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Impact of Tannery and Textile Effluent on the Chemical Characteristics of Challawa River, Kano State, Nigeria

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Abstract: The impact of effluent from tanneries and textile on the chemical characteristics of Challawa River was carried out for a periods of one year. Water samples were collected on quarterly basis beginning from the months of June to September, 2007 (Rainy season), November, 2007 – February, 2008 (Harmattan period) and March – May, 2008 (Dry season) to reflect the seasonal factors. Water samples from these areas were collected and designated S_1 to S_8 for the determinations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), Dissolved oxygen (DO) total dissolved solid (TDS), anions and trace element. These parameters were determined using standard procedures. The concentrations of BOD (40.20±42.65 to 33.91 ±678.36mg/l.), COD (158.00 ±3439.11 to 15.41 ±210.33mg/l), %TOC (0.21 to 5.54 %) were higher than the WHO limits for the protection of fish and other aquatic life. The concentrations of heavy metals in the water and sediment samples were higher than the WHO guideline values for the protection of aquatic life. This is expected owing to its location close to tanneries and textile industries. Results of Analysis of variance (ANOVA) results revealed that BOD, COD, DO, TOC, TDS, nitrate, nitrite, sulphate, phosphate, heavy metals and chloride were significantly different among the sampling points and seasons with exception of point S_1-S_3 where the was no marked seasonal variations. Point S_5 which is the control point (upstream) recorded the lowest concentrations for all the parameters studied. The relationship between %TOC with BOD and COD; TDS with BOD and COD were also observed. The Pearson linear correlation analysis showed that the mean concentrations of heavy metals in the water and sediment samples revealed significantly positive correlated values. Base on the above results, the study underscores the need for immediate remediation programs to control the discharged of tanneries and textile effluent into Challawa River.

Key words: Impact, Tannery and Textile Effluent, Chemical Characteristics, Challawa River.

INTRODUCTION

According to the Nigerian Federal Ministry of Environment (FME), there were 39 tanning industries around Kano Metropolis by the year 2001 that discharged their liquid and solid wastes into the immediate environment (consisting of land and water bodies). Chemical fertilizers are very expensive in the open market, which, according to Abubakar et al. (2004), is the main source of fertilizer for about 96% of farmers in Kano State. Government supplies and subsidy on fertilizers are by far inadequate, and so farmers resort to applying tannery sludge to 'fertilize' their crops particularly cereals. The tannery sludge is a combination of hair, fleshings, shavings, splits, hide/skin trimmings, leather trimmings, buffing dust, leather finishing residues, general plant wastes, and waste water treatment sludge (Owoeye, 1993; FME, 2001). Tannery sludge could be an excellent material for soil amendment as it was found to improve the physical properties of soil and contain considerable amounts of plant nutrients (Frank, 1998; Naidu et al., 1998; Tudunwada, 1998; Ogbonna et. al., 1998; Tiredstorm, 1997; Lewcock, 1994; Carre et al., 1983). According to Imamul Huq (1998), various chemicals are used during the soaking, tanning and post tanning processing of hides and skins. The main chemicals used include sodium sulphite and basic chromium sulphate including non-ionic wetting agents, bactericides, soda ash, CaO, ammonium sulphide, ammonium chloride and enzymes. Others are sodium bisulphate, sodium chlorite, NaCl, H_2SO_4, formic acid, sodium formate, sodium bicarbonate, vegetable tannins, syntans, resins,

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polyurethane, dyes, fat emulsions, pigments, binders, waxes, lacquers and formaldehyde. Various types of processes and finishing solvents and auxiliaries are used, as well. It has been reported that only about 20% of the large number of chemicals used in the tanning process is absorbed by leather, the rest is released as waste (UNIDO, 2005). Tanneries have been found to discharge not only Cr which is an inherent product of the tanning process but also significant amounts of Zn, Mn, Cu and Pb have been observed at the main waste disposal points exceeding the toxic range in soils (Imamul Huq, 1998). Ogbonna et al. (1998) reported that the wastes from the leather industry consist of tanned and untanned solids, waste waters (effluent) including the sludge and waste gases.

The sludge derived from the treatment of tannery effluent varies in composition but usually contains water (65-98%), lime, Cr, hydrate oxide, residual sulphides and organic matter (proteins, hair and grease). Common mineral elements such as Al, Fe, Ca, Na, K and Si are present in significant quantities in sludge. It may also contain trace elements and heavy metals such as Cd, Pb, Hg, As, Cr, Cu, Ni, Zn, B, Se, Mo as well as N and P in both organic and inorganic forms Ogbonna et al. (1998). Eventually the effluents and sludge from these operations are discharged onto land and into water bodies. The high sulphide content of tannery sludge, apart from being toxic, poses serious odour problems in the environment. The dissolved and suspended solids of the effluent would affect the quality of nearby streams, in addition to reduced clarity. There is also a great danger to man and livestock particularly from the high Cr content (Cr6+ has been found to be toxic to humans at levels as low as 0.1 mg/l (UNIDO, 2005).

Kano (Lat. 11^{O} 59m 18.3s N, Long 08^{O} 32m 05.8s E) 418meters above sea level is located in Kano State; it occupies a central position in Northern Nigeria. It is one of the developed industrial cities in Nigeria. Tannery and textile are some of the dominating industries and this could be one of the reasons for her high population density (Olanrewaju, 2001). River Challawa (Lat 11^{O} 52m 41s N, Long 08^{O} 28m 09s E) 515meters above sea level originates from the Challawa Gorge dam in Challawa village and stretches to River Kano that empties into Lake Chad. The river receives waste from tanneries and textile industries, urban water storm, and agricultural runoffs from farming communities along its course. River Challawa serves as fishing, farming and water supplies for the communities in the area. The domestic water supply for Challawa, Sharada, and Bompai industrial areas and the surrounding comes from River Challawa (Felsner, 2003). Hence, the need to monitor the pollutant levels of these areas.

MATERIALS AND METHODS

Sample and Sampling:

Samples were from Kano industrial area, industries from these areas discharge their effluents into canals, which converge at a confluent point and flow into the River Challawa. Water samples from these areas were collected and designated S_1 to S_8. Samples were collected from the confluence point at Challawa industrial estate (S_1); 300metres away from confluence point (S_2); and at 600metres away from confluence point (S_3). For River Challawa, water and sediment samples were collected at immediate point of effluent discharge from Challawa industrial estate into it (S_4); 200metres up-river from the discharge point into the river (S_5); 2 Km after effluent discharge point into river Challawa (S_6); 4 Km after effluent discharge point into river (S_7); and the new water work after effluent discharge point into river Challawa (S_8) which is 7Km.

Sediments samples from river Challawa (points S_4 to S_8) were collected using a plastic hand-trowel by scooping the top layer sediments (0.2cm dept). About 500-1kg of sediment samples were collected at each point, stored in polyethylene bags, labeled and transported to the laboratory for storage in freezers.

Determination of Organic Pollutant Indicators:

Dissolved oxygen of the effluent samples was determined using Jenway Model 9070 waterproof DO meter. The protective cap of the DO meter was removed from the probe. Membrane module was taken and held in the vertical position. The probe was calibrated prior to measurement with the appropriate traceable calibration solution of 5% sodium sulphate in accordance with the manufacturer's instruction. The probe was immersed into the effluent samples to be analyzed and the readings were recorded at the point of sample collection.

The biochemical oxygen demand (BOD) determination of the water sample in mg/l was carried out using the standard methods (1976). The dissolved oxygen content was determined before and after incubation. Sample incubation was for 5 days at $20^{O}C$ in BOD bottle and BOD_5 was calculated after the incubation period. Determination of chemical oxygen demand (COD) was carried out according to the method described by Ademoroti (1996). COD was determined after oxidation of organic matter in strong tetraoxosulphate VI acid medium by $K_2Cr_2O_7$ at $148^{O}C$, with back titration. Levels of total dissolved solid (TDS) was determined by using a C0150 conductivity meter at the point of sample collections.

Determination of total organic carbon was carried out according to the method described by Ademoroti (1996). The dried sediment sample was finely pulverized and 0.2grams was weight into 500ml conical flask, 10 ml of 0.5M $K_2Cr_2O_7$ was added and swirl gently. Concentration H_2SO_4 (20ml) was carefully into the suspension. The mixture was immediately swirled gently and allowed to stand for about 40 minute. Distilled water of 200ml was added follow by careful addition of 10ml concentration H_3PO_4. The mixture was allowed to cool, and three drops of ferroin indicator was added and this was then titrated with 0.25M FAS to wine-red end point.

A blank titration was carried out using the same procedure as above but without sediment sample. The %TOC of the sediments was obtained using the following expression (Ademoroti, 1996):

$$\% \text{ TOC} = \frac{(Vb - Vs) \times M \times 1.38}{W}$$

V_b = Volume of FAS for Blank, Vs = Volume of FAS for sample, M = Morality of FAS
W = Weight of the sample in gramme

Determination of Heavy Metals in Water and Sediment Samples:

The water samples were digested as follows. The samples ($100cm^3$) were transferred into a beaker and 5ml concentrated HNO_3 was added. The beaker with the content was placed on a hot plate and evaporated down to about 20ml. The beakers were cooled and another 5ml of concentrated HNO_3 was added. The beakers were covered with watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO_3 was added until the solutions appear light coloured and clear. The beaker wall and watch glass were washed with distilled water and the samples were filtered to remove some insoluble materials that could clog the atomizer. The volume of the samples was adjusted to $100cm^3$ with distilled water (Radojevic and Bashkin, 1999). A blank sample was digested so as to allow a blank correction to be made. This was done by transferring 100ml of distilled water into a beaker and digested as described above.

All sediment samples were oven dried at 80 to 100^oC, gentle crushed and sieved to collect < 63 µm grain size. Accurately (1g) of the sediment samples were weighed into acid washed glass beaker. Sediment samples were digested by the addition of $20cm^3$ of aqua regia (mixture of HCl and HNO_3, ratio 3:1) and $10cm^3$ of 30% H_2O_2. The H_2O_2 was added in small portions to avoid any possible overflow leading to loss of material from the beaker. The beakers were covered with watch glass, and heated over a hot plate at 90^oC for two hours. The beaker wall and watch glass were washed with distilled water and the samples were filtered out to separate the insoluble solid from the supernatant liquid. The volumes were adjusted to $100cm^3$ with distilled water. Blank solutions were handled as detailed for the samples.

Determination of Cu, Zn, Co, Mn, Mg, Fe, Cr, Cd As, Ni and Pb were made directly on each final solution using Perkin-Elmer AAnalyst 300 Atomic Absorption Spectroscopy (AAS) as described by Floyd and Hezekiah (1997).

Determination of Some Anions in Water Samples:

The concentration of nitrate, nitrite, sulphate and phosphate were determined using a DR/2010 HACH Portable Data Logging Spectrophotometer. The spectrophotometers were checked for malfunctioning by passing standard solutions of all the parameters to be measured; Blank samples (deionized water) were passed between every three measurements of water samples to check for any eventual contamination or abnormal response of equipment. Nitrate as N was determined by the cadmium reduction metal method 8036 (Standard methods, 1976., DWAF, 1992). The cadmium metal in the added reagent reduced all nitrate in the sample to nitrite; while sulphate was determined by using Sulfa Ver methods 8051 (Standard methods, 1976., DWAF, 1992).

In the determination of chloride, one hundred (100) milliliters of the water sample was measured into a 250ml conical flask and pH was adjusted to 8 with 1M NaOH. One ml of K_2CrO_4 indicator was then added and titrated with the $AgNO_3$ solution. A blank titration was carried out using distilled water. Chloride (mg/l) was calculated as follows (Ademoroti, 1996).

$$\text{Chloride (mg/l)} = 70900 \times M \frac{(V_1 - V_2)}{Vs}$$

V_1 = Volume of titrant for the sample, V_2 = Volume of titrant for the blank
M = Molarity of $AgNO_3$, Vs = Volume of sample used (100ml)

RESULTS AND DISCUSSION

The mean seasonal DO levels for samples analysed for point S_1 to S_8 are as presented in Figure 1. Point S_1 to S_8 decrease in the order $S_1 > S_2 > S_3 > S_4 > S_6 > S_7 > S_8 > S_5$. They were decrease in concentration from point S_1 to S_3, but no significant seasonal were observed during the sampling periods. Marked variations in dissolved oxygen among sampling points and seasons (point S_4 to S_8) along the river. The low values of dissolved oxygen (DO) in River Challawa when compared with the control (point S_5) might be due to influx of untreated effluents into the river, while the decrease in values from point S_4 to S_8 might be attributed to dilution, sedimentation and depuration factor due to immense volumes of fresh water. The seasonal variation between point S_4 to S_8 are in the following order rainy season > Harmattan period > dry season. The high levels of DO during the rainy and harmattan period might be attributed to dilution of the effluent by fresh water and due to lower temperature despite the fact that pollutant load may be high but has less adverse effect, while the low values within the dry season along Challawa River could be ascribed to lower oxygen carrying capacity in warmer water and increased bacterial multiplication due to high temperature. The low values of DO observed may also be due to the nature of the effluents discharge into the water from tanneries and textile industries that places a high demand on the dissolved oxygen there by reducing the levels of dissolved oxygen. DO contents in all the sampled points were above the safety limits for maintenance of aquatic life of 5.00mg/l. The mean BOD levels for samples analysed for point (S1-S8) are shown in Figure 2. The concentrations of BOD for point S1 to S8 ranged from 67.88±23.25 to 665.67±46.21 mg/l for rainy season (June - September, 2007)., 52.40±52.25 to 656.48±34.93 mg/l Harmattan period (November 2007 – February 2008)., 40.20±42.65 to 678.36±33.91 mg/l for dry season (March – may 2008). While the concentrations of COD for point S_1 to S_8 ranged from 3442.10±161.70 to 234.00±17.23 mg/l for rainy season (June - September, 2007)., 3449.00±166.70 to 216.23±18.45 mg/l Harmattan period (November 2007 – February 2008)., 3439.11±158.00 to 210.33±15.41 mg/l for dry season (March – May 2008) Figure 3. The percentage of total organic carbon in the sediment samples are presented in Figure 4. The percentage of TOC for points S4 to S8 ranged from 0.25 to 4.00 % for rainy season (June - September, 2007)., 0.32 to 4.76 % Harmattan period (November 2007 – February 2008)., 0.21 to 5.54 % for dry season (March – may 2008).

Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values were higher at the confluence point (S_1) and decrease toward point S_3. No significant seasonal variations were observed between point S_1-S_3, which shows an almost constant flow of effluent during the sampling periods. Significant variation was observed for points S_4 to S_8 (Challawa River). Point S_5 (control) recorded the lowest values of BOD, COD and TOC, while point S_4 recorded high value, which indicate high organic load. The high values BOD, COD and TOC in points S_4, S_6, S_7 and S_8 when compared with the control (point S_5) might be due to influx of untreated effluent from tanneries and textile industries which contain higher organic matter into the river, while the decrease in values from point S_4 to S_8 might be attributed to dilution, sedimentation and depuration factor due to immense volumes of fresh water.

The seasonal variation BOD, COD and TOC between point S4 to S8 are in the following order rainy season < Harmattan period < dry season. The high levels of BOD, COD and TOC during the dry and harmattan period might be attributed to reduction in the volume of water and the addition of both organic and inorganic substances from tanneries and textile industries within these areas, while the low levels of BOD, COD and TOC during the rainy seasons might be attributed to dilution of the effluent by fresh water during the rainy seasons. Generally, the BOD and COD levels recorded in the entire sampling points were higher than the EU guidelines of 3.0 to 6.0 mg/l (BOD) and 200mg/l (COD) for the protection of fisheries and aquatic life and for domestic water supply (Chapman, 1996).

Total organic carbon content for sediments are usually recycled or fixed by the biological and chemical agents both within the sedimentary compartment and in the water column (Sadasivan and Baskin, 2000). This suggests that the BO and TOC are related as illustrated in Figure 5.

An attempt was made to investigate any relationship between Biochemical oxygen demand (DO) and Dissolved oxygen (DO). The correlation coefficient as shown in Figure 6 and 7 revealed an inverse linear correlation showing that as BOD and COD increases in values DO decreases with correlation of $r = -0.93$ and $r = -0.90$. The correlation of -0.93 and -0.90 between BOD, COD and DO suggest similar sources.

The seasonal mean TDS levels for samples analyzed for points S_1 to S_8 are as presented in Figure 8. Total dissolved solid (TDS) value was higher at the confluent point (S_1) and fluctuates between 6300.20±121.23 to 6384.54±134.22 mg/l and decreases toward point S_3. No significant seasonal variation between locations S_1-S_3 were observed, which shows that there were almost constant flow of effluent from the industries during the sampling periods or the activities of these industries remained almost constant throughout the sampling periods.

Significant variations were observed for point S_4 to S_8. The mean TDS value (1121.65±125.00 to 1453.12±111.70 mg/l) obtained for point (S_5) is low since this location serves as control. The high values of TDS at points S_4, S_6, S_7 and S_8 when compared with the control (point S_5) might be due to influx of untreated effluent from tanneries and textile industries which originate from all stage of leather making; they comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors into the river, the impact of an effluent on the receiving river is predicted by its dissolved oxygen (DO). While the decrease in values from point S_4 to S_8 might be attributed to dilution, sedimentation and depuration factor due to immense volumes of fresh water. However, the TDS levels recorded in the entire sample points were higher than the WHO guideline of 1000mg/l for the protection of fisheries and aquatic life and for domestic water supply. The relationship between mean dissolved oxygen (DO) and total dissolved solid (TDS) in the effluent are as presented in Figure 9, while TDS and BOD are as presented in Figure 10. A plot of DO and TDS gives an inverse linear correlation showing that as TDS increases in values DO decrease. The TDS values were noted to be high corresponding to low DO values. The finding is in line with what (Ademoroti, 1996) reported that a low DO usually depicts a high TDS values. The plot of DO against TDS values also emphasized this fact, with correlation of r = -0.96. From the graph an increased in TDS correspond with a decrease in DO. High TDS concentration also corresponds to high COD Figure 11. A plot of TDS versus BOD, COD gives a linear correlation showing that as TDS increase BOD and COD also increase. These correlation shows that levels of TDS, BOD and COD are affected by same activities within the study area.

The mean seasonal variations of heavy metals concentrations in all the sample points under study are as illustrated in Figure 12. The concentrations of all the metals were higher at the confluence point (S_1) and decreases toward point S_3 throughout the sampling seasons. No significant seasonal variation between points S_1-S_3 were observed, which shows that the activities of these industries remain almost constant throughout the sampling periods. No significant variation was observed for points S_4 to S_8 (Challawa River). The levels of all the heavy metals reported for point (S_5) were low.

The mean concentrations of heavy metals in water samples for points S4, S6, S7 and S8 were 2.54 to 5.25 mg/l for Cr; 0.63 to 1.11 mg/l Mn; 0.83 to 2.33 mg/l Mg; 0.22 to 1.33 mg/l Fe; 0.23 to 1.26 mg/l Cu; 0.45 to 1.00 mg/l Co; 0.17 to 0.34 mg/l As, 2.11 to 12.00 mg/l Ni; 1.22 to 2.34 mg/l Pb; 0.91 to 4.21 mg/l Zn; and 0.07 to 1.00 mg/l Cd for rainy season (June - September, 2007). 3.11 to 6.33 mg/l for Cr; 0.89 to 1.87 mg/l Mn; 1.65 to 3.44 mg/l Mg; 0.33 to 2.33 mg/l Fe; 0.63 to 1.98 mg/l Cu; 0.44 to 1.22 mg/l Co; 0.19 to 0.46 mg/l As; 3.12 to 7.22 mg/l Ni; 1.45 to 2.99 mg/l Pb; 1.33 to 3.55 mg/l Zn; and 0.23 to1.00 mg/l Cd for Harmattan period (November 2007 – February 2008). 4.65 to 9.11 mg/l for Cr; 1.55 to 2.44 mg/l Mn; 1.65 to 3.44 mg/l Mg; 1.22 to 3.66 mg/l Fe; 0.88 to 2.00 mg/l Cu; 0.66 to 1.22 mg/l Co; 0.19 to 0.46 mg/l As, 4.22 to 9.33 mg/l Ni; 1.66 to 3.22 mg/l Pb; 2.54 to 4.76 mg/l Zn; and 0.45 to 1.55 mg/l Cd for dry season (March – May 2008).

The mean concentrations of heavy metals in sediment samples at points S4, S5, S6, S7 and S8 are presented in Figure 13. Which ranged from 54.00 to 1453.00 µg/g for Cr; 52.00 to 1095 µg/g Mn; 52.2 to 87.00 µg/g Mg; 54.00 to 1543 µg/g Fe; 51.00 to 1932 µg/g Cu; 51.23 to 456 µg/g Co; 45.76 to 654.00 µg/g As, 55.00 to 2321.00 µg/g Ni; 48 to 1023.00 µg/g Pb; 46 to 987.00 µg/g Zn; and 33 to 87 .00 µg/g Cd for rainy season (June - September, 2007). 34 to 1675 µg/g for Cr; 44.00 to 1321.00 µg/g Mn; 36 to 97 µg/g Mg; 34.54 to 1765.21 µg/g Fe; 32.00 to 2111.21 µg/g Cu; 33 to 488.33 µg/g Co; 34 to 688 µg/g As; 32.11 to 2576 µg/g Ni; 45.87 to 1232.00 µg/g Pb; 32.55 to 1102.22 µg/g Zn; and 24.21 to 99.65 µg/g Cd for Harmattan period (November 2007 – February 2008). 24.56 to 1897.21 µg/g for Cr; 28.43 to 1543.21 µg/g Mn; 26.23 to 123 µg/g Mg; 27.54 to 2341.33 µg/g Fe; 27.31 to 2777.32 µg/g Cu; 25.32 to 533.43 µg/g Co; 27.54 to 733.65 µg/g As, 29.43 to 2987 µg/g Ni; 29.00 to 1432.44 µg/g Pb; 27.65 to 1322.61 µg/g Zn; and 27.88 to 132.44 µg/g Cd for dry season (March – May 2008).

The seasonal variation in the concentrations of heavy metals between points S4 to S8 are in the following order rainy season <Harmattan period <dry season. The higher levels of heavy metals during the dry and harmattan period might be attributed to reduction in the volume of water and the addition of tanneries and textile effluent, while the low levels of these metals during the rainy seasons might be attributed to dilution of the effluent by fresh water. The levels of all the metals in the sediment samples were higher than that of the water samples, this variation may be attributed to the fact that sediments usually serve as repository of element in aqueous environment. This conforms to report by Stephen *et al.,* (2001), that sediment could act as sink for a wide range of contaminant including heavy metals from various sources.

Chromium concentration was generally very high in all the water and sediment samples analysed. Chromium is a relatively scarce metal that occurs in several states. The most toxic of these states is the chromium VI or hexavalent state. According to WHO/USEPA guideline value, the concentration values of 0.1

mg/l (water) and 25 µg/g (sediment) Cr is acceptable (Radojevic and Bashkin, 1999). The values above 0.1 mg/l and 25 µg/g a condition known as allergic dermatis could result (EPA, 1999). From the result of these analyses, the concentrations of chromium in water and sediment samples exceeded the regulating limits, indicating severe pollution of Challawa River by chromium.

Iron concentration was generally very high in the entire sample analyzed. Although, iron is one of the essential elements in human nutrition, however, their presence at elevated concentration in aquatic ecosystems, poses serious pollution and health problems. Toxicity of iron in humans has been found to bring about vomiting, cardiovascular collapse and diarrhoea. While iron deficiency may lead to failure of blood clotting to replenish (Turnland, 1988). According to USEPA guideline value and maximum contaminant level, concentration values of 0.30 mg/l (water) and 30 µg/g (sediment) Fe is acceptable (Radojevic and Bashkin, 1999). Above 0.3 mg/l and 30 µg/g a condition known as haemo-chromatosis could result. From the result of this study, the concentration of iron in water and sediment samples exceeded the guideline limit by a factor of 45% indicating severe pollution of Challawa River.

Lead is a non-essential trace element (Ewers and Schlipkoter, 1991). The toxicity of lead is dependent on the life stage of the organism, and the presence of organic material (Hellawell, 1986). Decreases in water pH can increase the bioavailability of lead in the system (Hellawell, 1986). Lead in aquatic environment is risky to life since aquatic organisms used as food are particularly very sensitive to lead and often retain about a percent of ingested lead which could be taken up by man through the food chain (Ewers and Schlipkoter, 1991). Lead can cause damage to the nervous system and the kidneys and it is suspected to be carcinogenic (Radojevic and Bashkin, 1999). Children exposed to high lead levels are particularly at risk. The levels of lead in the analyzed water and sediment samples showed that the limiting values by USEPA of 0.01 mg/l and 40 µg/g respectively were exceeded, indicating contamination of Challawa River and may pose a hazard to the aquatic biota. The presence of lead in Challawa River may be attributed to anthropogenic discharge of lead waste from industrial processes within this area.

Copper is a common environmental metal and is essential in cellular metabolism but at high concentrations it can be highly toxic to fish (Grosell *et al.,* 1997). Copper is an essential substance to human life, however, in high concentrations, it can cause anaemia, liver and kidney damage, stomach and intestinal irritation (Turnland, 1988). Copper is generally remobilised with acid-base ion exchange or oxidation mechanism (Gomez Ariza *et al.,* 2000). Long term exposure of copper may lead to liver and kidney damage (EPA, 1999). The levels of copper in the water and sediment samples were above the (WHO, 2004) standard values of 1.00 mg/l and 25 µg/g respectively for the survivor of aquatic organism.

Zinc is equally an essential element in the human diet. Zn deficiency in the diet may be more detrimental to human health than too much of it in the diet (ATSDR, 1994). In aquatic ecosystem, Zn is highly toxic to some aquatic organisms. Although Zn is not a human carcinogenic, ingestion of large doses can cause death (ATSDR, 1994). Zinc is also an essential micronutrient for all organisms and forms the active site for various metalloenzymes (DWAF, 1996). Excessive intake of Zn may lead to vomiting, dehydration, abdominal pain, nausea, lethargy and dizziness (ATSDR, 1994). The levels of Zinc in the water and sediment samples exceed the WHO guideline value of 3.00 mg/l and 123 µg/g. However, locations S4 to S8 did not exceed the USEPA maximum contamination levels of 5.0 mg/l for water samples.

Cobalt is an essential element which could be introduced anthropogenically into aquatic ecosystem as runoff from industrial activities. The levels of copper in the water and sediment sample did not exceed the WHO guideline value of 2.00 mg/l and 56 µg/g (location S4 to S8). This means that cobalt was relatively less in the water and sediment samples than other heavy metals. The toxicity of potentials of copper are quite low compared to many other heavy metals. However, exposure to very high doses could cause severe health effect.

The levels of nickel were spatially and temporary high in the water and sediment samples. The concentration of nickel in water and sediment were higher coming second after Cr. A comparism of Ni concentration in the water and sediment samples with WHO guideline values of 0.02 mg/l and 20 µg/g respectively, and USEPA maximum concentration level of 0.1 mg/l for water showed that the concentration of Ni in Challawa River is very high and indicate possible pollution. The relatively high concentration of nickel trapped in the sediment and detected in the water sample may be due to wastewater from textile and tanneries industries common in the area. However, nickel limiting levels were exceeded and Challawa River could be said to be contaminated by nickel. Long term exposure can cause decreased body weight, heart and liver damage and skin irritation.

Arsenic is a highly toxic metalloid element (Rodrigues *et al.,* 2003; Pizzaro *et al.,* 2003). It is widely distributed as a trace element in rocks and soils and is mainly mobilised by microbial activities (Garcia-Sanchez and Alvarez-Ayuso, 2003). The levels of arsenic in the analyzed water and sediment samples showed that the limiting values of WHO of 0.10mg/l and 27 µg/g respectively were exceeded, indicating contamination of Challawa River. The present of arsenic in Challawa River may be attributed to anthropogenic discharge of wastewater from industrial processes within this area.

Cadmium is a non-essential trace element that enters the environment via anthropogenic activities such as industrial effluent, sewage-sludge, fertilisers and pesticides (DWAF, 1996). Cadmium adsorbs strongly to sediments and organic matter (Sanders *et al.,* 1999). Cadmium has a range of negative physiological effects on organism, such as decreased growth rates and negative effects on embryonic development (Newman and McIntosh, 1991). Although cadmium is a sulphur seeking metal that tend to precipitate in anoxic sediments, experiments carried out at concentrations lower than values found in this study, show that cadmium can still be assimilated from anoxic sediments with high organic matter content (Griscom *et al.,* 2000; Chong and Wong, 2000; Lee *et al.,* 2000; Muniz *et al.,* 2004). The levels of copper in the water and sediment samples were above the (WHO, 2004) standard values of 0.01 mg/l and 6 µg/g respectively for the survival of aquatic organism.

Manganese is an essential element (Health and Welfare Canada, 1980) that is a functional component in nitrate assimilation and is used as a catalyst in many enzymatic systems in both plants and animals (DWAF, 1996). Manganese is readily oxidisable and settles out of the water column as MnO_2 (DWAF, 1996). The levels of manganese in the analyzed water and sediment samples showed that the limiting values of USEPA of 0.1 mg/l and 300 µg/g respectively were exceeded, indicating contamination of Challawa River and may pose a hazard to the aquatic biota. The presence of manganese in River Challawa may be attributed to anthropogenic discharge of manganese waste from industrial processes within this area.

An attempt was made to investigate any relationship between the metals in water and sediment. The correlation coefficient as shown in Table 1 and 2 revealed positive correlation between all the metals in water and sediment samples. Positive correlation between metals in the water samples suggests similar sources. The high positive correlation between metals in the sediment samples indicates that these elements were bound to the sediment within the same periods and could be said to have a common anthropogenic pollution origin (Ogunsola, 1994).

The correlation between Cr-Fe, Mg-Ni, As-Ni in the water samples and Cr-Zn, Mn-Ni, Fe-Pb in the sediment samples did not showed any significant relation but were positive related. These however do not mean that the metals may not have come from the above sources. Their week relations could be attributed to physical disturbance or diagenesis, thus causing them to be released into the lower layer of the surrounding environment.

The mean seasonal variations of nitrate, nitrite and phosphate concentrations in all the sample points are as illustrated in Figure 14. The values of nitrate, nitrite and phosphate were higher at the confluence point (S_1) and fluctuate between 92.23 to 97.12 mg/l nitrate, 193.54 to 196.45 mg/l nitrite and 19.01 to19.89 mg/l phosphate, and decreases toward point S_3 (72.12 to 80.33 mg/l nitrate., 177.23 to 179.66 mg/l nitrite and 17.22 to 17.96 mg/l) throughout the seasons. The mean levels of sulphate and chloride against different sample points are also presented in Figure 15. The values of sulphate and chloride were higher at the confluent point (S_1) and fluctuate between 994.01 to 994.21 mg/l sulphate and 366.11 to 367 mg/l chloride, and decreases toward point S_3. However no significant seasonal variations between point S_1-S_3 were observed for nitrate, nitrite, phosphate, sulphate and chloride, which show that the activities of these industries remain almost constant throughout the sampling periods. Significant variation was observed for points S_4 to S_8.

The levels of nitrate (18.34 to 23.43 mg/l), 16.34 to 21.43 mg/l nitrite, 5.00 to 6.34 mg/l phosphate, sulphate (19.33 to 23.21 mg/l) and 13.22 to 19.23mg/l for chloride reported for point (S_5) is low. The levels of nitrate, nitrite, phosphate, sulphate and chloride in river challawa decreases in the following order $S_4>S_6>S_7>S_8>S_5$. The high values of nitrate, nitrite and phosphate at point S_4, S_6, S_7 and S_8 when compared with the control (point S_5) might be due to the discharged of effluent from tannery and textile industries. While the decrease in values from point S_4 to S_8 might be attributed to dilution, sedimentation and depuration factor due to immense volumes of fresh water.

The seasonal variation between point S_4 to S_8 are in the following order rainy season <Harmattan period <dry season. The high levels of nitrate, nitrite, phosphate, sulphate and chloride during the dry and harmattan period might be attributed to reduction in the volume of water and the addition of tanneries and textile effluent, while the low levels of these anions during the rainy seasons might be attributed to dilution of the effluent by fresh water during the rainy seasons.

Generally, the levels recorded in the entire sample points (S_4-S_8) were higher than the USEPA guideline of 45 mg/l nitrate, 20 mg/l nitrite, 5 mg/l phosphate, 200 mg/l sulphate and 50 mg/l chloride for the protection of fisheries, aquatic life and for domestic water supply.

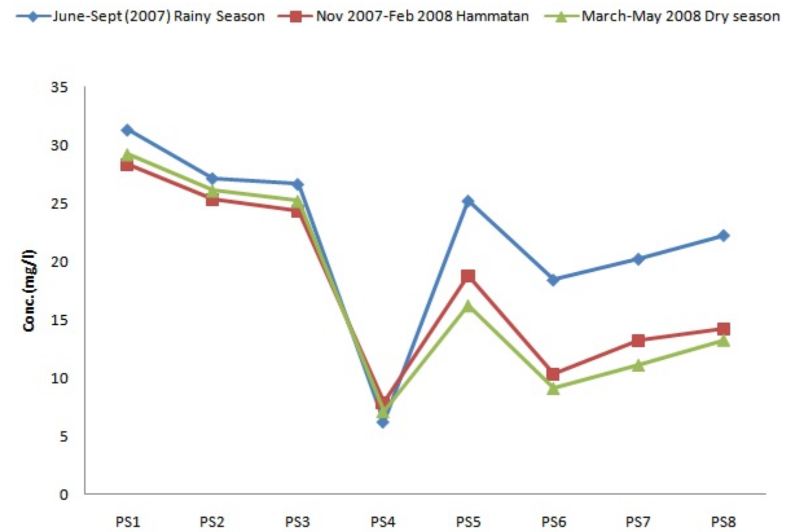

Fig. 1: Seasonal Variation of Dissolved Oxygen (mg/l) for water sample at different points of River Challawa.

PS1= Effluent Confluence Point at Challawa Industrial Estate
PS2= 300 Metres from Confluence Point
PS3= 600 Metres from Confluence Point
PS4= Point of Discharge of Effluent into River Challawa
PS5= 200 Metres Up-River from Discharge Point into River Challawa
PS6= 2Km after Effluent Discharge Point into River Challawa
PS7= 4Km after Effluent Discharge Point into River Challawa
PS8= 7Km after Effluent Discharge Point into River Challawa

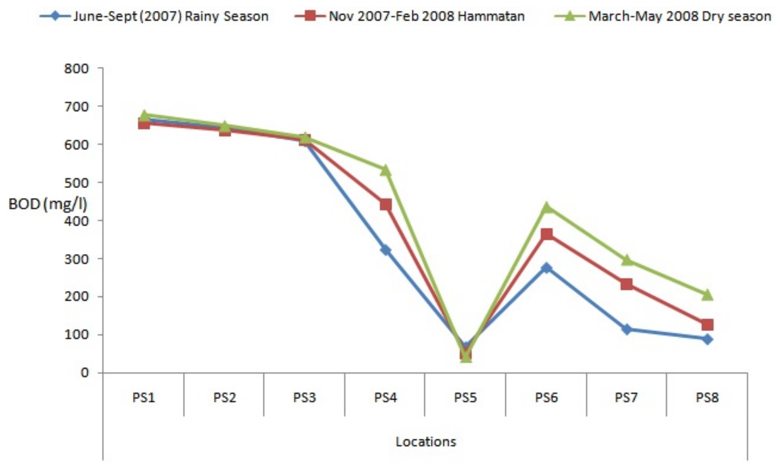

Fig. 2: Seasonal variations of biological oxygen demand (mg/l) for water samples at differnt points of River Challawa.

PS1= Effluent Confluence Point at Challawa Industrial Estate
PS2= 300 Metres from Confluence Point
PS3= 600 Metres from Confluence Point
PS4= Point of Discharge of Effluent into River Challawa
PS5= 200 Metres Up-River from Discharge Point into River Challawa
PS6= 2Km after Effluent Discharge Point into River Challawa
PS7= 4Km after Effluent Discharge Point into River Challawa
PS8= 7Km after Effluent Discharge Point into River Challawa

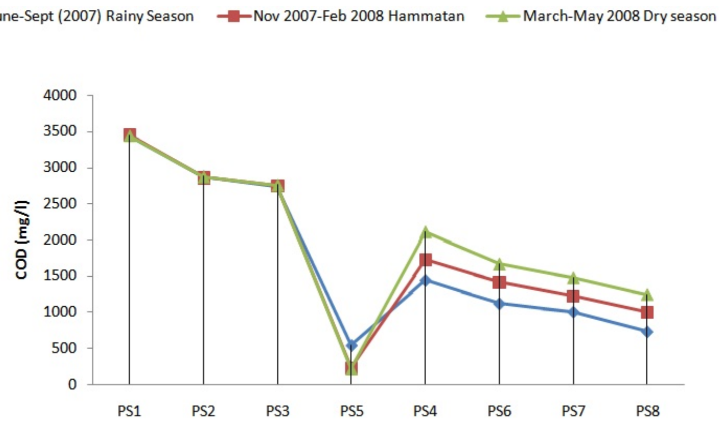

Fig. 3: Seasonal variations of chemical oxygen demand (mg/l) for water samples at differnt points of River Challawa.

PS1= Effluent Confluence Point at Challawa Industrial Estate
PS2= 300 Metres from Confluence Point
PS3= 600 Metres from Confluence Point
PS4= Point of Discharge of Effluent into River Challawa
PS5= 200 Metres Up-River from Discharge Point into River Challawa
PS6= 2Km after Effluent Discharge Point into River Challawa
PS7= 4Km after Effluent Discharge Point into River Challawa
PS8= 7Km after Effluent Discharge Point into River Challawa

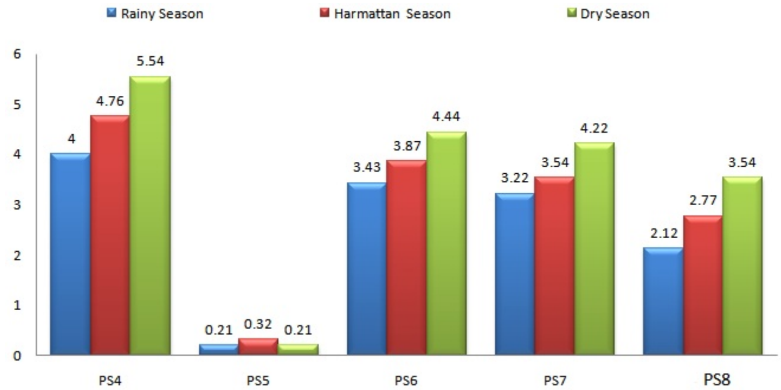

Fig. 4: mean seasonal variations of total organic carbon (%) in sediment samples at different points of River Challawa

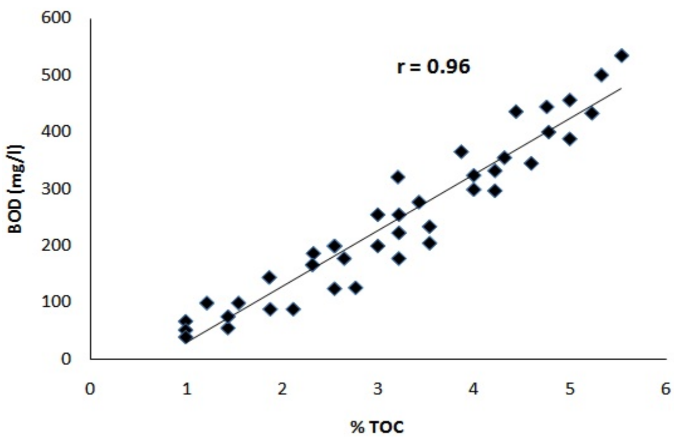

Fig. 5: Scatter gram of BOD and TOC for the sample points

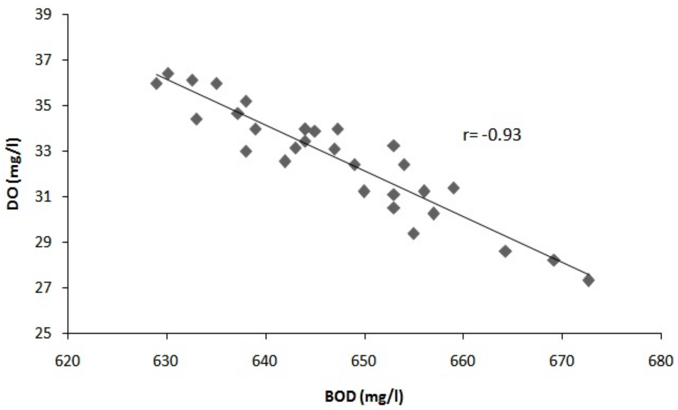

Fig. 6: Scatter gram of DO and BOD for the sample points

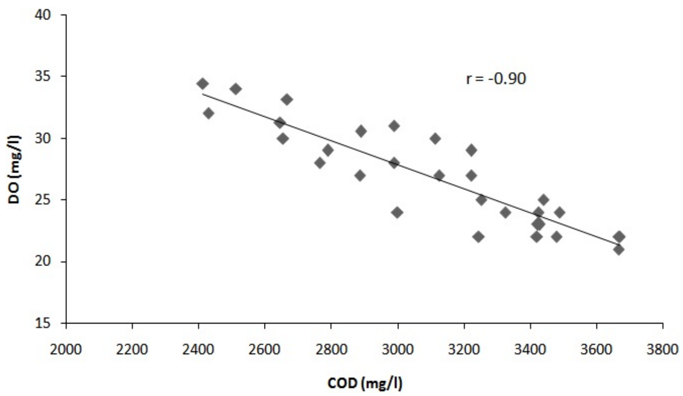

Fig. 7: Scatter gram of DO and COD for the Sample Points

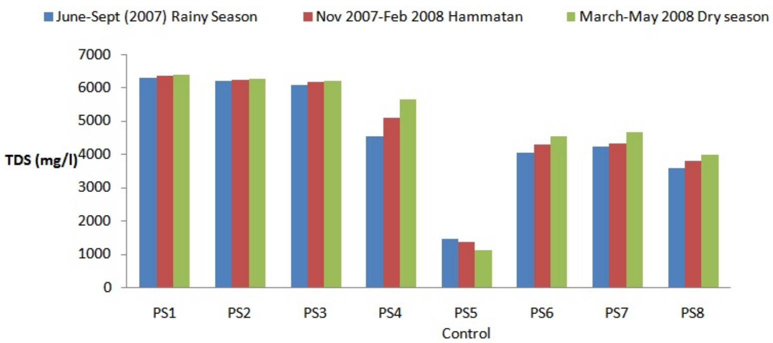

Fig. 8: Seasonal variations of Total dissolved solid in water samples at different points of River Challawa

PS1= Effluent Confluence Point at Challawa Industrial Estate
PS2= 300 Metres from Confluence Point
PS3= 600 Metres from Confluence Point
PS4= Point of Discharge of Effluent into River Challawa
PS5= 200 Metres Up-River from Discharge Point into River Challawa
PS6= 2Km after Effluent Discharge Point into River Challawa
PS7= 4Km after Effluent Discharge Point into River Challawa
PS8= 7Km after Effluent Discharge Point into River Challawa

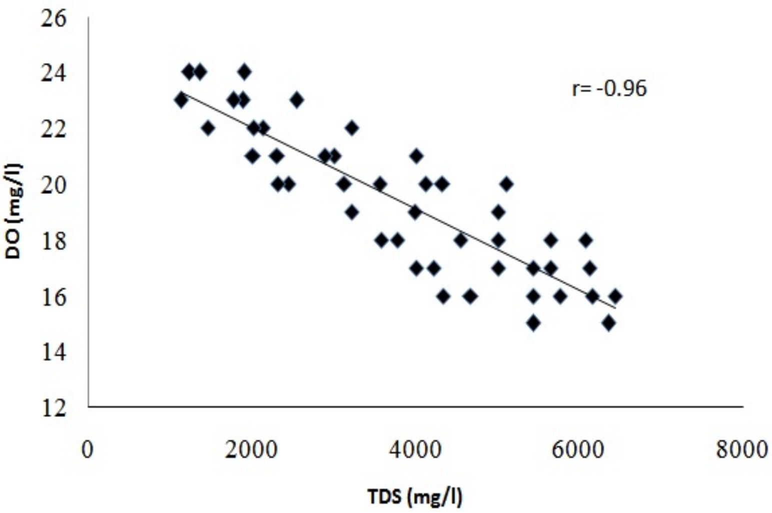

Fig. 9: Scatter gram of DO and TDS for the sample points

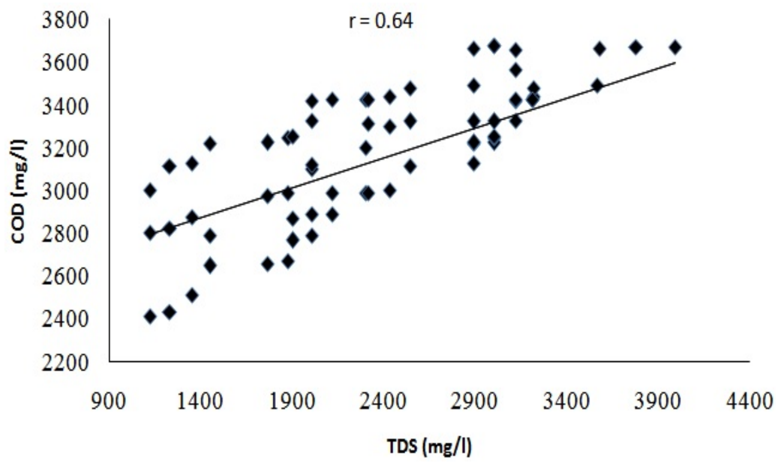

Fig. 10: Scatter gram of COD and TDS for the sample points

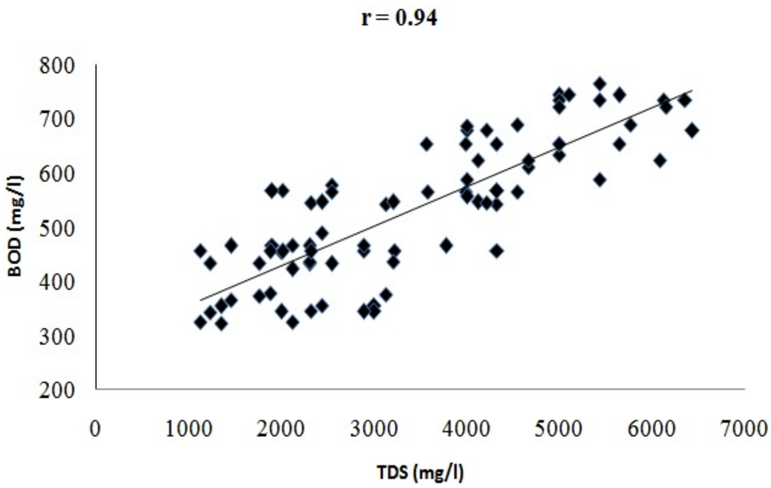

Fig. 11: Scatter gram of BOD and TDS for the sample points

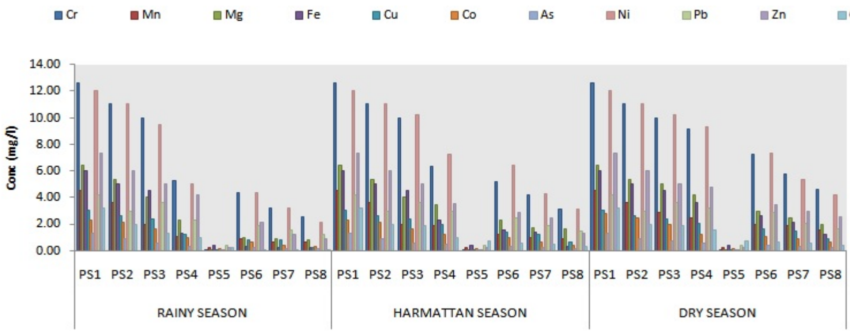

Fig. 12: Seasonal variation of Trace element concentrations (mg/l) in water samples at different points of River Challawa

PS1= Effluent Confluence Point at Challawa Industrial Estate
PS2= 300 Metres from Confluence Point
PS3= 600 Metres from Confluence Point
PS4= Point of Discharge of Effluent into River Challawa
PS5= 200 Metres Up-River from Discharge Point into River Challawa
PS6= 2Km after Effluent Discharge Point into River Challawa
PS7= 4Km after Effluent Discharge Point into River Challawa
PS8= 7Km after Effluent Discharge Point into River Challawa

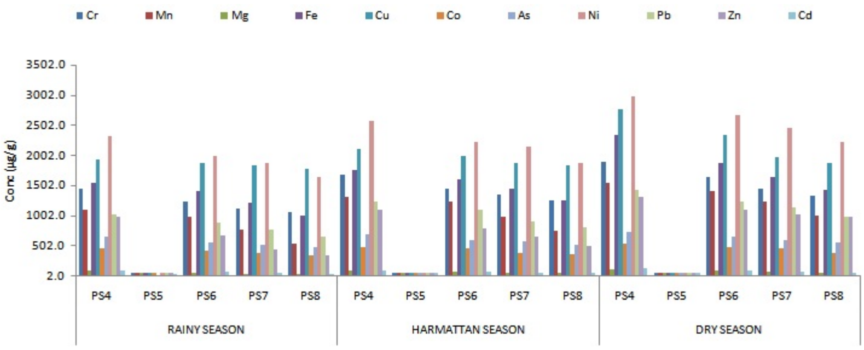

Fig. 13: Seasonal Variation of Trace element concentration (µg/g) in sediment samples at different points of River Challawa

Table 1: Correlation for water samples giving values of coefficient, r, for pairs of heavy metals

Element	Cr	Mn	Mg	Fe	Cu	Co	As	Ni	Pb	Zn	Cd
Cr	1										
Mn	0.79	1									
Mg	0.84	0.75	1								
Fe	0.44	0.93	0.68	1							
Cu	0.57	0.78	0.72	0.56	1						
Co	0.59	0.80	0.94	0.98	0.66	1					
As	0.92	0.78	0.95	0.91	0.64	0.98	1				
Ni	0.58	0.88	0.44	0.86	0.96	0.58	0.49	1			
Pb	0.76	0.77	0.82	0.76	0.62	0.56	0.706	0.68	1		
Zn	0.65	0.75	0.70	0.86	0.62	0.95	0.92	0.76	0.74	1	
Cd	0.89	0.97	0.65	0.95	0.57	0.97	0.78	0.82	0.51	0.85	1

Table 2: Correlation for sediment samples giving values of coefficient, r, for pairs of heavy metals

Element	Cr	Mn	Mg	Fe	Cu	Co	As	Ni	Pb	Zn	Cd
Cr	1										
Mn	0.85	1									
Mg	0.94	0.651	1								
Fe	0.60	0.708	0.824	1							
Cu	0.79	0.831	0.642	0.68	1						
Co	0.69	0.469	0.976	0.89	0.91	1					
As	0.50	0.801	0.612	0.98	0.72	0.84	1				
Ni	0.78	0.487	0.505	0.68	0.68	0.65	0.96	1			
Pb	0.99	0.569	0.893	0.41	0.85	0.88	0.67	0.87	1		
Zn	0.47	0.989	0.606	0.59	0.62	0.95	0.57	0.91	0.84	1	
Cd	0.70	0.500	0.543	0.63	0.95	0.84	0.77	0.77	0.94	0.90	1

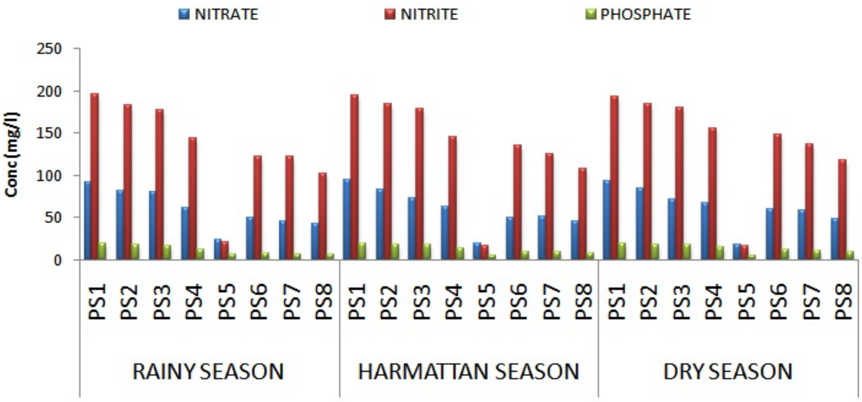

Fig. 14: Seasonal variation of nitrate, nitrite and phosphate (mg/l) in water samples at different points of River Challawa

PS1= Effluent Confluence Point at Challawa Industrial Estate
PS2= 300 Metres from Confluence Point
PS3= 600 Metres from Confluence Point
PS4= Point of Discharge of Effluent into River Challawa
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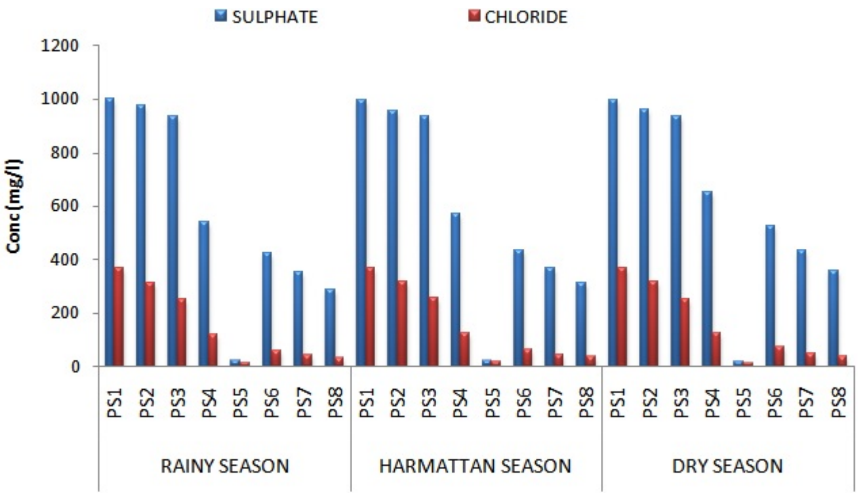

Fig. 15: Seasonal variation of Sulphate and Chloride in water samples at different points of River Challawa

PS1= Effluent Confluence Point at Challawa Industrial Estate
PS2= 300 Metres from Confluence Point
PS3= 600 Metres from Confluence Point
PS4= Point of Discharge of Effluent into River Challawa
PS5= 200 Metres Up-River from Discharge Point into River Challawa
PS6= 2Km after Effluent Discharge Point into River Challawa
PS7= 4Km after Effluent Discharge Point into River Challawa
PS8= 7Km after Effluent Discharge Point into River Challawa

Conclusion:

The levels of dissolved oxygen (DO), chemical oxygen demand (COD) and biological oxygen demand (BOD) in all the sampling points were found to be higher than ranged for the maintenance of aquatic life. The levels of heavy metals in surface water and sediment samples from different points of Challawa River were above the values set by WHO and UNEPA for the protection of fish and other aquatic organisms. The concentrations of sulphate, chloride, nitrate, nitrite and phosphate of were higher than the USEPA limits for the protection of aquatic environment.

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