of domains (biological toxicology, environmental chemistry as well as ecology) for the comprehensive evaluation of potential ecological risk caused by trace metals in sediments [5,51]. RI values

for water bodies are classified as: $RI < 150$ —low ecological risk; $150 < RI < 300$ —moderate ecological risk; $300 < RI < 600$ —considerable ecological risk and $RI > 600$ —very high ecological risk [1,5,10,51]. Sediment pollution was low except for the months of January and March which coincide with the highest rainfall recorded in the study area in 2014. Cd played a major role in the high levels of RI computed for the months of January-March. The overall ecological risk for all the metals evaluated was low. The major contributing factor to these high levels could be due to run-off from agricultural land, discharge of raw and partially treated water from the WSPs within the river catchment into the river.

4 Conclusion

Al and Fe were found in higher concentrations in the river water and sediments compared to the other metals investigated. In the water samples higher levels of metals were determined in the dry season except for Al, Cd and Cr. Conversely, higher levels were determined in the sediment samples of the river during the wet season than the dry season except for Mn and Pb. Possible sources of pollution include: run-off from settlements, agricultural soils, discharge of partially treated wastewater, poor solid waste management systems and several non-point sources. The Nzhelele River is not suitable for domestic purposes as most metals exceeded the benchmark compliance values. Apart from Cd, all metals investigated in the river water differed significantly with their levels in the sediments. Significant seasonal variations in the levels of the metals in the river water were only computed for Al, Pb and Cr while in the sediments only Cu and Cd varied significantly. It is believed that the levels of metals computed for Nzhelele River are influenced greatly by dilution and evaporation processes. Higher contamination levels and potential ecological risk were calculated for most of the metals in the wet season than in the dry season, however, the mean ecological risk for all the metals evaluated in the sampling period was low.

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Conflict of interest: Authors state no conflict of interest.

Table 3: Monthly average contamination factor (CF) of trace metals in Nzhelele River sediments.

		Al	Fe	Cr	Cu	Mn	Zn	Pb	Cd
January	Wet	0.06	0.09	0.57	0.60	0.33	0.53	0.08	13.5
February	Wet	0.06	0.06	0.36	0.49	0.18	0.37	0.07	4.33
March	Wet	0.05	0.05	0.34	12.58	0.20	2.13	0.14	7.33
April	Dry	0.05	0.11	0.50	0.33	0.61	0.19	0.11	0.27
May	Dry	0.04	0.07	0.31	0.13	0.33	0.09	0.05	0.03
June	Dry	0.03	0.02	0.09	0.05	0.14	0.03	0.01	0.03
Mean		0.05	0.07	0.39	2.36	0.30	0.56	0.08	4.25
Shale Average [10]		80000	47200	90	45	850	95	20	0.3

Table 4: Monthly average E' and RI of trace metals in Nzhelele River sediments.

		Cr	Cu	Mn	Zn	Pb	Cd	RI	Risk grade
January	Wet	1.14	3.00	0.33	0.53	0.40	405.00	410.40	considerable
February	Wet	0.72	2.45	0.18	0.37	0.35	129.90	133.97	low
March	Wet	0.68	62.90	0.20	2.13	0.70	219.90	286.51	moderate
April	Dry	1.00	1.65	0.61	0.19	0.55	8.10	12.10	low
May	Dry	0.62	0.65	0.33	0.09	0.25	0.90	2.84	low
June	Dry	0.18	0.25	0.14	0.03	0.05	0.90	0.74	low
Mean		0.72	11.82	0.30	0.56	2.30	127.45	141.10	low

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