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Human Health Risk Assessment of Trace Metals in Surface Water Due to Leachate from the Municipal Dumpsite by Pollution Index: A Case Study from Ndawuse River, Abuja, Nigeria

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Abstract: The study assessed the level of heavy metals in surface water across Ndawuse River near the dumpsite at Phase 1 District of the Federal Capital Territory (FCT), Abuja, Nigeria. The results indicated that oxygen demand, turbidity and heavy metals were above the standard limits set for drinking water. Multivariate analysis using principal component analysis and hierarchical cluster analysis revealed natural and anthropogenic activities as sources of heavy metal contamination. The estimated non-carcinogenic effects using hazard quotient toxicity potential, cumulative hazard index and daily human exposure dose of surface water through ingestion pathway were less than a unity. The estimated carcinogenic risks (CRing) exceeded the suggested potential risk limits, with lead (Pb) having the highest CRing value for all age groups. However, children were found to be more susceptible to heavy metals over a period of time according to the estimated values. The concentration of heavy metals in the investigated river could pose an adverse health risk to several communities that rely on this receiving water bodies for domestic purposes. Therefore, there is need for strict enforcement of environmental laws to protect aquatic ecosystem and to avoid long term cumulative exposure risk that heavy metals may pose on human health.

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Keywords: Carcinogenic risks, daily human exposure risk, heavy metals, Ndawuse River.

1 Introduction

Water is an important resource for human survival that has many uses, including recreation, transportation, hydroelectric power generation, domestic, industrial, and commercial purposes. About 97% of atmospheric water is saline and the available freshwater is inadequate to fulfill the needs of the growing world population [1]. Due to high growth rate, the demand and consumption of freshwater in the world increased six fold between 1900 and 1995. At present, approximately one-third of the world's people live in countries with moderate to high water stress. Additionally, many parts of the world are facing a water scarcity problem due to limitation of water resources coinciding with growing population [2].

The World Health Organization (WHO) and UNICEF reports for 2012 ranked Nigeria as the third country, after China and India, with the largest population without adequate water and sanitation conditions [3]. Reports have also shown that human health and environmental quality are undergoing degradation due to growth in population and rapid expansion of cities, which have resulted in generation of huge waste and indiscriminate waste disposal. This constitutes serious health and environmental problems. Sadly, land filling is the most widely used method for the disposal of municipal solid waste, accounting for approximately 95% of the total waste collected worldwide [4].

Wastes are complex in nature, depending on the sources and its environmental fate once it is generated. In the developed world, domestic sewage, industrial and agricultural wastes are treated at sewage central works to reduce its toxicity and subsequently discharged into rivers and streams. However, this is not the case in Nigeria [5]. Industrial and open dump of solid wastes disposal in the cities are some of the most significant sources of pollution [6,7,8]. Agriculture, as one of the backbones of any economy, has been greatly affected by upsurge in the indiscriminate dumping and disposal of wastes into land and water bodies. This has reduced the quality and quantity of both surface and underground water sources that are needed for general and agricultural demands during insufficient rainfall [9]. The challenge is critical as women and children travel long distances to fetch water from rivers, streams and ponds that are often contaminated.

When in contact with water, municipal solid waste dumpsites will generate leachate. The principal concern regarding leachate is related to the pollution of nearby surface water by uncontrolled leachate migration [109] and infiltration into groundwater aquifers. Leachate consists of many different dissolved or suspended organic and inorganic compounds that could cause more potential groundwater and surface water pollution, as well as public health hazards. Leachate was not considered a matter of concern until recently, when several water pollution studies linked the negative impact of leachate on physical, chemical, and biological properties of receiving water bodies [10,9,11]. Therefore, a risk assessment of daily human exposure is important. This involves the characterization of physical settings, identification of potential exposure populations and pathways as well as estimating the exposure concentrations and chemical intakes. Studies on possible human health related risk through the intake of both surface and groundwater have been reported [13-15].

This study is important in Federal Capital Territory (FCT) of Nigeria due to the rapid and continuous increase in population. According to the Master Plan, FCT was developed to include 2.0% area for government activity/usage, 32.5% as open/green/recreational areas, 49.0% for residential development and the remaining land (16.5%) is to be used for ancillary services. In 2001, the population of the Federal Capital, Abuja, increased from 378,671 (1991) to 1,724,205 people. Rapid increase in population exceeded the threshold in the Master Plan, which has now made Abuja in dire need of alternative water sources. Unfortunately, the population forecasted for Abuja region will increase to 5.8 million people by the year 2026. Currently, the demand for good quality water has increased the drilling of boreholes and the use of surface water in several residential and industrial areas as a complementary source of water supply.

The Ndawuse river is one of the rivers at Phase 1, District of the FCT, Abuja, Nigeria that could be used for domestic purposes. The Ndawuse river flows from Aso-buari route through Mpape dumpsite that has recently been evacuated. The water quality of this river is suspected to be deteriorating day by day due to anthropogenic input of dissolved nutrients and organic matter built up on its bank. Studies on pollution, human exposure pathways due to heavy metals and other related pollutants have been performed and reported in literature [13,14]. However, the effect the Mpape dumpsite has on the quality of surface water around it is yet to be investigated. Therefore, it is of vital importance to (1) monitor and simulate the water quality parameters of the river in order to ascertain whether the water is still suitable for domestic use; and (2) to assess the potential human exposure risk. The present study is aimed at investigating the effect of pollutant load from the Mpape dumpsite on the quality of surface water in FCT, with River Ndawuse as a case study over a period of time and the potential exposure risk to human beings. This is the first study to present water quality of Ndawuse River in connection with the impact of leachate from Mpape dumpsite as well as an assessment of health related risks to residents that depend on this river for domestic purposes.

2 Materials and Methods

2.1 Description of study area

The study area under investigation is Phase 1, Abuja, Federal Capital Territory, which lies between latitudes 90 10’_ 90 25’ North of the equator and Longitudes 70 10’ -70 20’ East of the Greenwich within the Gwagwa plain (Figure 1). Phase 1 is divided into five districts namely Wuse, Asokoro, Maitama, Central area and Garki District. It has an area of 250 square km that constitutes three percent of the FCT total land covered area [16].

2.2 Sampling and analysis

The drainage pathways from the dumpsite to surface water bodies were identified and surface water samples from five different points were taken along the River Ndawuse from the upstream and downstream of the river that runs adjacent to the Mpape dumpsite. Samples taken downstream represent the water quality condition after the mixing of leachate from the dumpsite with the stream. Finally, leachate from the dumpsite was taken through the

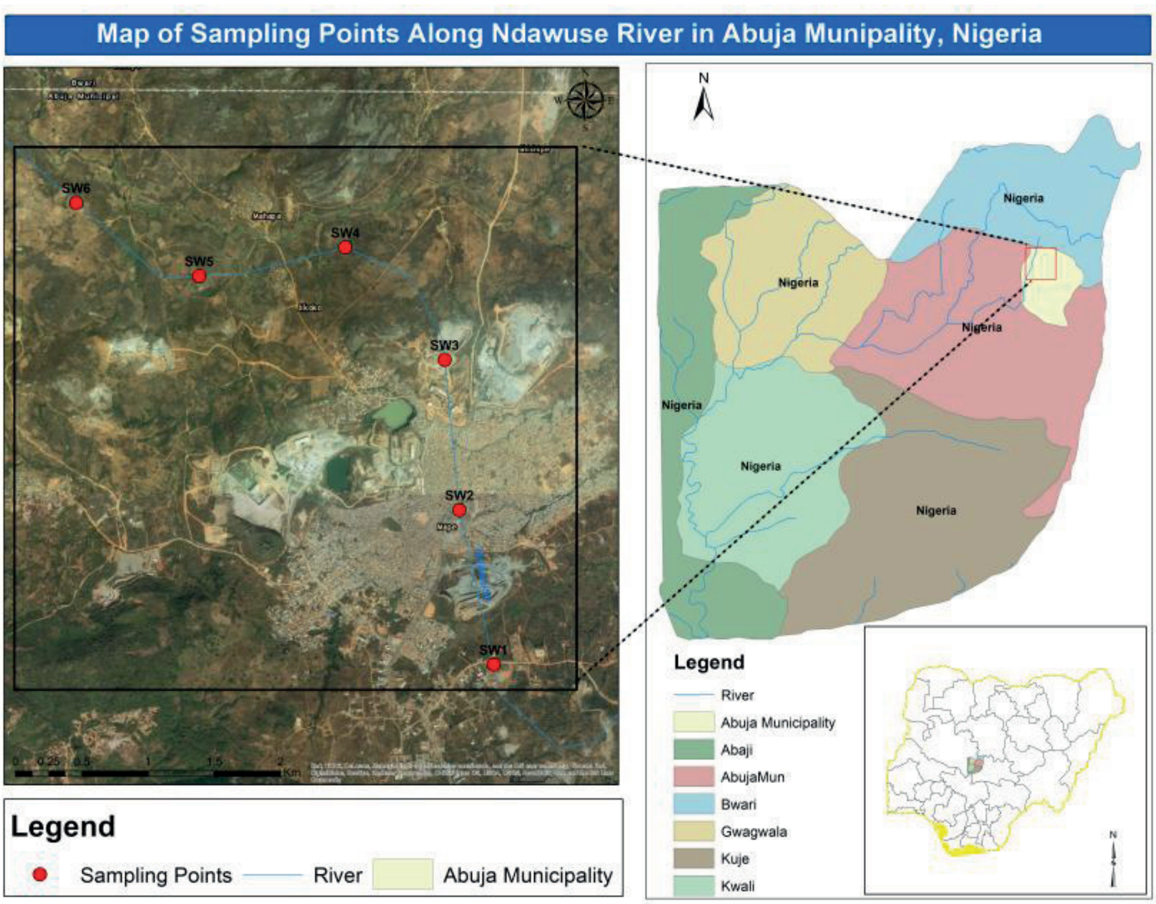

Figure 1: Map showing the sampling points along Ndawuse River in Abuja, the Federal Capital Territory (FCT), Nigeria.

drainage for analysis. The sampling locations were evenly demarcated on accessibility to the river, then labelled SW1, SW2 (Mpape dumpsite), SW3, SW4, SW5 and SW6 along River Ndawuse and at Mpape dumpsite (Table 1). The sample taken upstream of the dumpsite served as the control for all the analyses.

All sampling bottles were washed with acid and rinsed with deionized water. Bottles were later rinsed three times with surface water samples before collection. Triplicate samples were collected from each of the six sampling locations in 500 ml sterile bottles. The actual samplings were done midstream and the sampling bottles were labeled with dates and collection locations and transported to the laboratory at 4°C for analysis. A total number of 36 surface water samples were collected between March and August at the peak of rainy season. Samples were divided into two for physico-chemical and heavy metals analysis.

Temperature, pH and electrical conductivity (μS/cm) were measured *in*-situ during sampling using portable pH/conductivity meter (Model: Mettler Toledo MP 220, England). A microprocessor turbidity meter (NTU) (Model: HANNA, HI98703) was used for turbidity determination and total dissolved solid (TDS) was determined using the portable TDS meter. Biological oxygen demand (BOD) was measured after 5 days using DO Meter and chemical oxygen demand (COD) according to standard methods [17]. All equipment was calibrated according to the manufacturers' guidelines before use. Analysis of anions, nitrate-nitrogen

Table 1: Sample locations and codes used to denote the sampled sites.

Sample Code	Sampling Location	Distance from Landfill Site (km)
SW1	Upstream	1.2 km upward
SW2	Dumpsite	Mpape dumpsite
SW3	Downstream	1.2 km downward
SW4	Downstream	2.4 km
SW5	Downstream	3.6 km
SW6	Downstream	4.8 km

(NO_3-N), sulphate (SO_4^{2-}) phosphate (PO_4^{3-}) and chloride (Cl^-) in the collected surface water samples was conducted using a Thermo Gallery photometric analyser (Thermo Scientific, UK) according to standard methods for examination of water [17]. All chemicals used in the study were of analytical-reagent grade unless otherwise stated. Ultra-pure 6 M HNO_3 (2 mL/L; 65%, ultrapure grade) was added to acidify water samples to pH 1.5 and stored at 4°C for heavy metals analysis using inductively coupled plasma mass spectrometry (ICP-MS; Perkin-Elmer Sciex ELAN 6000, Canada). Good precision and reliability of the instrument was checked by frequent analysis of standards and blanks. All samples were analysed in triplicate and the means and standard deviations were determined.

2.3 Quantitative risk assessment analysis

Risk analysis considered the impact of the dumpsite on downstream sample measurements as compared with the upstream values. This observation was employed to assess the risk activities that are likely to contaminate surface water from the river or nearby catchments. Daily human exposure risk pathways of an individual to trace metals contamination could be through three main pathways including inhalation via nose and mouth, direct ingestion and dermal adsorption through skin exposure. The common exposure pathway to water is through ingestion pathway and this has been described in the literature [18-22]. In this study, human exposure risks (Exp_{ing}) through the intake of heavy metals were calculated separately for adults, children and infants (0 ≤ 2 months) because, water intake and exposure differs among different age groups. Equation 1 was used to calculate Exp_{ing} as adapted from the US EPA risk assessment Guidance for superfund (RAGS) methodology [19,20].

$$Exp_{ing} = \frac{C_{water} \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

where Exp_{ing}: exposure dose through ingestion of water (mg/kg/day); C_{water}: average concentration of the estimated metals in water (mg/L); IR: ingestion rate in this study (3 L/day for adults; 1.5 L/day for children and 250 mL/day for infant); EF: is exposure frequency (365 days/year); ED: exposure duration (70 years for adults; 6 years for children and 2 years for infants); BW: average body weight (60.7 kg for adults; 20 kg for children and 6 kg for infants); AT: averaging time (365 days/year x 70 years for an adult; 365 days/year x 6 years for a child and 365 days/year x 2 years for infant) [23,19,20,22].

Potential non-carcinogenic risks due to exposure to heavy metals were determined by comparing the calculated contaminant exposure with the reference dose (RfD) [19]. Equation 2 was used to estimate the hazard quotient (HQ) toxicity in order to determine the non-carcinogenic potential risks of an individual via the ingestion pathways.

$$HQ_{ing} = \frac{Exp_{ing}}{RfD_{ing}} \quad (2)$$

where RfD_{ing} is ingestion toxicity reference dose (mg/kg/day) and the values for the selected metals were obtained from the literature [22,19,23,20,2]. An HQ under 1 is assumed to be safe and taken as significant non-carcinogenic, but HQ value above 1 may be a major concern for potential health risks in association with over exposure of humans to the contaminants.

To assess the overall potential for non-carcinogenic effects posed by more than one metal through the pathway, the sum of the computed HQs across metals is expressed as a hazard index (HI) using equation 3 [19]. HI > 1 showed that exposure to the surface water could have a potential adverse effect on human health [22,25].

$$HI = \sum_{i=1}^{n} HQ_{ing} \quad (3)$$

In this study, the health risk associated with heavy metals in the daily intake of surface water from the Ndawuse River was ascertained by calculating the daily exposure dose using the modified equation of the United States Environmental Protection Agency [19] as mentioned by Elumalai et al. [13] in equation 4.

$$HE_{SW} = C_{water} \times \frac{IR}{BW} \quad (4)$$

where HE_{SW} is the daily human exposure dose through surface water (mg/kg/day), C is the concentration of heavy metals in the exposed surface water (mg/L), IR is the ingestion rate (L/day) and BW is the body weight (kg). $HE_{SW} < 1$ is considered safe for human health.

The carcinogenic risk (CR) associated with the ingestion pathway was estimated using equation 5:

$$CR_{ing} = \frac{Exp_{ing}}{SF_{ing}} \quad (5)$$

where CR_{ing} is the carcinogenic risk via ingestion route and SF_{ing} is the carcinogenic slope factor for Pb is 8.5×10^1, Cd is 6.1×10^3 and Cr is 5.0×10^2 μg/kg/day [25,20,24]. The CR_{ing} values for other metals were not calculated due to unavailability of the SF_{ing} values.

Table 2: Guidelines for drinking water quality by WHO and FEPA.

Parameter	WHO Values	FEPA
Temperature (˚C)	40	≤ 25
pH	6.5– 8.5	6-9
Electrical conductivity (µS/cm)	400	NIL
Turbidity (NTU)	-	1
PO_4	<6	5
SO_4	250 (>400 not permissible)	250
Cl	250	250
NO_3	50	20
TDS	500	500
COD	100	80
BOD_5 @ 20˚C	30	30
Fe	0.1	0.1
Mn	0.1	0.3
Cu	2.0	1
Zn	0.01	-
Pb	0.01	-
Cd	0.003 (>0.01 not permissible)	-
As	0.01 (0.05 not permissible)	-
Cr	0.05	-

Source: WHO [27] and Federal Environmental Protection Agency [26].
* pH has no unit and all parameters are in mg/L unless otherwise stated.

2.4 Statistical Analysis

GraphPad Prism version 5.0 for Windows (GraphPad Software, San Diego California, USA) was used for both statistical analysis at 95% confidence limit and the graphs. Mean values of the parameters obtained for the various locations were compared with the various permissible limits of the parameters set by WHO and FEPA in order to identify areas of problems in quality of drinking water from Ndawuse river (Table 2) [26,27]. Multivariate statistics, in terms of principal component analysis (PCA) and hierarchical agglomerative analysis (HAC), were performed using XLSTART statistical software [28]. The PCA was used to established the major variation and relationships among the different metals. Pearson correlation was calculated for different metals in the water samples and significant principal components (PC) was selected based on the varimax orthogonal rotation with Kaiser normalization at eigenvalues greater than one. The HAC was performed using Ward's method for linkages [29] and square Euclidean distance was used to identify

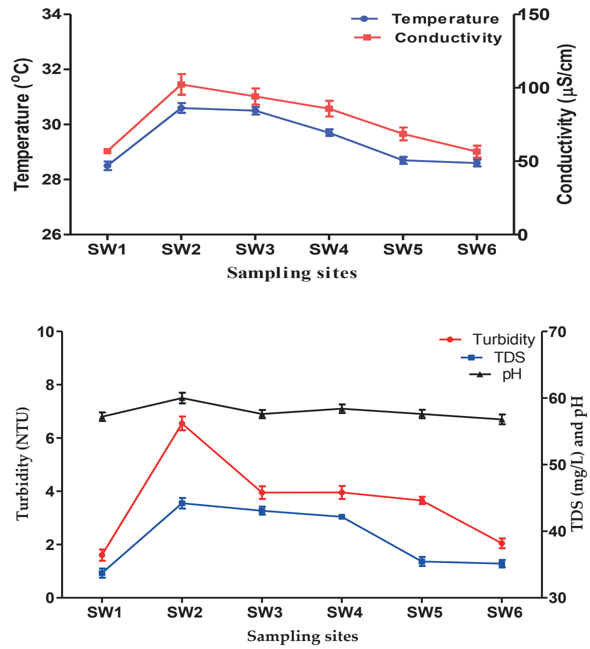

Figure 2: Temperature and Conductivity, pH, turbidity an TDS values for leachates from Mpape dumpsite and different surface water samples collected along Ndawuse River.

groups that shows similar characteristics or variables. Dendrogram was used to provide a visual summary of the results based on dimensionality of the original data [25].

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

3 Results and Discussion

3.1 Characteristics of leachate and surface water samples

The temperature during the study period showed little difference across the sampled sites. Figure 2a shows the recorded average temperature of the surface water samples obtained during the study. The recorded values ranged between 28.51˚C to 30.62˚C with no significant differences among the different locations (Figure 2a). A maximum temperature of 30.62˚C was recorded for leachate obtained at Mpape dumpsite and the minimum temperature of 28.51˚C was obtained for the upstream sample (SW1). The temperature is above the recommended limit of 25°C for domestic water quality set by FEPA, but is below 40°C set by WHO. Temperature of water has an impact on the acceptability of some other inorganic constituents and chemical contaminants and this may affect the taste of surface water [12]. Temperature also affects the conductivity of water, with warmer waters having higher values of conductivity as compared to cold water [30].

Electrical conductivity (EC) is a useful indicator of mineralization and salinity or total salt in a water sample. Reduction of conductivity in the area studied might be due to fresh water input from rain or the uptake of ions by organisms for their metabolism. The average conductivity measured at the upstream sampling point of the Ndawuse River was lower than the values recorded at the other sampling points (downstream) as shown in Figure 2a. The dumpsite had more net leaching effect on the surface water downstream along Ndawuse River as shown in the measured conductivity value of Mpape dumpsite (102.31 ± 7.01 µS/cm) and those of subsequent downstream sites when compared to the upstream value of 56.92 ± 1.13µS/cm (Figure 2a). It is also possible that lower conductivity is observed due to organic detritus, weed growth and biomass degradation in the benthic layer. In many cases, high EC indicates low water quality as EC of water is an indirect measurement of its dissolved chemical constituents. Electrical conductivity is therefore another method for measuring the dissolved ions in the samples and this is often used as a surrogate for TDS, since the EC of water is a function of the number of charged ions in a solution [31].

There was a significant difference ($p < 0.05$) in TDS among the different sites with the highest value of 3.55 ± 0.19 mg/L recorded at the dumping site, while the upstream sample, SW1, had the lowest value of 0.93 ± 0.17 mg/L (Figure 2b). The present study shows that the average recorded value of TDS is 2.24 ± 0.17 mg/L, which is below the permissible limit of 500 mg/L set by both WHO and FEPA for drinking water. The values of TDS generally decreased downstream from the dumping site. This may be attributed to the fact that the ions in the leachate are absorbed on the surface of suspended sediments along the river. The TDS could be used as an indication of aesthetic characteristics of drinking water and the presence of a broad array of chemical pollutants. It naturally gets into the surface water from weathering and dissolution of rocks, soils or through the primary sources such as agricultural runoff, residential runoff and leaching of soil contamination [32].

Figure 2(b) shows the results of turbidity of water samples taken from the sampling points. The values ranged between 36.42 and 56.19 NTU with a mean value of 44.51 ± 3.46 NTU. Generally, the lowest turbidity value (36.42 ± 1.31 NTU) was recorded at the source of the Ndawuse River catchment, SW1. However, as it flows along the course of the river and through the dumpsite that had the highest value (56.19 ± 3.52 NTU), it deposits debris, sediments and particles from the dumpsite towards the downstream of the river (Figure 2b). Based on this, it is evident that the turbidity of these sampling points along the investigated river is negatively influenced by the dumpsite. The turbidity of the surface water samples obtained is above standard limits (5 NTU and 1 NTU) by WHO [27] and FEPA [26] guidelines, respectively, for domestic water usage. These values made this receiving water body to be unfit for domestic purposes.

High or low pH values have been reported to influence aquatic life [33,34]. The pH of the surface water samples varied from 6.7 to 7.5 with a mean pH of 6.98. The highest pH (7.5) was recorded at the Mpape dumpsite (SW2), when compared with other samples obtained from the upstream and downstream of River Ndawuse. Leaching of Mpape dumpsite leachate could have contributed to increase in pH of surface water at the downstream when compared with the pH value of the water sample obtained from the upstream of River Ndawuse. pH values are within the acceptable limits of 6.5-8.5 and 6-9 set by both WHO and FEPA, respectively. This indicates that the pH values of water from the river could still support aquatic life. Healthy fish could still survive with pH of 6.7-8.6. Only a few fish can tolerate acidic pH of less than 5.0 or alkaline pH of greater than 9.0 [35].

The estimation of COD is of great importance for water having unfavourable conditions for the growth of microorganisms, such as the presence of toxic chemicals and oxidisable pollutants. BOD_5 is found to be more sensitive test for organic pollution and oxygen demand of biodegradable pollutants. The mean values of 106.96 ± 9.65 mg/L and 85.88 ± 3.27 mg/L were recorded for COD and BOD_5, respectively (Figure 3). The highest concentration for both parameters were measured at SW2 (dumpsite) and decreased downstream of the discharge points. These concentrations were above the safety limits set by WHO and FEPA for domestic water usage (Table 2). This is comparable to the work of Maiti et al. [36] who recorded high COD and BOD_5 concentrations in the leachate samples analysed in their study.

There was a significant difference in BOD_5 concentration and the results further showed the level of oxygen-depletion due to pollutant load in the water samples. The water samples had excessive organic matter that could not be self-purified, which caused a rapid decrease in DO concentrations at the sampling sites. This condition is an indication of a very poor aeration system and could cause damaging effect on the health of both human and animals, if the surrounding surface water are to be used for domestic purposes. Subsequently, it will

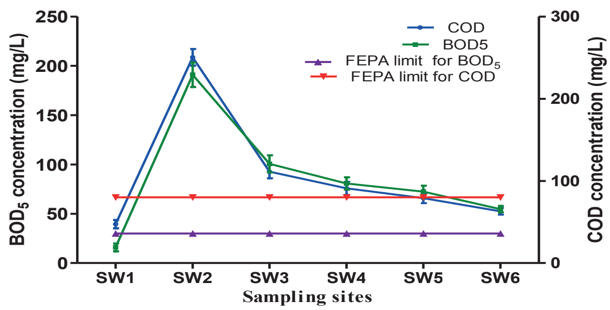

Figure 3: The BOD_5 and COD concentrations of leachate and sampled surface water in this study as compared to the standard limits set by FEPA.

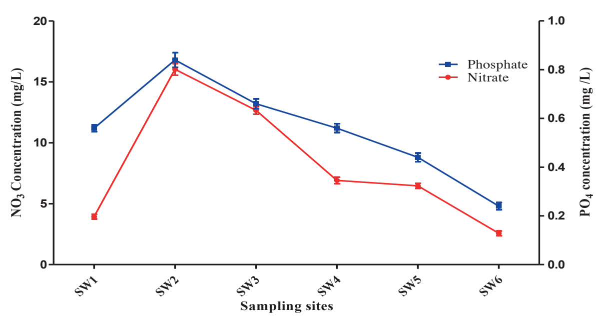

Figure 4: Nitrate and phosphate concentrations of surface water and leachate samples.

have negative effects on aquatic life especially reduction of fish diversity at the downstream [34]. According to Ogunfowokan et al. [37], increase in COD could be attributed to an increase in both organic and inorganic substances from the environment, as well as organic contaminants entering the systems from the municipal sewage.

3.2 Nutrients

The mean concentration of nitrate-nitrogen (NO_3-N) ranged between 0.58 ± 0.01 - 3.62 ± 0.04 mg/L with the mean value of 2.12 ± 0.01 mg/L. The concentration obtained for NO_3-N was converted to nitrate as shown in Figure 4 with nitrate ions (NO_3^-) ranging from 2.57 ± 0.19 to 16.03 ± 0.49 mg/L with the mean value of 8.09 ± 0.28 mg/L. This implies that it does not pose significant health risk since none of the water samples analysed is up to the standard limit (Table 2). The concentration of phosphate ranged from 0.24-0.84 mg/L with the mean of 0.53 ± 0.04 mg/L. The range and the mean values were below the stipulated limit of 5 mg/L for FEPA and < 6 mg/L for WHO for drinking water. Considering the WHO drinking water quality guidelines, all the measured nutrient elements were low, suggesting low level of nitrate-nitrogen and phosphate from the dumpsite to the surface water. If unpolluted natural water contains only minute amounts of nitrate, it is considered suitable concentration for the growth of aquatic ecosystem without posing any negative impact on human health [39,35]. Nitrate is the most highly oxidised form of nitrogen compounds that is commonly present in surface and groundwater, because it is the end product of aerobic decomposition of organic nitrogenous matter. Although nitrate and phosphate concentrations at the dumpsite are below standard limits, they are still slightly high compared to other samples. The relatively high concentrations at the dumpsite could result in leaching of nitrate and phosphate fertilizers into the river, thus causing eutrophication.

3.3 Major ions

The average concentration of measured sulphate during the study period range from 29.60 ± 0.41 mg/L to 45.10 ± 0.61 mg/L (Figure 5) with a mean value in the sampled water of 37.23 ± 0.52 mg/L. These are below the permissible range limits of 250 - 400 mg/L and 250 mg/L given by the WHO and FEPA, respectively (Table 2). All the samples have SO_4 and Cl^- values below the standard limits of 250 mg/L set by both WHO and FEPA for drinking and irrigation water (Figure 5). The recorded chloride concentrations range between 5.53-12.56 mg/L across the sampling sites for surface water and dumpsite as shown in Figure 5. The mean value of chloride was 9.05 ± 0.04 mg/L. The highest value is found at the SW1 (upstream), while the lowest value was recorded for SW2 (dumpsite) as compared to other sites. The concentration increased downstream from the dumpsite, though all the samples analysed had chloride values below the standard limit. Low concentration of chlorine promotes the growth of pathogenic organisms in the surface water, which could pose major health related problems. As observed in this study, Figure 5 shows that the sulphate concentration is indirectly proportional to chloride. As the water gets more polluted, the sulphate increases, while chloride reduces (Figure 5). The high chloride concentration justifies the range of COD concentration in the studied area, similar to the findings of Maiti et al. [36]. Generally, higher concentrations of all the measured parameters were observed downstream than upstream of the dumpsite along the river due to leaching of leachate from the dumpsite. The leachate could be one of the contributing factors to high concentrations of pollutants that was recorded at the downstream.

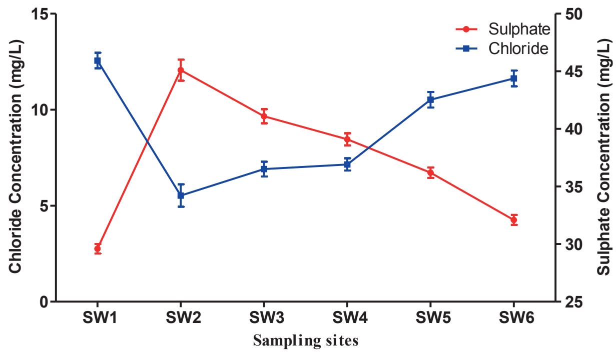

Figure 5: Indirect relationship between the measured sulphate and chloride concentrations in the surface water and leachate samples collected from Ndawuse River and dumpsite.

3.4 Concentration of heavy metals in the leachate and surface water samples

Chromium (Cr) concentrations at the different sampling sites were between 0.078 ± 0.001 mg/L and 0.140 ± 0.001 mg/L (Figure 6a) with an average concentration of 0.098 ± 0.002 mg/L. This shows that the Cr level is above the safety limit of 0.052 ± 0.001 mg/L set by the WHO (Table 2). Chromium concentration was higher at the confluence point, SW2 (0.135 ± 0.021 mg/L) and decreased downstream throughout the sampling points from 0.077 ± 0.005 mg/L (SW1) to 0.082 ± 0.003 mg/L (SW6). The range of iron (Fe) concentration was 0.014 ± 0.001 mg/L to 3.511 ± 0.191 mg/L with an average of 1.203 ± 0.383 mg/L, which means that Fe concentration for the sampled water is above the threshold limit of 0.1 mg/L set by both WHO and FEPA. There was a significant difference in the mean concentration of Fe in all the sampled sites at $p < 0.05$. The Fe concentration at the dumpsite greatly increased (3.511 ± 0.214 mg/L) when compared with the measured concentration (0.014 ± 0.013 mg/L) at the upstream of the river. The result showed that there was a decrease of Fe from the dumpsite downstream (Figure 6a) indicating the dumpsite to be the major contributor of Fe. The surface water from the river may be considered unsafe with respect to Cr and Fe content [30].

The ranges of Lead and Zinc concentrations were 0.133 ± 0.006 to 0.303 ± 0.018 mg/L and 0.165 ± 0.009 to 0.262 ± 0.013mg/L (Figure 6b) with means of 0.206 ± 0.041 mg/L and 0.194 ± 0.021 mg/L, respectively. In the study area, all the samples in the six sampling locations have values above the safety limit of 0.01 mg/L set by WHO for drinking water (Table 2). In this regard, it can be said that the water samples analysed were polluted with both Pb and Zn, which could be as a result of heavy metals

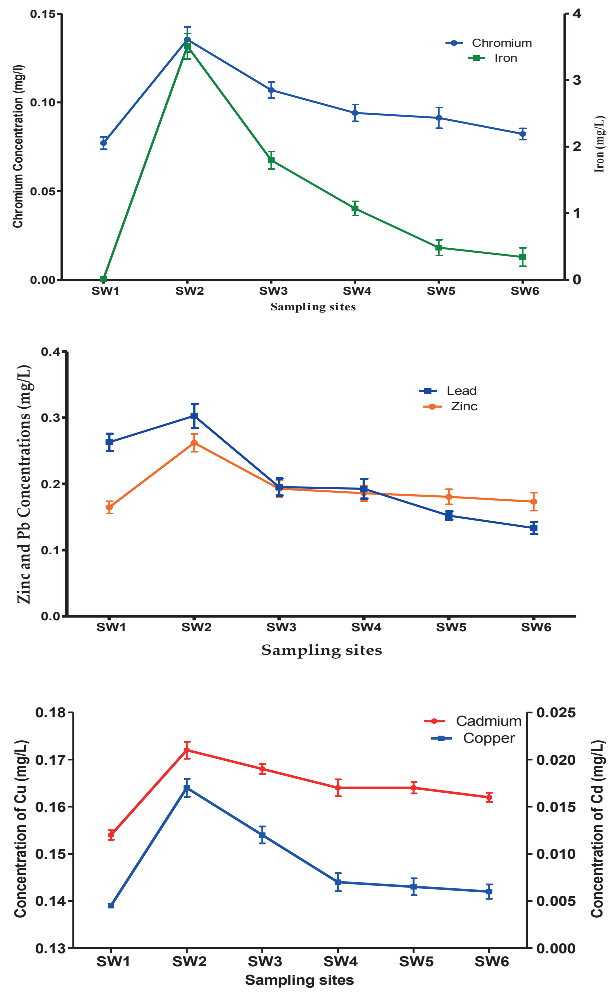

Figure 6: Average concentrations of (a) Chromium and Iron (b) Lead and Zinc (c) Cadmium and Copper in the leachate and surface water samples taken at the different sampling sites along Ndawuse River during the study period.

concentrations at the investigated dumpsite (Pb = 0.303 ± 0.021 mg/L and Zn = 0.262 ± 0.007 mg/L) as compared to the concentrations recorded at the upstream of the river SW1 (Pb = 0.263 ± 0.005 mg/L and Zn = 0.165 ± 0.006 mg/L) and downstream, SW6 (Pb = 0.133 ± 0.007 mg/L and Zn = 0.173 ± 0.004 mg/L). There was a significant difference in the measured concentrations ($p < 0.05$) for both parameters. This is comparable to the study of Maiti et al. [36] where the authors reported high concentration of Pb in leachate obtained from a closed dumpsite at Dhapa (Kolkata, West Bengal, India) and its negative effect on the receiving environment especially surface and groundwater quality. Dervišević et al. [30] also recorded high concentration of Zn in the leachate obtained from illegal landfill in Grabovac.

Arsenic concentrations at the different sampling points ranged between 0.003 ± 0.00 - 0.009 ± 0.0001 mg/L with a mean value of 0.005 ± 0.001 mg/L. There was negligible detection of As at the upstream (SW1), this shows that the dumpsite (SW2) where the highest concentration was recorded had a negative influence on the Ndawuse River as shown in the measured concentrations for SW3 up to SW6. The results indicate that there is migration of leachate and heavy metals into the river. However, the concentration of As is still below the WHO acceptable limit of 0.01 and < 0.05 mg/L (Table 2). The dumpsite contributed significantly to the concentrations of Mn and As in the downstream locations of the river. Furthermore, the range of manganese concentration of 0.215 ± 0.074 mg/L to 1.478 ± 0.153 mg/L with the mean value of 0.782 ± 0.045 mg/L is above the acceptable limits of 0.1 mg/L and 0.3 mg/L for WHO and FEPA guidelines, respectively (Table 2). There was a significant difference in the mean concentration of Mn between the dumpsite and other sampling sites ($p < 0.05$). The Mn concentration of the dumpsite (1.478 ± 0.152 mg/L) is five times the concentration of Mn recorded at the upstream (0.251 ± 0.001 mg/L) (Figure 6c).

The range of Cu concentrations was 0.139 – 0.164 mg/L (Figure 6c) with an average of 0.149 ± 0.032 mg/L. These are below the standard limit sets (2 mg/L and 1 mg/L) for drinking water by WHO and FEPA, respectively. There was a significant difference in the concentration of Cu between the leachate and the collected surface water. The range of Cd concentrations was 0.012 ± 0.001 mg/L to 0.021 ± 0.001 mg/L with an average of 0.017 ± 0.005 mg/L. These concentrations are above the acceptable limit of between 0.003 and 0.001 mg/L by WHO guideline (Table 2). Lower Cd concentration was recorded at the upstream (SW1), while the highest value of 0.021 ± 0.001 mg/L was measured at the dumpsite (SW2). The concentration gradually decreased down the sampling sites throughout the study period, similar to the results reported by Dervišević et al. [30]. Cadmium is one of the most unwanted metals in human body systems. Elevated concentrations of Cd could cause nausea, vomiting, salivation and renal failure as well as kidney, liver and blood damages [40]. Singh and Mosley [41] suggested that high concentrations of Cd may even cause mutations. Therefore, high concentrations of these metals in the surface water due to leaching of leachate poses a public health risk, if not addressed.

3.5 Correlation and multivariate principal component analysis

Inter-relationship between all metals in the water samples was determined using Pearson correlation analysis. High positive correlations with r values > 0.8 showed significant relationship between pairs of different metals except Pb, which has moderate correlation. The variation matrix showed strong association of metals, indicating that the dumpsite is the source of heavy metal pollution. Multivariate principal component analysis employed to depict the relationship between measured heavy metals generated two significant principal components (PCs) with total variance of 97.64% (Table 3). PC1 accounted for 86.33% of the variance with eigenvalue of > 6 and PC2 of 11.32% (eigenvalue > 0.9). Factor loading ranged from 0.896 to 0.998 for PC1 for all the metals except Pb with moderate PC loading of 0.598. This suggests that the origin of Pb is slightly different from other metals, as observed in the correlation and risk analysis. The dendrogram generated using hierarchical cluster analysis (HCA) detected similarities and differences amongst metals with two clusters (Figure 7). Cluster 1 has Cd, Zn, Pb, Cr and Cu, while Fe and Mn formed cluster 2. Arsenic (As) was alone without clustering with other metals, perhaps as a result of low concentration of measured As in the surface water and at the dumpsite.

Table 3: Principal component loadings of selected metals in surface water investigated at Ndawuse river and the dumpsite with eigenvalues.

Component matrix	Rotated Component matrix	
	PC1	PC2
Chromium	0.998	-0.007
Iron	0.997	0.034
zinc	0.963	0.116
Lead	0.578	0.813
Arsenic	0.972	-0.127
Manganese	0.973	-0.130
Cadmium	0.896	-0.442
Copper	0.982	0.037
Eigenvalue	6.906	0.905
Variability (%)	86.325	11.316
Cumulative %	86.325	97.641

3.6 Human health risk assessment

The water quality was found not to comply with the safety standards set by the WHO and FEPA for drinking water, there was a significant difference in the turbidity, BOD_5, Fe, Zn, Cd, Mn, Cr and Pb concentrations. In this study, the results showed that the water samples taken from the different locations along the river were unsafe for human consumption, in terms of metals concentrations due to

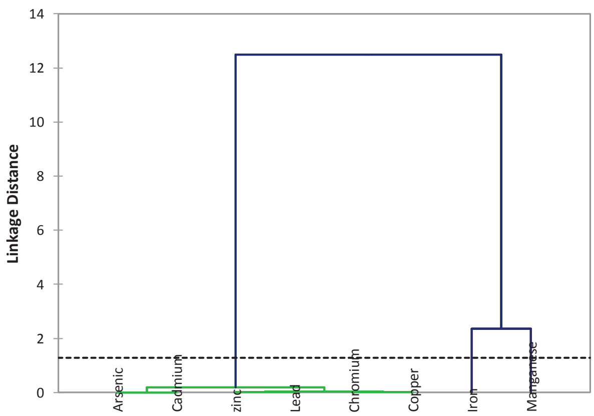

Figure 7: Dendrogram showing cluster analysis of heavy metals in the surface water samples from Ndawuse River based on the hierarchical cluster analysis.

the impact of leachate from the dumpsite. In this study, Cr was found in abundance above the acceptable limit for drinking water. Chromium toxicity is frequently the result of long term and low level exposure to pollutants in the environment: air, water, food and numerous consumer products. Exposure to chromium is associated with many chronic diseases such as dermatitis, kidney damage, chronic ulceration and perforation of the nasal septum, respiratory illness, nasal cancer, asthma and other skin surfaces [43]. Most significantly, Cr^{6+} has been reported for its carcinogenic effect when overly exposed to humans [44].

The upstream sampled value for Fe was observed to be lower than the recommended value set by WHO/FEPA, but there was a decrease of Fe from the dumpsite to downstream. This is in agreement with the report of Hossain et al. [45]. This may have positive impact and unpleasant ferrous smell to the water as well as bittersweet taste. Human beings could absorb this metal when consumed through drinking, food or air. It is important to indicate that iron is one of the essential elements for human metabolism. Long-term exposure could lead to biotoxic effects due to accumulation of heavy metals above the recommended levels thereby leading to degenerating disease conditions [46]. Therefore, appropriate concentration is required and this could not be achieved due to the effect of leachates from the dumpsite. Research has shown that iron is the second most abundant metal on the earth‘s crust, of which it accounts for about 5%. Elemental iron is rarely found in nature, as the ferrous ion Fe^{2+} and ferric ion Fe^{3+} readily combine with oxygen and sulfur containing compounds to form oxides, hydroxides, carbonates and sulfides. Iron (as Fe^{2+}) concentrations of 40 μg/L can be detected by taste in distilled water [12]. Aeration of iron-containing layers in the soil can affect the quality of both groundwater and surface water if the groundwater table is lowered or nitrate leaching takes place. Dissolution of iron can occur due to oxidation and decrease in pH.

On the other hand, Pb is the most notable of all unwanted metals in human body. Adverse health effects of high level of Pb include cancer, interference with Vitamin D metabolism, toxicity to the central and peripheral nervous systems, adverse reproductive outcomes, as well as adverse mental development in infants [42]. Similar investigation on higher concentration of Pb above the WHO recommended limit for domestic uses has been reported by some authors [12]. Research has shown that the main adverse health effects of As are laryngitis, tracheae bronchitis, pharyngitis, shortness of breath and nasal congestions [47]. Copper is an essential nutrient, but at high doses it has been shown to cause stomach and intestinal distress, liver and kidney damage and anaemia [48,49]. However, Cu is below the limit for drinking water as compared to other measured metals. Hence, high concentrations of Cr, Cd, Pb, As and Fe is a serious concern as it renders the water unsuitable and unsafe for human consumption in terms of heavy metals toxicity according to standard limits for water quality set by FAO/WHO and it should not be used for domestic and recreational purposes [50]. Oluwande et al. [51] and Uyom et al. [12] reported high concentrations of some heavy metals in Nigerian rivers. High level of metals has been a serious problem in the environment due to toxicity in most aquatic biota in the last few decades.

In addition to the magnitude of heavy metals contamination in surface water due to leaching from the dumpsite, the average estimated human health risk index through the intake of heavy metals were calculated separately for adults, children and infants due to different water intake or exposure rate among different age groups. Table 4 shows the results of Exp_{ing} HQ_{ing}, HI and CR_{ing} of heavy metals for adults, children and infants through ingestion pathway. The average exposure pathway for children has the highest levels of risk for all the sampling sites with the lowest estimated values for infants. The HQ_{ing} for all ages through the aforementioned pathway were less than one unity (Table 4), indicating little or no health risk is posed by ingesting the surface water by an individual. The HQ_{ing} decreased in the order of Pb > Cd > Cr/Mn > As > Zn > Cu > Fe for adults, Cr > Pb > Cd > Mn > As > Zn > Cu > Fe for children while, infants decreased in the order; Pb > Cd > Cr/Mn > As > Zn > Cu > Fe. The main contributors to non-carcinogenic health risks in this investigation were Pb, Mn, Cr and Cd. Lead is the

Table 4: Potential non-carcinogenic risks assessment of all heavy metals and carcinogenic risk values (CR_{ing}) of Cr, Pb and Cd for adults, children and infants in consuming surface water around Ndawuse River through ingestion pathway.

Metals	RfD_{ing} (µg/kg/day)	Adults EXP_{ing}	HQ	H1	CR_{ing}	Children EXP_{ing}	HQ	HI	CR_{ing}	Infants EXP_{ing}	HQ	HI	CR_{ing}
Cr	3	4.84×10^{-3}	1.61×10^{-3}	9.67×10^{-3}	9.67×10^{-6}	7.34×10^{-3}	$^{a}1.87 \times 10^{-1}$	3.01×10^{-1a}	1.47×10^{-5}	2.01×10^{-4}	6.71×10^{-5}	4.03×10^{-4}	4.03×10^{-7}
Fe	700	5.95×10^{-2}	8.50×10^{-5}	5.10×10^{-4}	ND	9.03×10^{-3}	1.29×10^{-4}	7.74×10^{-4}	ND	2.48×10^{-3}	3.54×10^{-6}	2.12×10^{-5}	ND
Zn	30	9.55×10^{-3}	3.18×10^{-4}	1.91×10^{-3}	ND	1.45×10^{-2}	4.83×10^{-4}	2.90×10^{-3}	ND	3.98×10^{-4}	1.33×10^{-5}	7.96×10^{-5}	ND
Pb	1.4	1.02×10^{-2}	7.29×10^{-3}	4.38×10^{-2}	$^{b}1.20 \times 10^{-3}$	1.55×10^{-2}	1.11×10^{-2}	6.64×10^{-2}	$^{b}1.82 \times 10^{-3}$	4.25×10^{-4}	3.04×10^{-4}	1.82×10^{-3}	$^{b}5.00 \times 10^{-5}$
As	0.3	1.84×10^{-4}	6.14×10^{-4}	3.69×10^{-3}	ND	2.80×10^{-4}	9.33×10^{-4}	5.60×10^{-3}	ND	7.68×10^{-6}	2.56×10^{-5}	1.54×10^{-4}	ND
Mn	24	3.86×10^{-2}	1.61×10^{-3}	9.66×10^{-3}	ND	5.86×10^{-2}	2.44×10^{-3}	1.47×10^{-2}	ND	1.61×10^{-3}	6.71×10^{-5}	4.03×10^{-4}	ND
Cd	0.5	8.40×10^{-4}	1.68×10^{-3}	1.01×10^{-2}	1.38×10^{-7}	1.28×10^{-3}	2.55×10^{-3}	1.53×10^{-2}	1.76×10^{-7}	3.50×10^{-5}	7.0×10^{-5}	4.20×10^{-4}	3.88×10^{-9}
Cu	40	7.31×10^{-3}	1.83×10^{-4}	1.10×10^{-3}	ND	1.11×10^{-2}	2.77×10^{-4}	1.66×10^{-3}	ND	3.04×10^{-4}	7.61×10^{-6}	4.57×10^{-5}	ND

* Carcinogenic risk values (CR_{ing}) of Cr, Pb and Cd for adults, children and infants based on the available data for SF, ND= not determined, a = means high non-carcinogenic risk while b = means high carcinogenic risk.

most abundant element that is common for both adults and infants. This shows the presence of external sources of surface water pollution due to anthropogenic activities such as industrial effluents and untreated urban wastes from the dumpsite [24,13]. The results suggested that the metals may pose little health threat to the people of all ages with potential non-carcinogenic concern. The calculated cumulative hazard quotients (HI) indices on exposure to surface water at different sites were less than one. The calculated HI for heavy metals ranged between 5.10 x 10^{-4} – 4.38 x 10^{-2} for adults, 7.74 x 10^{-4} – 3.01 x 10^{-1} for children (≥ 6 years) and 2.12 x 10^{-5} – 4.20 x 10^{-4} for infants (≤ 2 years) (Table 4). Therefore, exposure to heavy metals through ingestion may likely exert little negative or cumulative adverse health risk on adults and people using this water [25]. The health risk through ingestion of surface water for infants between the ages of 0 ≤ 2 years and adults were consistently lower than the exposure of children above 6 years. Children above 6 years may consume more heavy metals in the surface water during their outdoor play activities [52].

The daily human exposure risk through surface water (HE_{SW}) for heavy metals in the surface water samples around River Ndawuse through ingestion pathway is shown in Table 5. The maximum daily HE_{SW} values for the selected metals were found to be in the order of Fe > Mn > Pb > Zn > Cd > Cr > Cu > As for all age groups. The daily exposure risk assessment index was < 1 for all metals across the age groups. In general, health risk assessment indices below one (< 1) showed that the concentration of heavy metal is less or has no health threat via ingestion route to humans [20,23]. The risk is therefore less significant, though cumulative long term exposure or trace effect is a threat to human health, hence measures should be made to avoid accumulation of heavy metals that could pose any health risk, especially in children.

Carcinogenic risk (CR_{ing}) is defined as the incremental probability that an individual will develop cancer during one's lifetime due to exposure under different scenarios. The CRing of only Cr, Pb and Cd via ingestion of Ndawuse surface water were calculated for all ages, because the value of cancer slope for other selected metals are not available in the literature [21]. The average estimated values of CR_{ing} for Cr, Pb and Cd are shown in Table 4. The maximum estimated Pb values for 1.76 x 10^{-3} for adults, 2.67 x 10^{-3} for children and 7.34 x 10^{-3} for infants exceeded the target carcinogenic risk value of 10^{-4} - to 10^{-6}. The CR_{ing} of Pb suggested potential risk, if the groundwater is consumed by all the residents. The results further indicated that the investigated Ndawuse River could pose little carcinogenic health risk to adults, children and infants, but the leachates from the dumpsite would pose more risk to human beings. Thus, government should ensure safety measures to protect the users using this river.

4 Conclusion

The dumpsite investigated poses great threat to the surrounding environment and is a major source of pollution to surface water from Ndawuse river. Based on the results obtained, it can be concluded that physical parameters such as the turbidity, COD and BOD_5 are above the standard limits across the river. Most of the metals analysed in this study have concentrations above the safety limits set by WHO/FEPA for drinking water, especially at the dumpsite. This shows that the water quality is unacceptable for domestic purposes and the emphasis on waste management practices as well as construction of appropriate engineered sanitary landfill sites to restrict surface water contamination is highly needed. Human health risk assessment through the intake of heavy metals was calculated separately for adults, children and infants to estimate the magnitude of heavy metals in surface water due to leaching from the dumpsite on humans. The calculated non-carcinogenic effects (HQ_{ing}), HI and HE_{SW} were less than a unity which shows that consumption of the surface water pose little or no significant health risk. However, precaution needs to be taken due to human activities and the potential carcinogenic exposure risk (CR_{ing}) over a period of time especially for the children using this fresh water.

Hence, it is strongly suggested that government should enforce National environmental laws on solid waste disposal /management in order to avoid improper disposal of waste and geophysical conditions that create enormous pressure on safe water sources and provide continous monitoring of the water bodies in order to prevent water contamination in Nigeria. Currently, National Environmental Standards and Regulations Enforcement Agency (NESREA) Act has the responsibility and powers to enforce compliance with policies, environmental issues, laws and regulations. Good management measures should also be employed to make sure that the river regains its fitness for the support of aquatic life and for other domestic purposes as well as to avoid long-term cumulative exposure risk on health. Waste sites should be placed at safe distance with respect to the river to prevent or minimise indiscriminate leaching of leachate from the environment into the river.

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