

Full Length Research Paper

Impact assessment of effluent discharge on physico-chemical parameters and some heavy metal concentrations in surface water of River Challawa Kano, Nigeria

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In order to understand bioavailability of heavy metals in water, surface water samples were collected from River Challawa, Nigeria, with the view of determining the effect of industrial effluents on the water quality of the river. The fractional concentration of heavy metals (Cd, Cr, Pb and Zn) in water were analysed using Atomic Absorption Spectrophotometer. The water samples were also analysed for physico-chemical parameters. The results show that all physico-chemical parameters determined: Total Solids, Total Dissolved Solids, Total Suspended Solids, pH, Temperature, Chloride, Sulphate, Phosphate with exception of Dissolved Oxygen, Biochemical Oxygen Demand, Chemical Oxygen Demand and Electrical Conductivity are within the recommended standard limits for these contents in drinking water. Also, results obtained from this study indicates the pollution tendencies of the surface waters of river Challawa, attributable to high levels of Pb, Cr and Cd recorded. Generally, elevated levels of Pb and Zn were recorded at control site, which indicates that other sources, than industrial effluents could be responsible. Also, the results showed that with continuous discharge of waste and waste water, pollution event especially with high Cd and Cr within the study area is likely to have severe but localized effects. It is therefore recommended that more strict methods of waste effluent management should be adopted to reduce further inputs into the area.

Key words: Contents, fractionation, river, water, challawa

INTRODUCTION

Recent public of environmental issues in Nigeria tops agenda at both international and national level. This has occurred as a result of environment degradation, environmental deterioration and underdevelopment (Ekweozor and Agbozu, 2001). The rapid industrialization is also having a direct and indirect adverse effect on our environment (Nasrullah et al., 2006). Industrial development manifested due to setting up of new industries or expansion of existing industrial establishments resulted in the generation of industrial effluents, spatially small scale cottage industries which discharge untreated effluents

which cause, water, sediment and soil pollution. In advanced countries, environmental monitoring agencies are more effective and environmental laws are strictly followed. General environmental quality monitoring is compulsory and the monitoring of the quality of water resources is done on a regular basis (Robson and Neal, 1997; USEPA, 2000; Neal and Robson, 2000). As a result, any abnormal changes in the water quality can easily be detected and appropriate action taken before the outbreak of epidemics. In developing like Nigeria, the case is quite the opposite. Environmental laws are rarely observed. Industrial growth and its associated environmental problem such as soil, plant and air contamination is fast increasing (Fakayode and Onianwa, 2002; Fakayode, 2005). Bichi (2000) indicated that Kano is a booming industrial centre in Nigeria, with over 320 indus-

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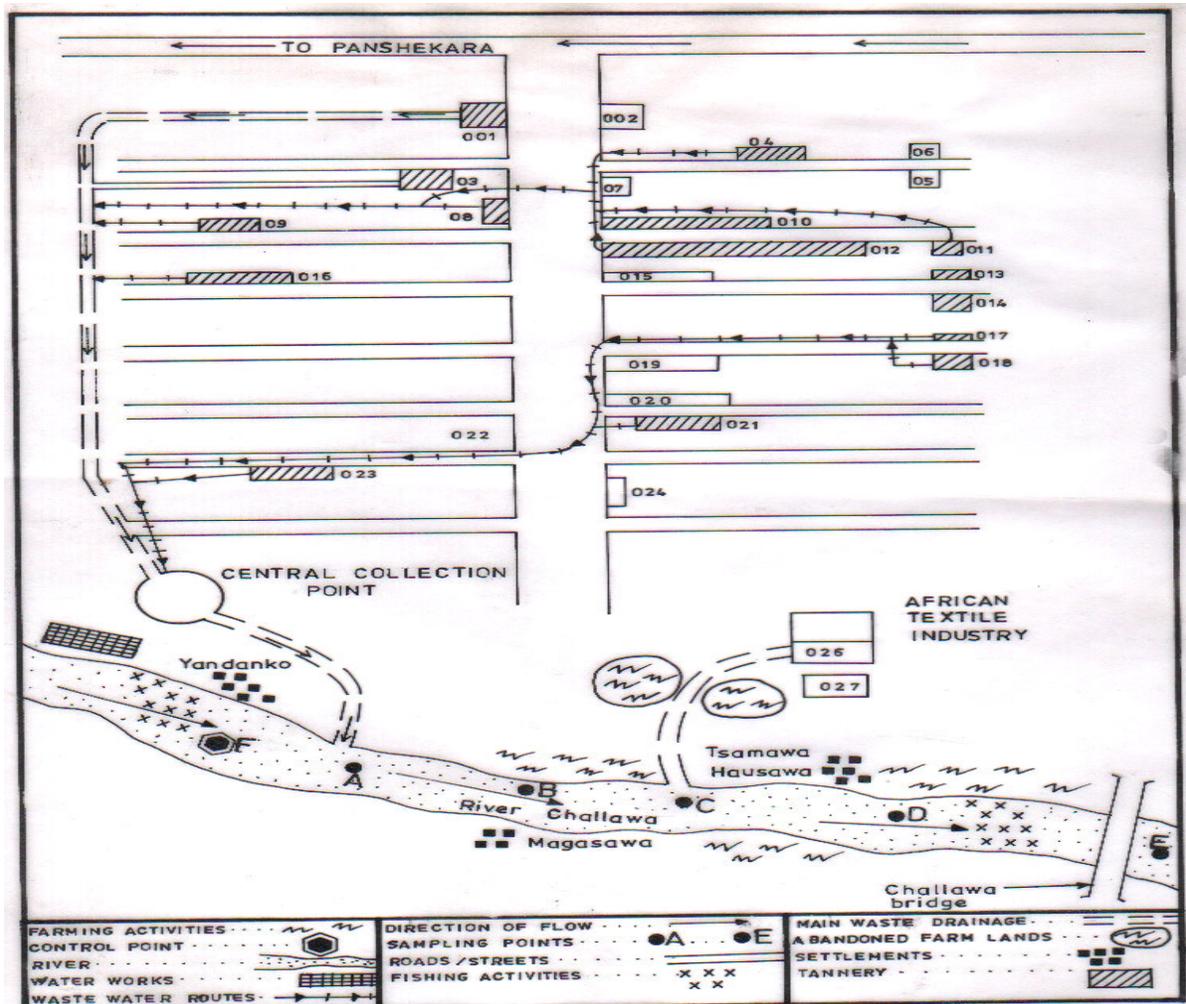


Figure 1: A sketch map of river challawa showing the sampling points.

trial 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 receiving river.

Dada (1997) carried out industrial survey which showed that 60 industries discharged untreated effluent into river and only 6 industries surveyed (10%) had primary treatment plants ranging from oxidation tanks, sedimentation tanks. This is considered inadequate and water analysis showed excessive amounts of heavy metals such as Pb, Cr and Fe (Ahmed, 2000).

Although, water quality is to some extent an index of water pollution, the indices presently used in Nigeria are inadequate to indicate the damage that is done by heavy metals (Arimoro et al., 2008). Data on Challawa River water quality are available (Ahmed, 2000) but little or any information have been provided on the bioavailable heavy metal fractions of the river. Hence, the present research were carried out on Challawa river to determine

the physico-chemical characteristics and fractionation of heavy metal in surface water, this planned research will be helpful to assess the impact of the industrial effluent in Challawa industrial estate on the surrounding water bodies.

MATERIALS AND METHODS

Study area

Challawa River is located in Challawa Industrial Estate in Kumbotso local Government of Kano State. Kano State is located in the Northern part of Nigeria covering an area extending between latitude $12^{\circ} 40'$ and $10^{\circ} 30'$ and longitude $7^{\circ} 40'$ and $9^{\circ} 40'$. 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 in to Challawa River as a point source as shown in Figure 1. The climate of the area is dominated by the cyclirial migration inter tropical convergence zone. The marked season of climate, the dry season is longer than

Table 1. Mean (\pm SD) of physicochemical parameters measured at various sampling sites.

Parameters	Sites					
	A	B	C	D	E	F
Total Solids (TS) mg/l	562.00 \pm 1.00	310.00 \pm 4.36	523.33 \pm 0.47	373.67 \pm 0.58	227.00 \pm 8.03	257.33 \pm 4.93
Total Dissolved Solid (TDS) mg/l	34.67 \pm 1.15	96.67 \pm 0.58	215.67 \pm 0.58	171.00 \pm 7.32	260.00 \pm 1.00	26.33 \pm 1.53
Total Suspended solids (TSS) mg/l	426.67 \pm 0.58	215.33 \pm 1.15	241.67 \pm 3.62	202.67 \pm 7.65	167.00 \pm 17.78	231.00 \pm 3.46
pH	8.37 \pm 0.01	7.97 \pm 0.58	9.38 \pm 0.01	10.46 \pm 0.01	8.37 \pm 0.01	7.21 \pm 0.02
Temperature $^{\circ}$ C	24.96 \pm 0.02	23.27 \pm 0.06	24.01 \pm 0.01	26.15 \pm 0.01	26.15 \pm 0.01	23.91 \pm 0.01
Electrical Conductivity μ Scm $^{-1}$	677.25 \pm 0.01	193.93 \pm 0.31	292.97 \pm 0.15	120.07 \pm 0.12	120.07 \pm 0.12	52.61 \pm 0.02
Dissolved Oxygen mg/l	3.30 \pm 0.20	2.90 \pm 0.00	3.20 \pm 0.10	2.67 \pm 0.15	2.67 \pm 0.15	3.10 \pm 0.10
Biochemical Oxygen Demand (BOD)mg/l	30.00 \pm 1.00	10.00 \pm 1.00	60.00 \pm 2.00	70.00 \pm 1.00	70.00 \pm 1.00	20.00 \pm 2.00
Chemical Oxygen Demand (COD) mg/l	260.00 \pm 1.00	270.00 \pm 5.00	170.00 \pm 2.00	570.00 \pm 0.00	570.00 \pm 0.00	260.00 \pm 2.00
Turbidity (NTU)	300.33 \pm 0.58	510.00 \pm 0.00	480.00 \pm 1.00	300.00 \pm 0.00	300.00 \pm 0.00	560.00 \pm 1.00
Chloride mg/l	14.90 \pm 0.10	14.90 \pm 0.20	24.90 \pm 0.00	19.87 \pm 0.15	19.87 \pm 0.15	9.90 \pm 0.10
Sulphate mg/l	655.00 \pm 2.00	515.00 \pm 1.00	640.33 \pm 0.58	466.67 \pm 2.89	466.67 \pm 2.89	640.00 \pm 3.00
Phosphate mg/l	0.55 \pm 0.01	1.10 \pm 0.10	0.35 \pm 0.01	1.20 \pm 0.10	0.33 \pm 0.05	1.20 \pm 0.20

wet, with highest rainfall in July and August (Kabiru, 2007).

Sample collection

Surface water samples for this analysis were collected during the winter season of 2006 (November). Surface water was collected as a composite sample at each sample station as shown in Figure 1. At each time of surface water collection, two separate set of samples were collected, one for the determination of heavy metals and the other for the determination of physico-chemical parameters. At each sampling location, the surface water sample was collected at the middle of the river and stored in a clean polythene bottles that have been prewashed with 10% nitric acid and thoroughly rinsed with deionized water.

Water quality analysis

pH, temperature, electrical conductivity (EC) and total dissolved solid (TDS) were determined at the time of sampling in the field using a portable HANNA, HI991301 Model. Total Solid (TS), Total Suspended Solid (TSS), Sulphate, phosphate-phosphorus ($\text{PO}_4^{3-}\text{-P}$) and Chloride were determined according to APHA (1985) methods. Chemical oxygen demand (COD), Dissolved Oxygen (DO) and Biological oxygen demand (BOD) were also determined following the procedure of Hamer (1986).

Chemical fractionation of water samples

Chemical fractionation of water samples was carried out on the principle proposed by Bäckström et al. (2003). Samples were subjected to extraction using 2% nitric acid separately. The

extraction was aimed at differentiating fractions in 3 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 h.

Fraction III (Total): 2% nitric acid was added directly into the sample vessel and shaken rigorously to suspend all particulate matter. The solution was filtered after 24hr through 0.50 μm Teflon filters. The particulate concentration was calculated as the difference between Fraction III and Fraction I. Analysis of Cd, Pb, Zn and Cr were then performed on an AAS-650 (Shimadzu Double Beam). The validation of the procedure for metal determination was conducted by spiking samples with multielement standard solution containing 0.5 mg/l of all metals analysed. Spiked samples were analysed under the same experimental conditions used for procedural blanks and samples. Acceptable (>90%) recoveries from the spiking experiment validate the experimental procedure.

RESULTS AND DISCUSSION

A summary of the physico-chemical parameters obtained in Challawa River for the different sites are presented on Table 1. The value of TS ranged from 227.00 – 562.00 mg/l for the polluted site with Site E having the lowest mean value and Site A having the highest mean value. The control Site F has a mean value of 257.33 mg/l lower

Table 2. Heavy metal concentrations (Mean \pm SD), mg/l) in each fractions of water samples of six sites.

Fractions	Sites					
	A	B	C	D	E	F
Cd						
Dissolved	BDL	BDL	0.05 \pm 0.04	0.13 \pm 0.04	0.13 \pm 0.04	0.08 \pm 0.00
Mobile	BDL	0.21 \pm 0.12	0.05 \pm 0.04	0.05 \pm 0.04	BDL	BDL
Total	0.10 \pm 0.09	BDL	0.15 \pm 0.00	0.15 \pm 0.00	0.15 \pm 0.04	0.10 \pm 0.04
Particulate	0.10	BDL	0.10	0.02	0.02	0.02
Cr						
Dissolved	5.00 \pm 2.50	BDL	5.83 \pm 3.82	2.33 \pm 0.29	BDL	BDL
Mobile	5.00 \pm 0.00	5.00 \pm 2.50	5.00 \pm 4.33	1.67 \pm 1.44	BDL	BDL
Total	12.50 \pm 2.50	6.67 \pm 2.89	11.67 \pm 1.44	11.67 \pm 1.44	BDL	BDL
Particulate	7.50	6.67	5.84	9.34	BDL	BDL
Pb						
Dissolved	BDL	2.33 \pm 1.53	BDL	BDL	1.33 \pm 1.15	3.00 \pm 2.00
Mobile	0.67 \pm 0.58	2.67 \pm 2.31	1.33 \pm 1.15	BDL	1.33 \pm 1.15	2.67 \pm 1.53
Total	2.00 \pm 0.00	9.00 \pm 1.00	3.00 \pm 1.00	4.33 \pm 0.58	5.00 \pm 1.00	9.00 \pm 1.00
Particulate	2.00	6.67	3.00	4.33	3.67	6.00
Zn						
Dissolved	0.26 \pm 0.13	BDL	BDL	0.26 \pm 0.06	BDL	0.26 \pm 0.17
Mobile	BDL	BDL	0.07 \pm 0.06	0.19 \pm 0.06	0.19 \pm 0.06	0.56 \pm 0.22
Total	0.44 \pm 0.11	0.15 \pm 0.13	0.22 \pm 0.19	0.67 \pm 0.11	0.30 \pm 0.06	0.96 \pm 0.13
Particulate	0.18	0.15	0.22	0.41	0.30	0.70

BDL: Below Detection Limits

than the highest value of 526.00mg/l obtained from the polluted sites. Statistical analysis using ANOVA indicated that TS was significantly different ($p < 0.001$) among the sites sampled. The marked difference among sites might be due to deposition of solid particles from the effluent through the river course which could lead to the reduction in the volume of water and also impede the free flowing of the river. Also, as compared to other studies, it was lower than 1379.3mg/l reported in a similar study (Fakayode, 2005). Although higher than 328.8 mg/l reported in the same study for unpolluted sites. However, the mean values obtained in this study were within 1000mg/l limits recommended by WHO (1999) and FEPA (1991) for total solids (TS) for municipal water.

Also, contrary to reported values by Arimoro et al. (2008), TSS values were higher than the TDS values in all the sites sampled. Generally TDS and TSS fluctuated between 34.67 – 215.67 mg/l and 167.00 – 426.67 mg/l for the polluted sites respectively. There were significant differences ($p < 0.001$) in the values of TSS and TDS among the different sampling sites. Similar to TS, value obtained for TDS from the control Site F is lower than the values obtained from the polluted sites. While TSD obtained for the control site is slightly higher than the polluted sites with exception of Sites A and C.

The pH value as presented in Table 1 for polluted site varied from 7.97 – 10.46. Maximum pH 10.46 was of the sample of Site D. The maximum pH value recorded in this study is slightly higher than maximum pH of 8.22, 8.1, and 7.4 reported in similar water bodies in Nigeria (Arimoro et al., 2008; Fakayode, 2005; Davies et al., 2006; Ekweozor and Agbozu, 2001). All the sites except

Sites C and D were within the permissible limits of USEPA (2000) and WHO (1999) for drinking water.

Temperature of the water samples ranged from 23.23 – 24.96°C. The lowest value was found in Site D and the highest temperature was that of Site A. The temperatures of the polluted and control sites were normal with significant difference ($p < 0.001$) among sites. The highest temperature 24.96°C was about the value of the ambient air temperature.

Electrical conductivity (EC) of water is also an important parameter for water quality. The values of EC ranged from 120.07 – 677.25 μScm^{-1} for the polluted sites. However, these values are generally higher than 52.61 μScm^{-1} reported for the control Site F. Higher conductivity of 677.25 μScm^{-1} from Site A could indicate high amount of ions that exceed the recommended limit by WHO (1999).

Dissolved oxygen (DO) is a very crucial parameter for the survival of aquatic organism and is also used to evaluate the degree of freshness of a river. However, the DO concentration of the river examined showed that the river was poorly aerated, irrespective of sites. The highest mean value of 3.30 mg/l recorded in this study falls short of the relatively high values reported by Egborge et al. (1986) and Umeham (1989). These low values observed may be as a result of the nature of the effluent discharge into the water that places a high demand on the DO (Arimoro et al., 2008). Again, the raw effluents discharge into the water resulted to high COD and BOD.

BOD and COD sampled ranged from 10.00 – 70.00 mg/l and 170.00 – 570.00 mg/l respectively. The lowest value of BOD and COD was recorded in sites B and C respectively. The highest value of BOD and COD was re-

corded in (D and E) and E respectively. The observed BOD levels were noted to be above maximum permissible limit of 10mg/l recommended by FEPA (1991) for drinking water. In addition the high levels of DO and TSD in the water systems increased the BOD and COD, which depleted the DO in the water system. The results indicate that the water bodies sampled had suffered deterioration and degradation due to continuous discharge of partially treated effluents into the environment (Ekweozor and Agbozu, 2001) and could be classified as polluted surface water.

The observed turbidity ranged from 300.00 – 510.00NTU for polluted sites. The maximum value obtained from the polluted sites was lower than 560.00NTU recorded for Site F. The results revealed that the water were quite turbid and would affect the surface water quality. This remarkably high value might be connected with continuous discharge of organic wastes discharged into the aquatic ecosystem from the surrounding swampy environment. However, the mean values reported in this study were higher than 1NTU recommended by FEPA (1991).

The maximum level of chloride was 24.90 mg/l (Site C) and minimum level of 14.90 mg/l of the studied. Generally chloride values obtained from the studied sites are higher than the control Site F. The sources of chloride in the studied sites were likely to be from hydrochloric acid, common salt (NaCl) and other chloride containing compounds, which are usually used as raw materials particularly in the textile and tanning industries. Compared to standard limits, the values obtained in this study are lower than 200.00 – 500.00 mg/l recommended limits by WHO (1999).

Sulphate levels downstream ranged from 466.67 – 640.33 mg/l while the level upstream is 640.00 mg/l, slightly higher than 640.33 mg/l recorded in the studied sites. The levels were higher than the natural background sulphate levels of 1 -3 mg/l reported in other unpolluted rivers elsewhere (Kudryavtseva, 1999). The high level of sulphate obtained in this study could be ascribed to the use of sulphuric acid or sulphate salts, which are commonly used in several industries. However, it was comparatively lower than the sulphate levels of 622 mg/l, reported from other pollution studies elsewhere in rivers receiving industrial water or effluents of higher sulphate contents (Seleznev and Selezneva, 1999).

The highest level of phosphate of 1.20 mg/l recorded from Sites D and F compare to other studies (Fakayode, 2005) indicates that the level of phosphate in the samples were not too high. However, values obtained from this study were comparable to reported value by Arimoro et al. (2008).

Chemical fractionation of metals in waters

From the results as presented on Table 2, the availability of Cd in extractable fractions across the site follows the

order;

Dissolved: $D = E > F > C > A = B$
 Mobile: $B > C = D > E = F = A$
 Total: $D = E = C > A = F > B$
 Particulate: $D = E = F > C = A > B$

Analysis of variance results showed dissolved and mobile fractions of Cd were significantly different ($p < 0.05$) among the various sampling sites. This observation suggests that the distribution of Cd depends partly on sources of contamination along the river course. Compared to standard limits of 0.01 and 0.05 mg/l, the result showed higher values with few exceptions. Cd identified as one of the trace metals implicated as a metal which has the capability to accumulate along the food chain. It has also been known to be very hazardous and of no use to biological processes. The Cr concentration in the four fractions of the water is presented on Table 2. The bioavailability of the metal is in the following order across the sites:

Dissolved: $C > A > D > E = F = B$
 Mobile: $A = B = C > D > E > F$
 Total: $A > C > D > B > E = F$
 Particulate: $D > A > B > C > E = F$

Analysis of variance (ANOVA) for all fractions with exception of dissolved fraction showed significant difference ($p < 0.05$) among the various sampling stations. Similar explanation as incase of Cd fractions could also be responsible. However, values obtained were higher than 1.0 mg/l recommended limit (WHO, 1999) with few exceptions. Cr been a major constituent of chemicals use in tanning industries in this area a contributing factor to the high level of Cr. Contrary to other studies (Gasparon and Burgess, 2000; Tsareva et al., 1999), high level of Cr was obtained before the point of effluent discharge. This could indicate other source of contamination other than effluents from tanning industries. Metal tear and wear from Lorries use in carrying river sediment could be responsible, since this is a common phenomenon along the river bank.

Also, as shown on Table 2, the result of available Pb in the extractable fractions across the sampling sites reveal pattern as follows:

Dissolved: $F > B > E > A = C = D$
 Mobile: $B = F > C = E > A > D$
 Total: $F > B > E > D > C > A$
 Particulate: $B > F > D > E > C > A$

Analysis of variance (ANOVA) across the sites for all fractions showed that concentrations of dissolved, total and particulate fractions were significantly ($p < 0.05$) varying, with Site F having the highest concentration for the total fraction. The reported values were found to be higher than mean value of 0.023 and 0.14 mg/l reported for unpolluted and polluted sites in a similar study in

Nigeria (Fakayode, 2005). The relatively elevated levels of Pb in the fractions could indicate other sources other than effluents from industries. Compared to standard limits, the levels recorded in this study were higher than 0.05 mg/l (USEPA, 2000; WHO, 1999). According to Ajiwe et al. (2000), Pb is easily distributed in the aquatic ecosystem through surface runoffs or overflow during flood. Thus, the reported values if allowed to accumulate will pollute aquatic resources and pose health hazards to the inhabitants of the area.

The extractable fractions of Zn are shown in Table 2. The results of extractable fractions showed the following profile.

Dissolved: A = D = F > B = C = E
 Mobile: F > D > E > C > A = B
 Total: F > D > A > E > C > B
 Particulate: F > D > E > C > A > B

Significant variation ($p < 0.01$) of all extractable fractions across the sites were obtained. The results show that the mean total extractable from Site F was higher than those of the other sites. The observed higher values may not be connected with the continuous discharge of effluents in other sites. However, based on the mean values obtained, it does not seem that Zn was highly concentrated in the surface water samples, since the levels were below 5 mg/l limits (USEPA, 2000; WHO, 1999). The observed levels tend to agree with those recorded elsewhere in rivers (Kakulu and Osibanjo, 1992; Fakayode, 2005; Adefemi et al., 2008). However continuous discharge of wastes containing Zn metal should be discharge, since Zn has been known to induce vomiting, dehydration, abdominal pain, dizziness and lack of muscular co-ordination in man (WHO, 1999).

Conclusion

The results obtained from this study indicates the pollution tendencies of the surface waters of river Challawa, attributable to high levels of Pb, Cr and Cd recorded. Generally, elevated levels of Pb and Zn were recorded at Site F (control), which indicates that other sources, than industrial effluents could be responsible. Also, the results showed that with continuous discharge of waste and waste water, pollution event especially with high Cd and Cr within the study area is likely to have severe but localized effects.

All the heavy metals study are known to be toxic to man at certain levels of intake and with the observed increase of industrial activities in the area, it will be recommended that more strict methods of waste effluent management should be adopted to reduce further inputs into the area.

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