*Original Research Article*

# An assessment of the heavy metal status of River Galma around Dakace industrial layout, Zaria, Nigeria

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## Abstract

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The concentrations of some heavy metals were determined in surface water from River Galma to evaluate the influence of effluents from Dakace industrial layout, Zaria on the water quality of the river. Four sampling stations were established, with sampling station 1 (control) upstream before effluent discharged points from the industrial layout. Cadmium (Cd) Manganese (Mn), Chromium (Cr) and Cobalt (Co) concentrations were analyzed using Schimadzu atomic absorption spectrophotometer (model AA-6800, Japan) after wet digestion. The range of concentrations (mg/l) of each metal was Cd (0.00-0.076), Cr (0.04-0.42), Mn (0.01-2.00) and Co (0.10-1.83). The heavy metals concentrations determined were found to be above World Health Organization (WHO) and Nigerian Standard for Drinking Water Quality (NSDWQ). They were also above the Australian and New Zealand Environment and Conservation Council's guidelines for irrigation waters. Statistical analysis shows that effluents discharged into the river from Dakace industrial estate had no significant influence on the overall Cadmium, chromium, manganese and cobalt contents of the River. The implications of these findings for public health are fully discussed.

**Keywords:** Dakace, Heavy metals, public health, River Galma, surface water

## INTRODUCTION

Surface water pollution describes the introduction by man of foreign substances capable of causing harm to man, hazard to other living organism or interference with the legitimate use of the environment into the surface water bodies (Oze et al., 2006). Population explosion, rapid urbanization, industrial and technological expansion, energy utilization and wastes generation from domestic and industrial sources have rendered many water resources unwholesome and hazardous to man and other living resources. Water pollution is now a significant global problem (Anetor, 2003). Industrial effluents are a main source of direct and often continuous input of pollutants into aquatic ecosystems with long-term implications on ecosystem functioning including changes in food availability and an extreme threat to the self-purification capacity of the surface water bodies. These industrial discharge or wastes include heavy metals, pesticides, polychlorinated biphenyls (PCBs), dioxins,

poly-aromatic hydrocarbons (PAHs), petrochemicals, phenolic compounds and microorganisms (Fakayode, 2005; Davies et al., 1988; Nubi et al, 2008; Vesiland et al., 1990; Botkin et al., 1998). While most people in urban cities of the developing countries have access to piped water, several others still rely on borehole and river water for domestic use. Most of the rivers in the urban areas of the developing world are receptacles for effluents discharged from the industries (Mumba, et al., 2005; Olayinka, 2004). Aquatic contamination by heavy metals is very harmful since these elements are not degradable in the environment and may accumulate in living organisms (Jardim, 1983). Some heavy metals can continue to accumulate in the tissue of organisms until they reach intolerable levels resulting in morbidity or mortality (Offem and Ayotunde, 2008). In the human body, they may undergo biotransformation, metabolism and excreted without the risk of toxicity depending on the
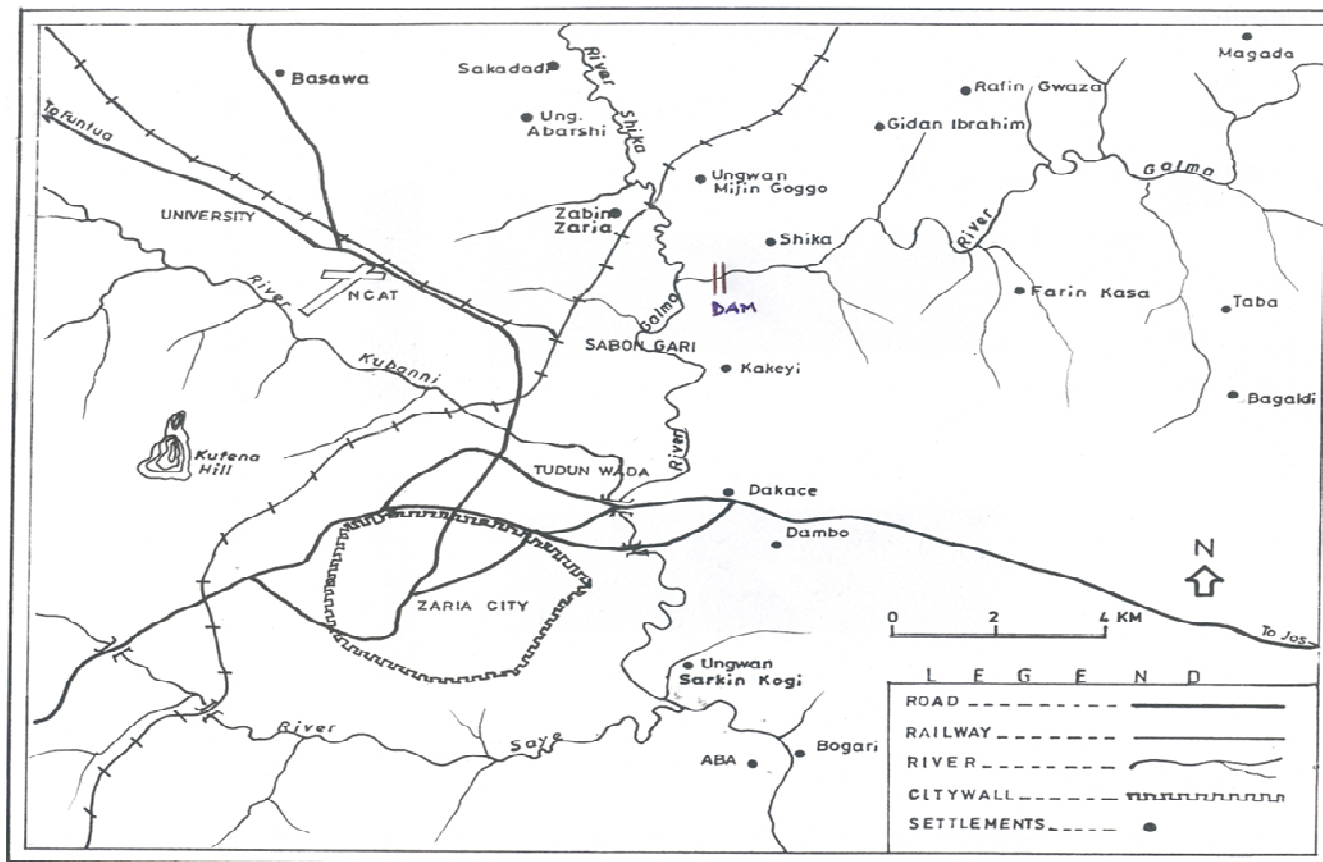
**Figure 1.** Zaria showing rivers and settlements

chemical characteristics of the metal and the dose. However, some of the metals resist chemical and biological transformation and accumulate in the tissues to cause toxic effects (Oze et al., 2006). Man being higher in the food chain stands the risk of higher bioaccumulation. The adverse effects of these pollutants on the nerves give rise to neurotoxicity. Some heavy metals are neurotoxic. For instance lead, mercury, nickel, zinc, cadmium, chromium and manganese (Oze et al., 2006). Environmental data concerning the levels and prevalence of heavy metals in inland water used extensively as a source of domestic or industrial water supply is of utmost importance in view of the danger associated with it. River Galma supplies the bulk of water used by people in Zaria and its environs for different activities depending on the point of contact.  There is therefore need for a periodic, rational and systematic assessment of heavy metals in the river system environment. In this study, the concentration of Cadmium (Cd), Manganese (Mn) and Chromium (Cr) and Iron (Fe) were thoroughly examined in water samples collected from River Galma around Dakace industrial layout, Zaria, in order to establish their current status and the influence of Dakace industrial estate on the quality of the river.

## MATERIALS AND METHODS

### Sampling Area

River Galma is the main drainage channel in Zaria since other rivers and streams discharge into it. Zaria is in the North central Kaduna state of Nigeria and is located at latitude 11º3'N and longitude 7º40'E, 128 km South- East of Kano and 64 km North-East of Kaduna City (Nnaji et al 2011). River Galma is located at the southeastern part of Zaria and its source is the Jos Plateau. The Zaria dam is located on River Galma (Nnaji et al 2007). Dakace industrial area habours a number of wet industries such as oil mills, packaging, food and beverages industries. Effluents from these industries are discharged through drains and canal that empties into the River. The Galma river basin is a booming agricultural area. Crops are planted on both sides of the riverbank through-out the year. Fertilizers, herbicides and insecticides are used on these crops and are eventually washed into the river via surface runoff (Nnaji et al., 2011). The river is a major source of water supply to a number of communities located along its course. It is used for irrigation, fishing, bathing and even drinking. (Figure 1)

**Table 1.** Results of analysis of reference material (Lichen IAEA -336) compared to the certified reference value (mg/kg).

| Element (mg/kg) | Pb | Cd | Cu | Mn | Zn |
|---|---|---|---|---|---|
| A Value | 5.25 | 0.140 | 4.00 | 55.78 | 29.18 |
| R value | 4.2-5.5 | 0.1-2.34 | 3.1- 4.1 | 56-70 | 37-33.80 |

*A Value = Analyzed value  R Value = Reference value.*

## Sample collection and Preservation

The procedure for sample collection and analysis was adopted from APHA (2005)**.** Four sampling points 200 meters apart were established along Galma River around Dakace industrial area after identifying effluent discharge points (point sources) from the industries. Sampling point A was 200 meters upstream from the first point source. Sampling point B was at the first point source. Sampling point C was after the second and third identified effluent discharge points and sampling point D was 200 meters from sampling point C. Sample containers were thoroughly washed with detergent, rinsed with water followed by distilled water before soaking in 5% nitric acid for about 24 hours. Water sample was collected from each of the four sampling points by simple scooping using plastic bucket on monthly basis. Collected water sample was poured into the washed 2-litre polypropylene container. Temperature was determined on site using HACH conductivity / TDS meter (model 44600.00, USA), pH was also determined on site electronically using Zeal–tech digital pH meter (model 03112, India). Each sample was fixed with 5mls of concentrated nitric acid and kept in cooler stock with ice block and transported to the Environmental Laboratory of National Research Institute for Chemical Technology, (NARICT) Zaria, Nigeria, at temperature of $< 4^{o}C$.

## Sample preparation

The samples were digested according to Standard methods for the examination of water and wastewater, American Public Health Association (APHA, 2005). Each sample was thoroughly mixed, 20ml was transferred into a conical flask, 10ml concentrated nitric acid was added and brought to slow boiling before evaporating on a hot plate to lowest volume (5 – 10ml). Concentrated nitric acid was added as necessary until digestion was complete as shown by light colour clear solution. The digest was filtered into 50ml volumetric flask and made up to the mark.

## Sample Analysis

Metal concentration in the digests was determined by Atomic Absorption Spectrophotometry, using Schemadzu Atomic Absorption Spectrophotometer (model AA-6800, Japan) equipped with Zeaman background correction and graphite furnace at National Research Institute for Chemical Technology (NARICT), Zaria-Nigeria. The calibration curve was prepared by running different concentrations of standard solutions. The instrument was set to zero by running the respective reagent blanks. Average values of three replicates were taken for each determination and were subjected to statistical analysis

## Analytical Quality Assurance

In order to check the reliability of the analytical methods employed for metal determination, one blank and combine standards were run with every batch to detect background contamination and monitor consistency between batches. The result of the analysis was validated by digesting and analyzing Standard Reference Materials, Lichen coded IAEA-336 following the same procedure. The analyzed values and the certified reference values of the elements determined were compared to ascertain the reliability of the analytical method employed. The reagent used for sample preservation and digestion, viz. $HNO_3$ (Riedel-deHaën, Germany), was of analytical grade.

## Statistical Analysis:

All statistical analyses were done by SPSS software 17.0 for windows.

## RESULTS AND DISCUSSION

To evaluate the accuracy and precision of the analytical procedure employed, standard reference material of Lichen coded IAEA -336 was analyzed in like manner to our samples. The analyzed values and the certified reference values of the elements determined were very close (Table 1), suggesting the reliability of the method employed.

The Mean concentration and standard deviation of Cadmium, Chromium, Manganese and Cobalt alongside pH and Temperature of water samples from the four established sampling points along River Galma, around Dakace Industrial Estate,  are presented in Table 2. The

**Table 2.** Physico-chemical parameters of water samples collected from River Galma round Dakace Industrial Estate, Zaria, Nigeria.

| Sampling Stations / Parameters | Sampling Point 1 | | Sampling Point 2 | | Sampling Point 3 | | Sampling Point 4 | |
|---|---|---|---|---|---|---|---|---|
| | Dry Season | Wet Season | Dry Season | Wet Season | Dry Season | Wet Season | Dry Season | Wet Season |
| pH | 6.63±1.05 | 6.78±0.18 | 6.44±1.23 | 6.69±0.10 | 6.54±0.99 | 6.67±0.30 | 6.26±1.40 | 6.65±0.28 |
| Temperature | 28.26±4.47 | 28.47±3.13 | 28.16±4.63 | 27.03±2.26 | 28.18±4.81 | 27.31±2.36 | 28.48±4.81 | 27.26±2.48 |
| Cadmium | 0.03±0.01 | 0.01±0.01 | 0.04±0.03 | 0.03±0.01 | 0.04±0.02 | 0.02±0.01 | 0.03±0.01 | 0.02±0.02 |
| Chromium | 0.26±0.27 | 0.24±0.12 | 0.44±0.30 | 0.20±0.07 | 0.28±0.25 | 0.13±0.12 | 0.21±0.19 | 0.30±0.02 |
| Manganese | 0.28±0.28 | 0.07±0.01 | 0.85±1.00 | 0.12±0.17 | 0.70±0..53 | 0.22±0.28 | 0.44±0.30 | 0.12±0.09 |
| Cobalt | 0.94±0.77 | 0.63±0.69 | 0.96±0.08 | 0.69±0.26 | 0.60±0.25 | 0.49±0.38 | 0.47±0.27 | 0.30±0.25 |
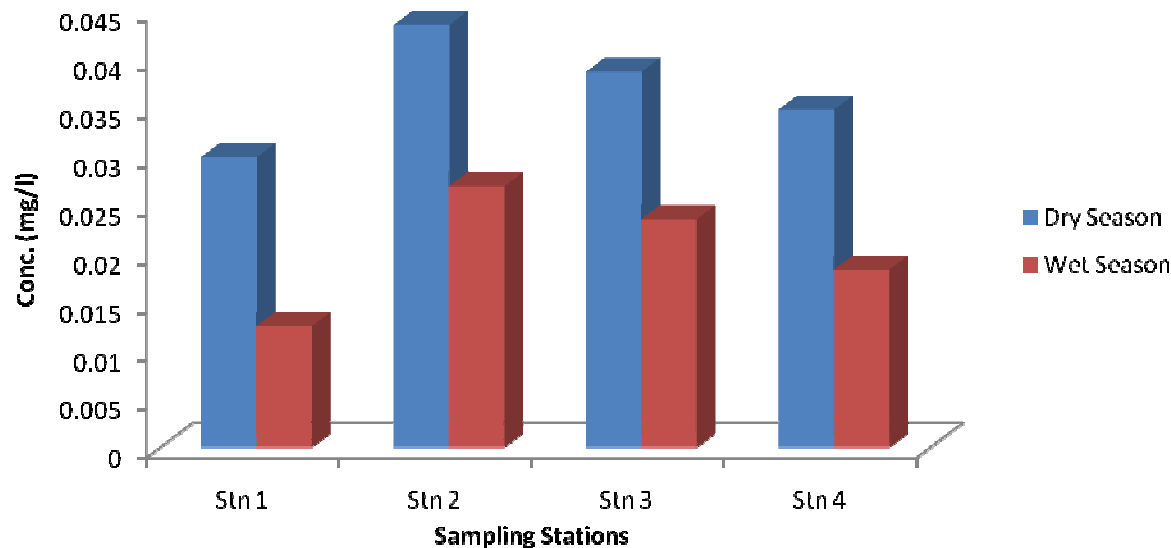


**Figure 2.** Spatio-seasonal variation of Cadmium in River Galma around Dakace industrial area, Zaria, Nigeria.

spatial and seasonal distributions of the elements in the river are shown in Figures 2, 3, 4 and 5 respectively.

The overall temperatures ranged from 21.4°C to 35.2°C with a mean value of 28.27±4.32°C during the dry season and from 22.3°C to 31.5°C with a mean value of 27.02±2.43°C during the wet season. The mean temperatures observed in the study were above World Health Organization (WHO) and European Union (EU) standard of 25°C for domestic water supply. Surface Water temperature above 40 °C depicts polluted water (FEPA 1991). The water temperature observed in this study is therefore within the permissible limit of water temperature for inland waters. Increase in temperature leads to increase in solubility. At high temperatures total dissolved solid is increased as more solute goes into solution (Udiba et al., 2013). No statistically significant seasonal or spatial variation in temperature was also observed in the study (ANOVA, P > 0.05). Similar temperatures have been reported for other rivers in Nigeria. Average temperatures of 28°C and 26°C were reported for River Ona and river Alaro in Ibadan, Nigeria (Osibanjo et al 2011). A mean temperature of 28.5°C was reported for down-stream area of River Galma while 25.7°C was recorded for upstream area of river Galm in 2011(Nnaji et al 2011). Udiba et al (2012) reported arrange of 25.5-31.4 for the Calabar river

estuary.

The pH of water is very important in the determination of water quality since it affects other chemical reactions such as solubility and metal toxicity (Udiba et al., 2013). pH ranged from 4.00 to 7.68 with a mean value of 6.47±1.09 in the dry season and from 6.17 to 7.00 with a mean value of  6.70±0,21 in the wet season.  Mean pH value was found to be higher in the wet season than dry season but the difference was not statistically significant at 95 % confidence level. All through, pH of surface water from station 1 (200 meters from the first identified effluent discharge point) fell within the pH range (6.5-8.5) assigned by assigned by World Health Organization (WHO) and United State Environmental protection Agency (US EPA) as standard pH of water, making it suitable for portability with respect to pH (US EPA, 211). Sampling stations 2, 3 and 4 recorded slightly acidic pH values that were outside the acceptable range of pH values for unpolluted waters in the dry season. This observation may be attributed to the discharge of effluents with low pH values into the river. A similar range of pH values (5.94-7.34) was reported for Calabar River (Udiba et al 2012). pH ranges of 7.43-7.60 and 6.88-7.59 were reported for River Ona and River Alaro in Ibadon, Nigeria (Osibanjo et al 2011). Mean value of 6.98±0.36 was reported for the downstream area of river Galma and 7.5±0.27 for the upstream area in 2011 (Nnaji et al 2011). pH has profound effect on water quality as it affects the solubility of metals, alkalinity and hardness of water. Metals tend to be more soluble and more reactive at lower pH.

Cadmium Concentration in the study ranged from 0.015 mg/l to 0.076 mg/l with a mean value of 0.037±0.017 mg/l during the dry season and from 0.00 mg/l to 0.04 mg/l with a mean value of 0.020±0.012 mg/l during the wet season (Table 2). The mean cadmium concentration per sampling points for the dry and wet seasons were 0.30±0.01 mg/l and 0.01±0.01 mg/l for station 1, 0.04±0.03 mg/l and 0.03±0.01 mg/l for sampling station 2, 0.04±0.02 mg/l and 0.02±0.01 mg/l for sampling station 3 and, 0.03±0.01 mg/l and 0.02±0.02 mg/l for sampling station 4 (Figure 2). The difference in cadmium concentration between dry and wet season was found to be statistically significant (P < 0.05), dry season's concentration being significantly higher than wet season concentration.  No statistically significant spatial variation in cadmium levels was also observed in the study (ANOVA, P > 0.05).  Sampling station 1 was established 200 meters upstream from the first point source to act as control. That the difference in cadmium concentration between sampling station 1 and the other sampling stations was not significant indicates that effluents discharged into the river from Dakace industrial estate did not have any significant influence on the overall cadmium levels of the River. Cadmium content of River Galma observed in this study was found to be higher when compared to World Health Organization (WHO) and the

Nigerian Standard for Drinking Water Quality (NSDWQ) of 0.003 mg/l for portable water (WHO, 1984; NSDWQ, 2007). The water thus poses serious toxicological risk with respect to cadmium intoxication. The mean cadmium concentration of River Galma for both wet and dry season was above the Australian and New Zealand Environment and Conservation Council limit of 0.01 mg/l for irrigation water (ANZECC, 2000). It follows therefore that the river is not fit for irrigation purposes as cadmium uptake by plants and subsequent transfer into the food chain cannot be completely ruled out. Cadmium accumulates in the kidney and liver causing kidney dysfunction and liver failure, interferes with the metabolism of Calcium and Phosphorus, causing painful bone diseases, in addition to being a teratogenic and carcinogenic agent. Eating food or drinking water with high Cadmium concentration irritates the stomach causing vomiting and diarrhea. Chronic exposure can also cause irreversible damage to the lungs (Udiba et al., 2013). A higher concentration of cadmium ranging from 0 to 0.39 mg/l and from 0.22 to 0.52 mg/l were reported for Warri River, Nigeria by Ayenimo  et al.,( 2005) and Owamah, (2013) respectively. Our observation is in agreement with Owamah (2013) who reported a range of 0.01to 0.05 for River Ikpoba  in Niger Delta, Nigeria.  A mean value of 0.05 ± 0.02 mg/l was reported for lower river Niger drainage in North central Nigeria (Olatunji and Osibanjo 2012). (Figure 2)

Chromium concentration in the present study fluctuated from 0.06 mg/l to 0.42 mg/l with a mean value of 0.30±0.24 in the dry season and from 0.04 mg/l to 0.37 mg/l with a mean value of 0.22± 0.10 mg/l in the wet season (Table 2). The mean concentration of chromium per sampling points for the dry and wet seasons were found to be 0.26±0.27 mg/l and 0.24±0.12 mg/l for sampling station 1, 0.44±0.30 mg/l and 0.20±0.07 mg/l for sampling station 2, 0.28±0.25 mg/l and 0.13±0.12 mg/l for station 3, and 0.21±0.19 mg/l and 0.30±0.02 mg/l for sampling station 4 (Figure 3). No statistically significant seasonal or spatial variation in chromium levels was observed in the study (ANOVA, P > 0.05). Chromium levels actually reached their maximum value in the month of February when the water level was considerably low and minimum value in the month of July at the peak of the wet season.  The fact that the difference in chromium levels between Sampling station 1 (control) and the other sampling stations downstream was not significant also indicates that, effluents discharged into the river from Dakace industrial estate had no significant influence on the overall chromium levels of the River. However the chromium content of River Galma observed in this study was found to be higher than the World Health Organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) of 0.05 mg/l (WHO, 1984; NSDWQ, 2007). The mean chromium concentration of River Galma was above the Australian and New Zealand Environment and Conservation Council
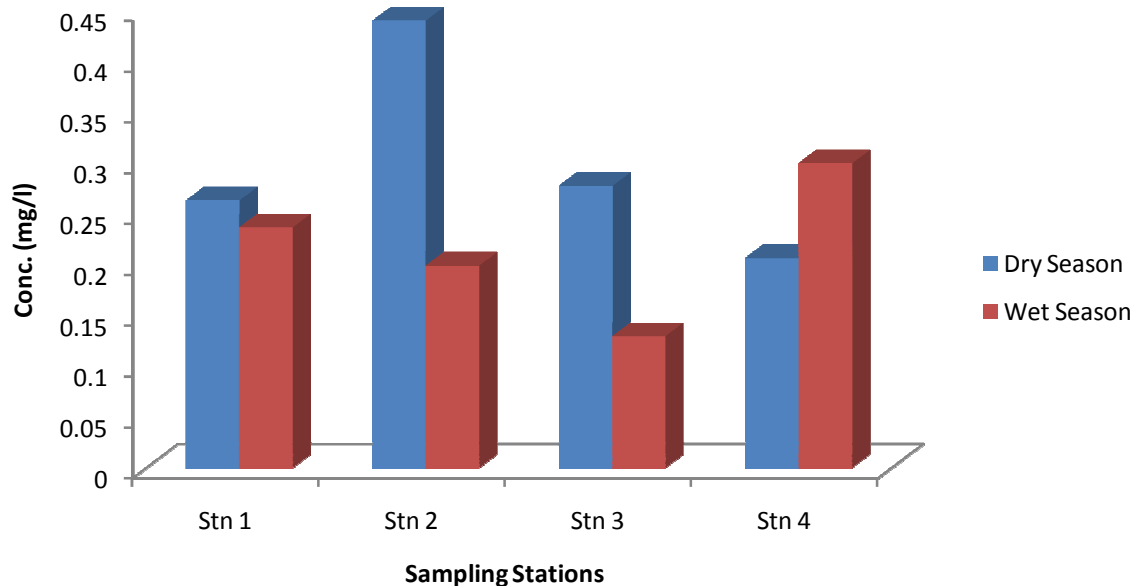
**Figure 3.** Spatio-seasonal variation of Chromium in River Galma around Dakace industrial area, Zaria, Nigeria

limit of 0.10 mg/l for irrigation water (ANZECC, 2000). The river therefore poses significant risk with respect to chromium contamination when used for domestic or agricultural purposes. Chromium (Cr) is considered an essential nutrient and a health hazard. Hexavalent chromium is considered harmful even in small intake quantity (dose) whereas trivalent chromium is considered essential for good health in moderate intake. Ingestion of high concentration of chromium (vi), often result in lung function and blood system problem, death may be the result of pulmonary or cardiac arrest. Ingestion of chromium (VI) also leads to gastrointestinal burns, hemorrhage, generalized oedema, Pulmonary oedema, liver damage and kidney damage that may ultimately lead to death. Other symptoms are diarrhea, ulcers, abdominal pain, indigestion, and vomiting (ATSDR, 2000; Udiba et al., 2012). Lower chromium concentration ranging from 0.01 to 0.14 mg/l was reported for Warri River (Ayenimo et al., 2005) and 0.11 to 0.17 mg/l for River Ikpoba, in Niger Delta, Nigeria (Owamah, 2013). Higher concentration ranging from 0.213 to 0.924mg/l was reported for River challawa, Kano, Nigeria (Dan'azumi and Bichi, 2012) and 0.33 to 1,56mg/l for River Warri, Niger Delta, Nigeria (Owamah, 2013). A mean value of 2.08 ± 1.27 mg/l was reported for lower river Niger drainage in North central Nigeria (Olatunji and Osibanjo 2012).

The results obtained in the present study showed that manganese content in water samples ranged from 0.08 mg/l to 2.00 mg/l with a mean value of 0.57±0.56 mg/l during dry season and from 0.01 mg/l to 0.54 mg/l with a mean value of 0.12±0.16 mg/l during the wet season (Table 2). The mean manganese concentration per sampling points for the dry and wet seasons were

0.28±0.28 mg/l and 0.07±0.01 mg/l for station 1, 0.85±1.00 mg/l and 0.12±0.17 mg/l for sampling station 2, 0.70±0.53 mg/l and 0.22±0.28 mg/l for sampling station 3 and, 0.44±0.30 mg/l and 0.12±0.09 mg/l for sampling station 4 (Figure 4). Statistically significant ($P < 0.05$) seasonal variation was observed in the study, manganese concentration in the dry season being significantly higher than wet season concentration. manganese concentration was slightly higher at sampling stations 2 and 3 (the point sources) when compared to sampling station 1(200 meters before the effluent discharge points) suggesting anthropogenic input but the variation was not statistically significant (ANOVA, $P > 0.05$) indicating that the influence of industrial activities at Dakace industrial estate on the manganese levels of river Galma was not statistically significant. Except at the peak of the wet season when the average levels was slightly less than the Nigerian Standard for Drinking Water Quality (NSDWQ) maximum allowable limit, manganese concentration recorded in the study was found to be above the maximum contaminant Levels of 0.05mg/l and 0.2mg/l established by US Environmental Protection Agency (US EPA) and the Nigerian Standard for Drinking Water Quality (NSDWQ) respectively (US EPA, 2011; NSDWQ, 2007). The Australian and New Zealand Environment and Conservation Council's limit for manganese for Irrigation water is 0.2 mg/l (ANZECC, 2000). River Galma around Dakace industrial estate is thus fit for irrigation purposes only at the peak of the wet season. Manganese is a redox sensitive metal that can exist in water as the manganese (II) ion ($Mn^{2+}$), or in the oxidized state as manganese (IV) ion ($Mn^{4+}$). Mangaese in water can be significantly bioconcentrated by aquatic biota at lower trophic levels. Uptake by aquatic
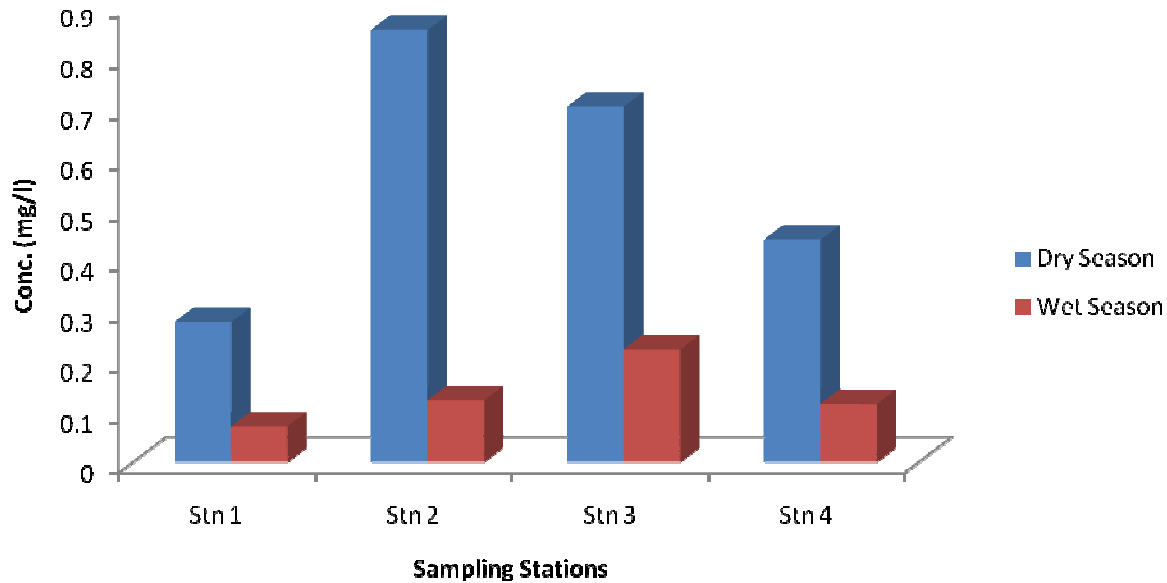
**Figure 4.** Spatio-seasonal variation of Manganese in River Galma around Dakace industrial area, Zaria,Nigeria
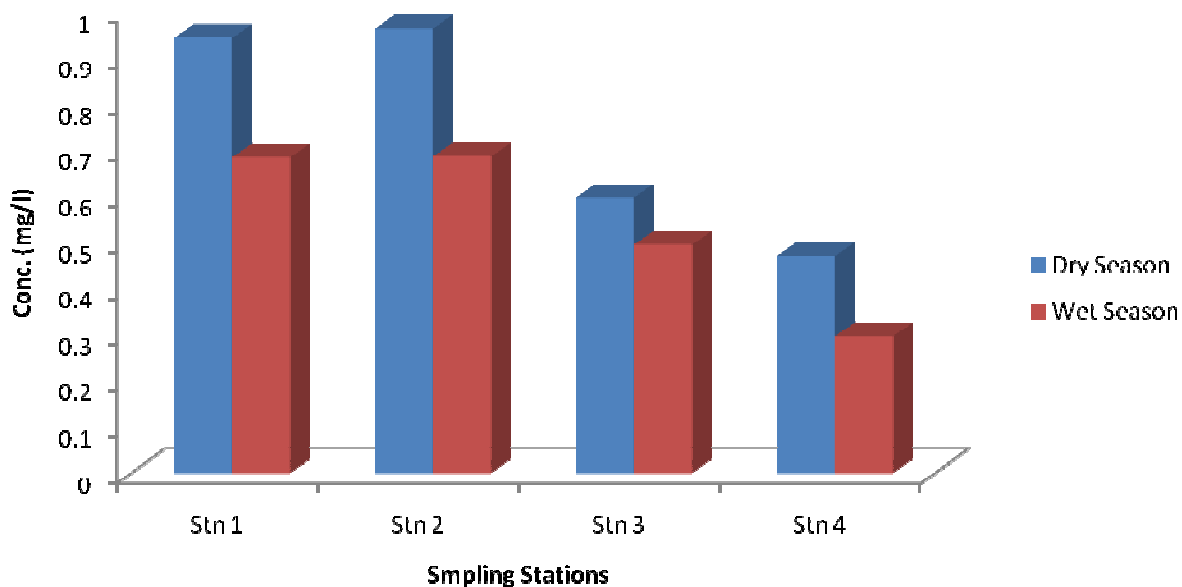


**Figure 5.** Spatio-seasonal variation of Cobalt in River Galma around Dakace industrial area, Zaria, Nigeria

invertebrates and fish greatly increases with temperature and decreases with pH, subsequent transfer to man higher up in the food chain cannot therefore be ruled out. In its worst form, Manganese toxicity can result in a permanent neurological disorder with symptoms similar to those of Parkinson's disease, including; tremors, difficulty in walking, and facial muscle spasms. Individuals with chronic liver disease are uniquely susceptible to Manganese toxicity (Udiba, 2013; Keen, 2001). Our observation is in agreement with Dan'azumi and Bichi (2012) who reported manganese concentration ranging from 0.249 to 1.681 mg/l for River Challawa in Kano

Nigeria. A mean value of 3.85± 0.93 mg/l was reported for lower river Niger drainage in North central Nigeria (Olatunji and Osibanjo 2012).

Cobalt concentration ranging from 0.17 to 1.83 mg/l with a mean value of 0.74±0.43 mg/l in the dry season and from 0.10 to 1.47 mg/l with a mean value of 0.54±0.41 mg/l in the wet season was recorded in the study (Table 2). The mean cobalt concentration per sampling points for the dry and wet seasons were 0.94±0.77 mg/l and 0.63±0.69 mg/l for station 1, 0.96±0.08 mg/l and 0.69±0.26 mg/l for sampling station 2, 0.60±0.25 mg/l and 0.49±0.38 mg/l for sampling station 3

and, 0.47±0.27 mg/l and 0.30±0.25 mg/l for sampling station 4 (Figure 5). Cobalt concentration in the dry season was found higher than the wet season but the difference was not statistically significant at 95% confident level. The decrease in cobalt levels during the wet season may be as a result of dilution due to large volume of water in the wet season. The difference in cobalt levels across the sampling stations was not statistically significant (ANOVA, P > 0.05). Cobalt content of water samples from River Galma was found to be higher than both the World Health Organization (WHO) standards for drinking water quality of 0.05mg/l (WHO, 2008) and the Australian and New Zealand Environment and Conservation Council's limit of 0.05 mg/l for irrigation water (ANZECC, 2000). The use of this water for drinking and irrigation purpose therefore constitutes serious health and environmental risk with respect to cobalt intoxication. Cobalt is found to have reproductive and developmental effect in animals. Bronchial asthma, cardiomyopathy, lungs diseases, eye, nose and throat irritation are some of the effects of cobalt toxicity (Kinn et al., 2006). Lower concentration ranging from 0 to 0.05 ppm was reported for Warri River (Ayenimo et al., 2005), 0.11 to 0.14 mg/l also for Warri River, Niger Delta, Nigeria (Owamah, 2013)and 0.01 to 0.04 mg/l for river Ikpoba, in Niger Delta, Nigeria (Owamah, 2013).

Metals concentration in River Galma around Dakace industrial layout followed the trend Cobalt > Manganese > chromium > cadmium. A statistically significant positive correlation was observed between chromium and manganese (r = 772) at 99 % confidence level and between chromium cobalt (r = 478) at 95 % confidence level indicting that increase in chromium concentration is associated with increase in the concentration of manganese and cobalt. This suggests that same source may be responsible for the present of these three elements at concentration determined.

## CONCLUSION

The present study has shown that River Galma is contaminated and that effluents discharged into the river from Dakace industrial estate had no significant influence on the overall Cadmium, chromium, manganese and cobalt contents of the River. Surface water temperatures were found to be above World Health Organization (WHO) standards for domestic water supply but below 40 °C which depicts polluted water. The water was generally acidic in the dry season. Concentrations of Cadmium, chromium, manganese and cobalt were found to be above World Health Organization (WHO) and Nigerian Standard for Drinking Water Quality (NSDWQ). The Australian and New Zealand Environment and Conservation Council's guidelines for irrigation waters showed that water from the river is not fit for Irrigation purposes. Use of the water under study for domestic and

agricultural purposes thus poses serious toxicological risk.

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