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Research Article

Bioavailability Studies of Metals in Surface Water of River Challawa, Nigeria

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Due to industrialization of Kano City, more industries located within Challawa industrial estate have discharged waste informed of effluents into River Challawa, which is the main source of irrigation water for agricultural land. Hence, this study is aim at assessing the bioavailable fractions of the metals zinc (Zn), lead (Pb), copper (Cu), chromium (Cr) and cadmium (Cd) in surface water of river Challawa, Kano, Nigeria, across seasons. It was found that the concentrations of most metals increased significantly during the dry seasons. Concentrations of Cu and Zn are within the standard limits of EPA and WHO for these metals in drinking water while Pb, Cr, and Cd have their concentrations higher than EPA and WHO standard limits. Analysis of relationship between metals indicated significant positive correlation ($P < 0.05$) between Cr and Zn, in all seasons with exception of warm and dry season. This might explain the consistent variation of these metals in the sites in a particular season. Also, significant negative correlation was observed between Cd and Cu (hot and dry season). The chemical fractionation trends were found to be dominated by particulate fractions of metals studied except Zn (cool and dry season) and Cd. The highest percentages of all metals analysed were found in the particulate fraction with exception of Cd. This could reflect less availability of this metal to the immediate environment. However, availability of metals such as Cd, Cr, and Pb in the dissolved and mobile fractions reflects the greater tendency to become available to the aquatic system and through the food chain to man.

1. Introduction

The pollution of surface waters is significant, though on a local scale. However, the heavy runoff associated with perennial rainfall may mitigate the impact. Several small and heavy industries involved in activities such as battery, textiles, tanning, and paint manufacturing are now being located haphazardly mostly near metropolitan centers [1]. No centralized sewage systems exist, and the industrial effluents from the factories are usually discharged untreated into streams, rivers, and other water bodies. This has resulted in high alarming levels of lead (Pb), cadmium (Cd), copper (Cu), and chromium (Cr) in some localized areas.

Bichi [2] indicated that Kano is a booming industrial center in Nigeria, with over 320 industrial establishments comprising of chemical industries, tanneries, textiles, and food processing factories which release waste water into rivers. This, according to Bichi, has led to the deterioration of water quality with Challawa River, one of the receiving rivers. Dada [3] carried out industrial survey which showed that 60 industries discharged untreated effluents into river and only 6 surveyed industries (10%) had primary treatment plants ranging from oxidation tanks to sedimentation tanks. This is considered inadequate and water analysis showed excess amounts of heavy metals such as Pb, Cr, and iron (Fe) [4].

Pollution of water with heavy metals is of grave consequence because both terrestrial and aquatic lives may be poisoned; it may cause disease due to the presence of some hazardous substance which may distort the water quality, add odours, and significantly hinder economic activities

[5]. According to Izonfuo and Bariweni [6], several human activities have been identified to result in water pollution: agriculture, irrigation, urbanization, mining, and industrialization. Though several studies on Nigerian surface waters have been conducted [7–14], recently, the understanding of the biogeochemistry of heavy metals in marine environments has changed considerably during the last two decades [15]. A more thorough comprehension of heavy metal cycling in the environment could, however, require information on the chemical speciation of metals in solution, that is, the specific physicochemical forms that are part of the total concentration of metal in solution.

On the other hand, metal speciation determines the bioavailability and/or toxicity of the metals for aquatic organisms, in addition to affecting the cycle of metals in aquatic environments and in the water-sediment interface. According to Bäckström et al. [16], three fractionation stages were defined for heavy metals in runoff from roadside: dissolved fraction, mobile fraction, and total fraction; particulate fraction is the difference between total fraction and dissolved fraction. The mobile fractions of heavy metals are more available for environmental functions than other fractions. In the ecological context, the mobile fractions rather than the total metal content are important. Further the chemical species especially in aquatic medium play important role in transfer of metals along the water-sediment, aquatic animals, and plants to human chain. Hence, this research was initiated to study seasonal variations of impact of industrial effluents on total, dissolved, mobile, and particulate concentrations of some selected heavy metals in surface water of river Challawa in attempts to establish both long- and short-term concentrations effects.

2. Materials and Methods

2.1. Description of Study Area. Challawa River is located in Challawa industrial estate (11°45′42N, longitude 8°46′17E) in Kumbotso local Government of Kano State. Kano State is located in the Northern part of Nigeria covering an area extending between latitudes 12°40′ and 10°30′ and longitudes 7°40′ and 9°40′. Challawa River is one of the receiving rivers of effluents from Challawa industrial estate. The industries in the Challawa industrial estate range from tanneries and textile to foods and packaging industries. The effluents from the industries in the estate were connected by a canal and channeled directly into Challawa River as a point source. The climate of the area is dominated by the cyclical migration intertropical convergence zone, which is marked with longer dry than wet season, and the highest rainfall in July and August [17]. The relevant human activities in the River are commercial sand dredging, fishing, washing, and recreation during hot hour of the day.

2.2. Sample Collection. The River was divided into upstream and downstream areas as shown in Figure 1. Five sampling sites were chosen on downstream (polluted sites) and one sampling site was chosen on upstream (control site) giving a total of six sampling points. Each sampling site comprises of five sampling points composite to form a core for a site. In choosing the sites for the polluted sites, preference was given to such factor as points of effluent discharge into the river. Surface water was collected at the six sites on a seasonal basis between October 2006 and August 2008. Surface water was collected at the middle of the river and stored in clean polythene bottles prewashed with acid and rinsed thoroughly with deionized water. Once collected, the samples were immediately stored on ice in an ice box and transported to the laboratory for analysis.

Seasons

Warm and dry season—September–November

Cold and dry season—December–February

Hot and dry season—March–May

Warm and wet season—June–August.

2.3. Analysis. Chemical fractionation of water samples was carried out on the principle proposed by Bäckström et al. [16]. Samples were subjected to extraction using 2% nitric acid separately. The extraction was aimed at differentiating fractions in three stages as follows.

Fraction I (dissolved): 50 mL was decanted from the sampling vessel and filtered through 0.50 μm Teflon filters before acidification with 2% nitric acid.

Fraction II (mobile): 50 mL was decanted from the sample vessel and acidified with 2% nitric acid followed by filtration through 0.50 μm Teflon filters after 24 hrs.

Fraction III (total): 2% nitric acid was added directly into the sample vessel and shaken rigorously to suspend all particulate matters. The solution was filtered after 24 hrs through 0.50 μm Teflon filters. The particulate concentration was calculated as the difference between Fraction III and Fraction I.

Analysis of Cu, Zn, Pb, Cr, and Cr was performed on an atomic absorption spectrophotometer (AAS). The validation of the procedure for metal determination and efficiency of AAS was conducted by spiking a sample with multielement standard solution containing 0.5 mg/L of all metals analysed. All acid and reagents used were of analytical grade quality control certified by the use of procedural blanks and spikes. The spike recovery for each metal was >96%. All samples were run in triplicates.

3. Results

The results of total heavy metals concentration of surface water across the seasons were presented in Table 1. Zn values ranged between 0.88 mg/L (Site D, during the cool and dry season) and 3.86 mg/L (Site E, during hot and dry season). Season variations were observed with the highest value of Zn obtained during the hot and dry season. In the same vein, Pb concentration varied between 1.10 mg/L (Site E,

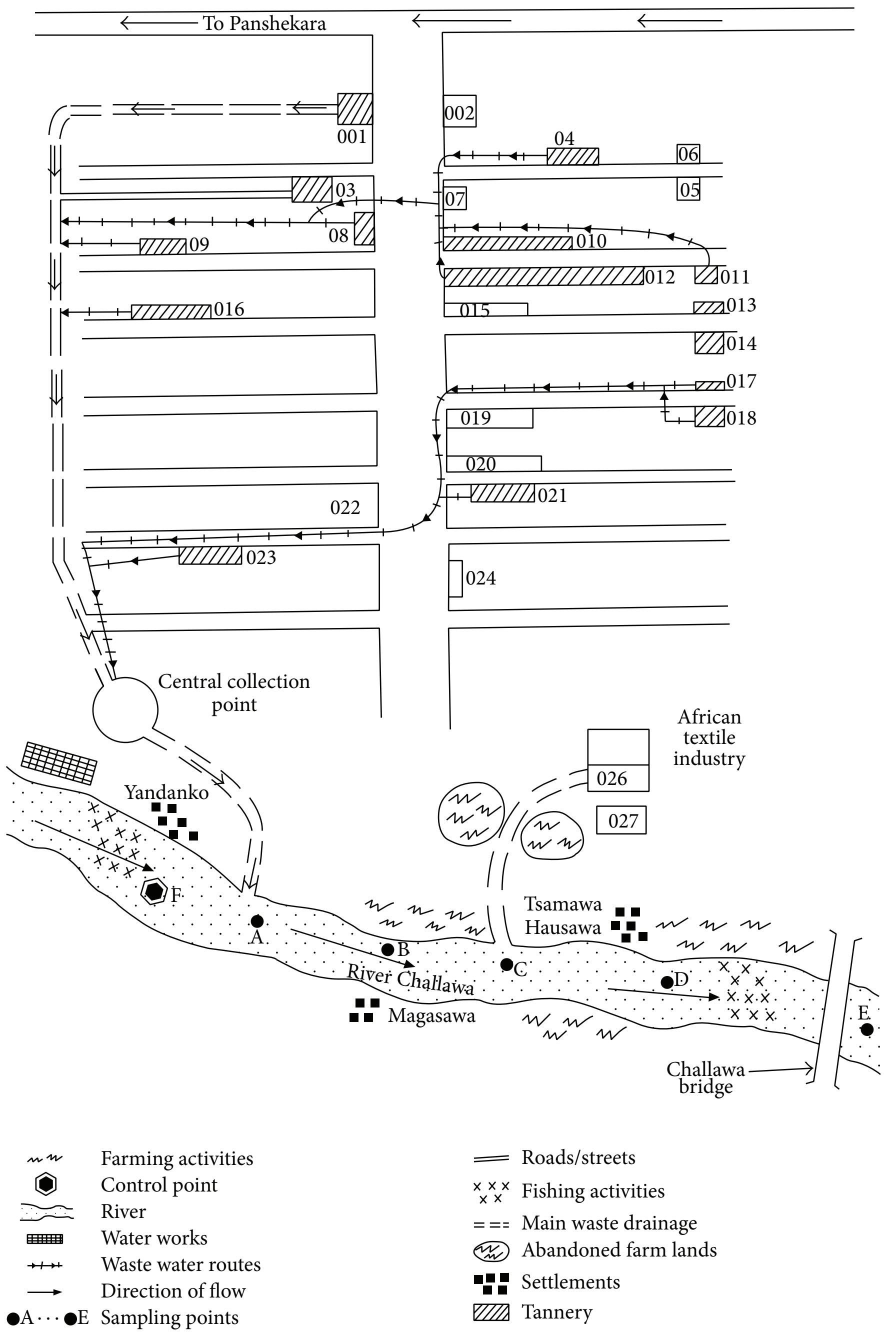

Figure 1: Study area map.

during wet season) and 9.00 mg/L (Site F, during dry season). The distribution of Pb concentrations as shown in the table showed that Pb is higher in all sites during the dry seasons. Similar reasons as Zn could also imply. Cu, Cr, and Cd mean concentrations in the water body ranged between 0.00 mgL^{-1} (Site F in all season) and 0.51 mgL^{-1} (Site B, during dry season); 0.00 mgL^{-1} (Site F, during dry season) and 12.51 mgL^{-1} (Site A, during dry season); and 0.00 mgL^{-1} (Site F, during wet season) and 0.71 mgL^{-1} (Site C, during dry season), respectively. Also, highest concentrations of Cu and Cr are recorded during the warm and dry season while Cd recorded maximum concentration during the hot and dry season. The highest concentrations of Cu, Cr, and Cd during the dry seasons could be due to the volume of water available, which is a function of pollutant concentration. Analysis of variation across the seasons was significant ($P < 0.05$) for all metals except Cu. Correlation analysis as shown in Table 2 indicates significant positive correlation ($P < 0.05$) between Cu and Pb across the seasons with exception of warm and dry season, Cr and Zn, Cr and Pb, and Pb and Zn. This may explain the consistent variation of these metals in the sites in a particular season. Also, significant negative correlation

Table 1: Mean (±SD) of total metal concentrations in surface water of River Challawa (mgL^{-1}).

	A	B	C	D	E	F
			Warm and dry season			
Zn	0.44 ± 0.01	0.15 ± 0.00	0.14 ± 0.01	0.67 ± 0.01	0.31 ± 0.01	0.97 ± 0.01
Pb	2.05 ± 0.07	9.05 ± 0.07	3.05 ± 0.07	4.34 ± 0.01	5.00 ± 0.00	9.00 ± 0.00
Cu	0.35 ± 0.07	0.51 ± 0.01	0.41 ± 0.01	0.10 ± 0.00	0.09 ± 0.01	0.00 ± 0.00
Cr	12.51 ± 0.01	6.68 ± 0.01	11.68 ± 0.01	11.68 ± 0.01	0.00 ± 0.00	0.00 ± 0.00
Cd	0.11 ± 0.01	0.22 ± 0.00	0.16 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	0.11 ± 0.01
			Cool and dry season			
Zn	2.05 ± 0.01	3.12 ± 0.01	2.26 ± 0.01	0.88 ± 0.01	2.69 ± 0.01	1.64 ± 0.01
Pb	2.63 ± 0.01	2.05 ± 0.07	2.15 ± 0.07	2.35 ± 0.07	2.20 ± 0.00	3.05 ± 0.07
Cu	0.21 ± 0.01	0.14 ± 0.01	0.15 ± 0.01	0.07 ± 0.01	0.08 ± 0.00	0.00 ± 0.00
Cr	3.10 ± 0.14	4.25 ± 0.01	3.30 ± 0.14	4.59 ± 0.02	2.47 ± 0.00	0.10 ± 0.00
Cd	0.47 ± 0.01	0.40 ± 0.00	0.71 ± 0.01	0.24 ± 0.00	0.30 ± 0.00	0.08 ± 0.00
			Hot and dry season			
Zn	1.08 ± 0.01	0.90 ± 0.00	1.99 ± 0.01	0.92 ± 0.01	3.86 ± 0.01	1.83 ± 0.01
Pb	3.45 ± 0.07	4.07 ± 0.01	2.51 ± 0.01	2.16 ± 0.01	2.15 ± 0.07	3.36 ± 0.01
Cu	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.01	0.31 ± 0.01	0.04 ± 0.01	0.00 ± 0.00
Cr	3.15 ± 0.07	3.20 ± 0.00	3.10 ± 0.14	6.00 ± 0.00	0.55 ± 0.07	0.00 ± 0.00
Cd	0.62 ± 0.00	0.15 ± 0.01	0.58 ± 0.01	0.19 ± 0.01	0.14 ± 0.01	0.06 ± 0.01
			Warm and wet season			
Zn	1.71 ± 0.01	1.30 ± 0.00	3.01 ± 0.01	1.56 ± 0.01	1.75 ± 0.01	2.85 ± 0.07
Pb	1.43 ± 0.01	2.60 ± 0.00	2.15 ± 0.07	2.25 ± 0.01	1.10 ± 0.00	1.25 ± 0.07
Cu	0.02 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.00 ± 0.00
Cr	3.75 ± 0.07	4.05 ± 0.07	4.25 ± 0.07	7.10 ± 0.14	0.61 ± 0.01	0.31 ± 0.01
Cd	0.10 ± 0.01	0.07 ± 0.01	0.06 ± 0.01	0.14 ± 0.01	0.09 ± 0.01	0.00 ± 0.00
Standard limit		Pb	Cr	Cu	Zn	Cd
WHO		0.1	0.1	—	—	0.01
EPA		0.05	0.1	1.3	5	0.01
FEPA		<1	0.05	<1	<1	<1

WHO [19], FEPA [20], and EPA [21].

was observed between Cd and Cu (hot and dry season), also this could explain the different sources of these metals in the environmental samples. Generally higher values were obtained in the dry season than in wet season (Table 1). This situation is expected in view of the reduction in the pollution in the wet season arising from increased dilution and water flow. This is also similar to report by Obasohan [18] that the river is at its highest volume and flow in the wet season.

From Figures 2, 3, 4, 5, and 6 the chemical partitioning trends were found to be dominated by particulate fractions of metal studied except Zn (cool and dry season) and Cd. Data obtained from the extraction procedure shows the following metal distribution pattern of the fractions across the seasons.

Warm and Dry Season

Zn: Particulate > Mobile > Dissolved

Pb: Particulate > Mobile > Dissolved

Cu: Particulate > Mobile > Dissolved

Cr: Particulate > Mobile > Dissolved

Cd: Dissolved > Particulate > Mobile.

Cool and Dry Season

Zn: Dissolved > Mobile > Particulate

Pb: Particulate > Mobile > Dissolved

Cu: Particulate > Dissolved > Mobile

Cr: Particulate > Dissolved > Mobile

Cd: Particulate > Mobile > Dissolved.

Hot and Dry Season

Zn: Particulate > Dissolved > Mobile

Pb: Particulate > Mobile > Dissolved

Cu: Particulate > Mobile > Dissolved

Table 2: Intermetal relationships in surface water across seasons.

Metals	Zn	Pb	Cu	Cr	Cd
			Warm and dry season		
Zn	1.000				
Pb	−0.020	1.000			
Cu	0.100	0.070	1.000		
Cr	0.312	0.400	0.407	1.000	
Cd	−0.233	−0.200	−0.100	0.100	1.000
			Cool and dry season		
Zn	1.000				
Pb	−0.112	1.000			
Cu	−0.298	0.416*	1.000		
Cr	0.512*	0.123	−0.121	1.000	
Cd	0.314	0.142	−0.344	0.298	1.000
			Hot and dry season		
Zn	1.000				
Pb	−0.109	1.000			
Cu	−0.113	0.500*	1.000		
Cr	−0.333	0.616*	0.414	1.000	
Cd	0.102	−0.211	−0.512*	−0.314	1.000
			Warm and wet season		
Zn	1.000				
Pb	0.500*	1.000			
Cu	0.109	0.522*	1.000		
Cr	0.222	0.200	0.010	1.000	
Cd	−0.100	0.100	−0.111	−0.126	1.000

*Significantly at $P < 0.05$.

Cr: Particulate > Mobile > Dissolved

Cd: Particulate > Dissolved > Mobile.

Warm and Wet Season

Zn: Particulate > Mobile > Dissolved

Pb: Particulate > Mobile > Dissolved

Cu: Particulate > Mobile > Dissolved

Cr: Particulate > Mobile > Dissolved

Cd: Dissolved > Mobile > Particulate.

The highest percentages of all metals analysed are found in the particulate fraction with exception of Cd. This could reflect less availability of this metal to the immediate environment. However, availability of metals such as Cd, Cr, and Pb in the dissolved and mobile fraction reflects the greater tendency to become available to the immediate environment.

4. Discussion

As identified from various literatures, main source of Pb is the alkyl derivatives in petroleum which is gradually phasing off. Also, it comes from other sources like metal manufacturing sewages, paints, fertilizer, pesticides, and ashes [22]. Leaded gasoline was used in Nigeria until recently. This is probably could be the mechanism of anthropogenic Pb contributions into the river. In particular, in dry season nearly in all sites from where samples were taken, Pb levels were found to be higher than mean values reported for polluted and unpolluted sites in a similar study in Nigeria rivers [5, 23]. The elevated levels of Pb in Site F (control) could indicate other sources than effluents discharged from industries within Challawa. As shown in Table 1, high level of Cr was obtained from Site A, point of discharge of tanning effluents into the river. Cr being a major constituent of chemicals use in tanning industries in this area may explain reason for the high level of Cr. Pb and Cr levels observed in this study far exceeded the WHO [19], EPA [21], and FEPA [20] recommended limits for Pb and Cr. Pb is the most ubiquitous toxicant in the environment [24]. Pb may impair renal function, red blood cell production, and the nervous system and causes blindness [5]. Though Cr is an essential trace nutrient and a vital component for the glucose tolerance factor, Cr toxicity damages the livers and lungs and causes organ hemorrhages [25]. The high value of Cr might be attributed to the careless

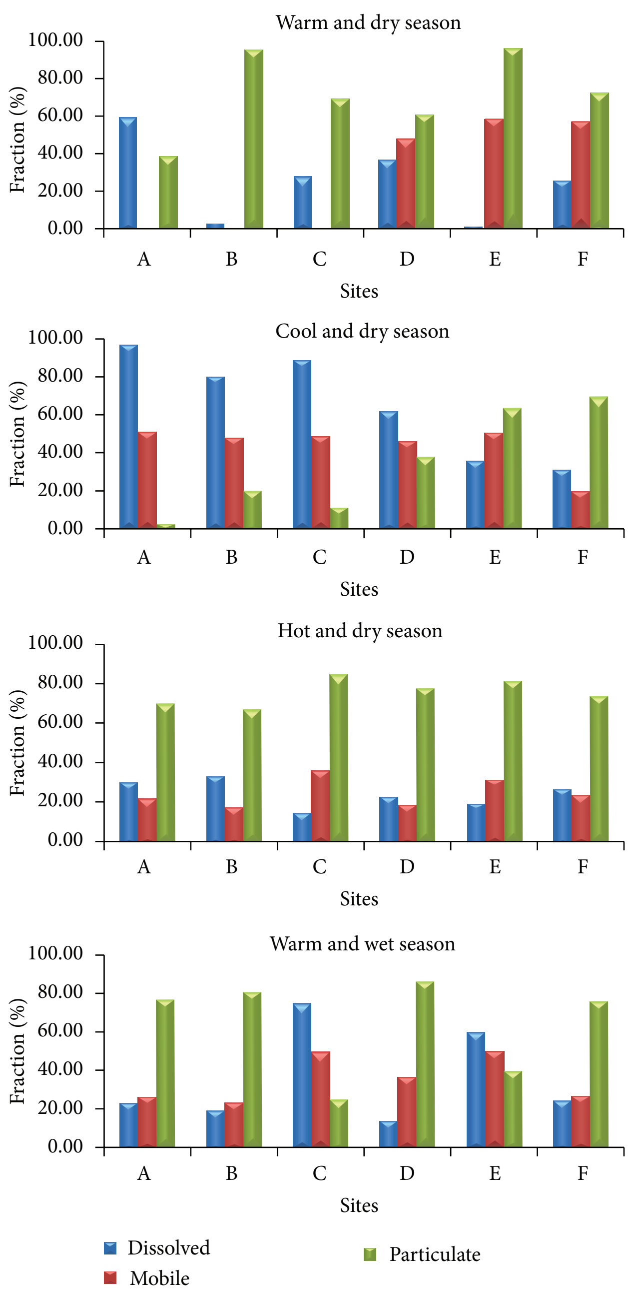

FIGURE 2: Percentage of Zn in fractions.

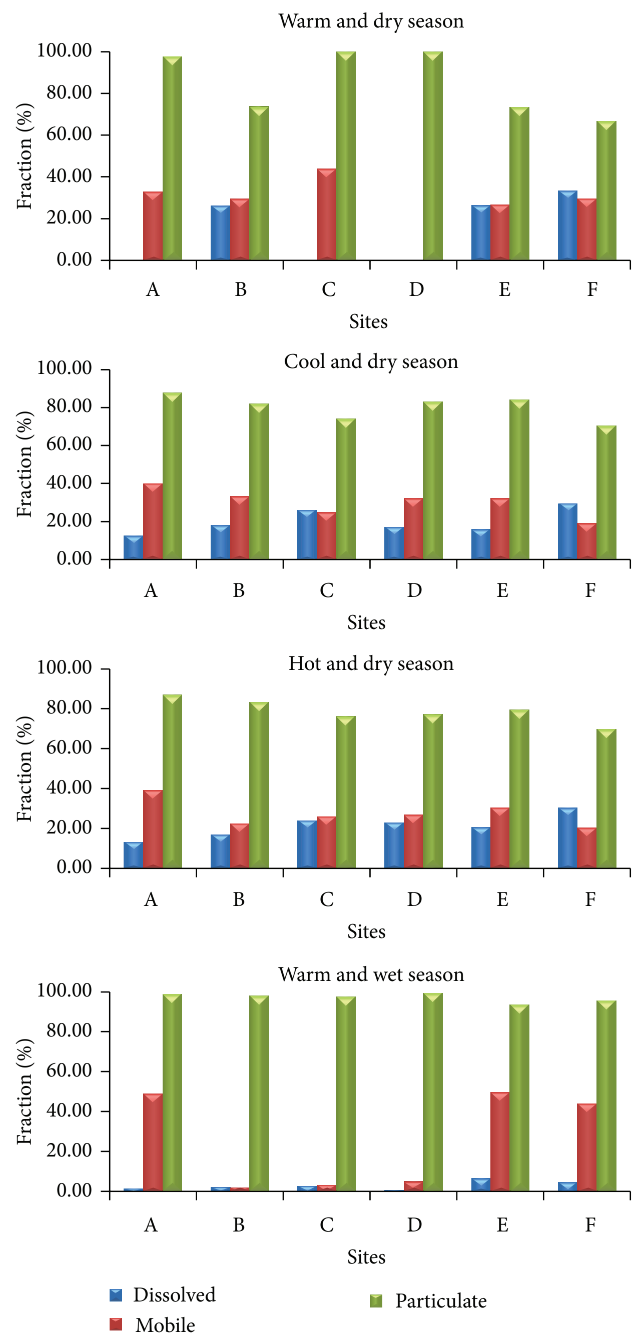

FIGURE 3: Percentage of Pb in fractions.

discharged of tannery and textile effluent from industries located within this area into the river.

All samples contained Zn. However, values obtained in the study indicated that Zn does not seem to be concentrated in water samples, since the levels were below WHO and EPA standards limit, though higher than FEPA standard limits. The observed levels tend to agree with those reported elsewhere in Nigeria rivers [23, 26, 27]. But it is important to mention Zn pollution in rivers. There are many sources of Zn like fossil fuels, metal manufacturing, and fertilizers [22]. Excessive Zn has also been known to induce vomiting, dehydration, abdominal pains, dizziness, and lack of muscular coordination in man [28]. For Cu, the recommended standard limits in water are 1.3 mgL^{-1} (EPA) and <1 (FEPA). For all samples analysed, Cu was generally within the recommended limits. Though widely distributed and being an essential element, acute toxicity of Cu results in hypotension, coma, and death. From research, Cu has been known to participate in the ecosystem from many sources like household tools, wood and metal manufacturing, pesticides applications, fertilizers, and septic tanks waste [29].

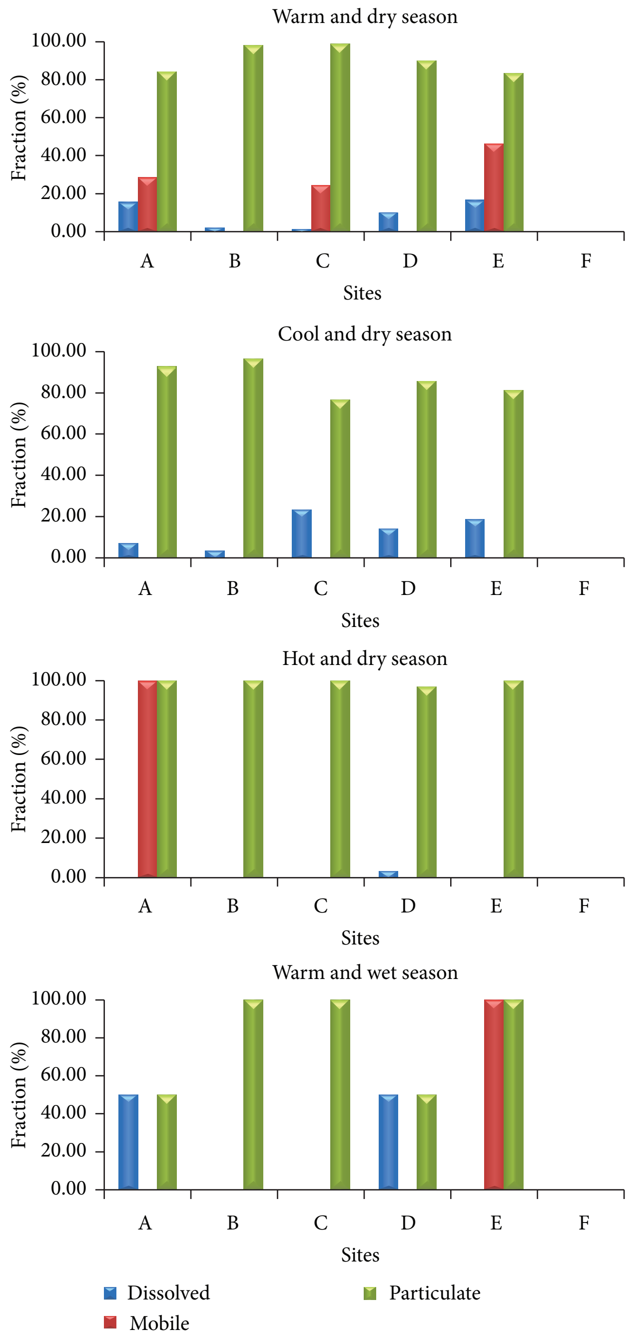

Figure 4: Percentage of Cu in fractions.

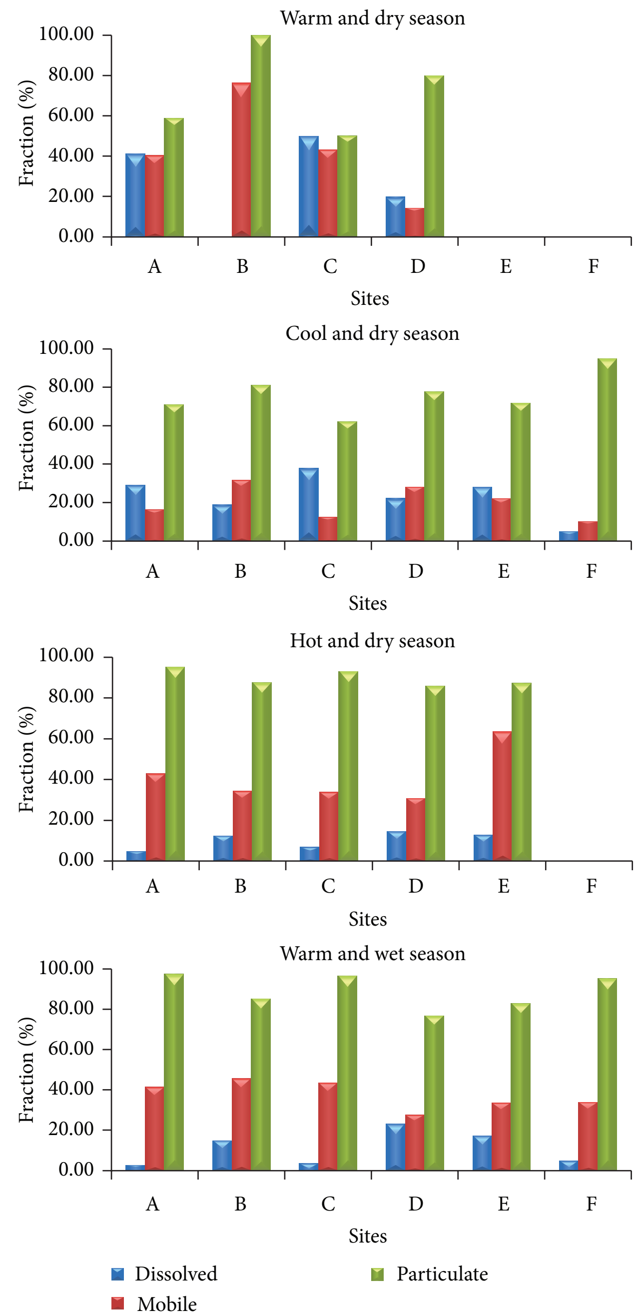

Figure 5: Percentage of Cr in fractions.

For all the samples, Cd was detected to be higher when compared to WHO and EPA standard limits, although within the FEPA [20] standard limits. Cd has a long biological life of 20–30 years in the kidney [19]. Chronic exposure may eventually accumulate to toxic levels as a result of high level obtained in this study. This may lead to anaemia, damage of proximal tubules, severe bone pain, and mineral loss [30].

As observed from Table 1, concentrations of metals obtained from this study showed increase in metal concentration of surface water of river Challawa compared to report of Akan et al. [13] in the same river water with exception of Cu and Zn. The increase could arise due to increase in indiscriminate discharge of waste into the river.

5. Conclusion

From the results, metals concentrations in the mobile and dissolved fractions which are easily bioavailable were high. This metal could leach during changes in environmental conditions and pose threat to the surrounding groundwater quality. Also, with elevated levels of some metals in Site F

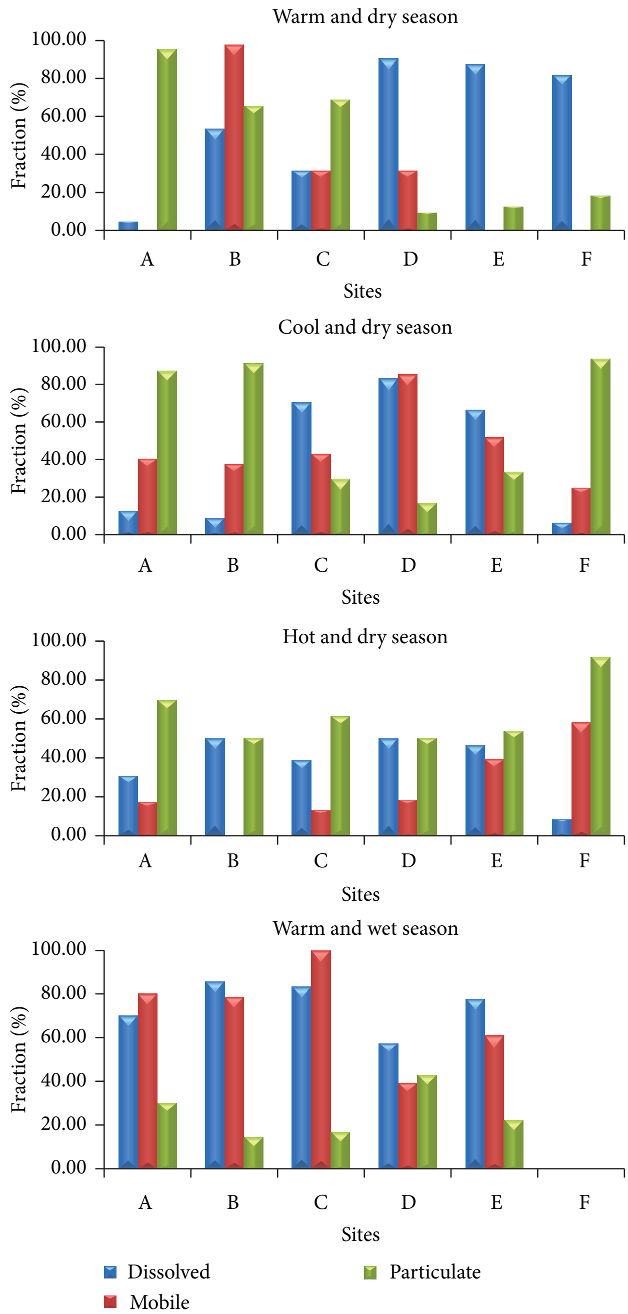

Figure 6: Percentage of Cd in fractions.

(control), it is indicated that sources other than industrial effluents could be responsible. With the continuous discharge of waste and waste water, pollution event especially with Cr, Pb, and Cd with the study area is likely to have a severe but localized effect.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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