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Impact of tannery effluent and climate change on physico-chemical characteristics of Ganga river at Kanpur (U.P.), India

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Abstract: An investigation has been made to ascertain the effect of tannery effluent associated with climate change on river water samples collected from confluence point, upstream and downstream located near Jajmau area at Kanpur. All the samples analyzed for physico-chemical parameters including estimation of chromium. The pH at confluence point (Q) was significant ($P<0.05$) alkaline (7.9±0.13) during summer as compared to upstream point P3 due to dumping of untreated tanneries effluent, which suggested that utilization of salts for leather tanning process. Study shows that a significant ($P<0.05$) decrease in DO values (3.79±0.101 mgL^{-1}) at summer, although the higher level of DO (6.76±0.13) during monsoon season might be attributed to the dilution of the effluent by rain water. The level of BOD (41.07±1.268 mgL^{-1}) shows a significant ($P<0.05$) increase at confluence point during as compared to upstream point (P3) during summer. Although the level of COD at different sampling points affected with climate changes but it was not significant. However this study also revealed a significant negative correlation showing that as BOD and COD increases in values DO decreases with correlation of $r = -0.944$ ($t= 6.978$, $P<0.05$ for BOD) and $r = -0.970$ ($t= 9.696$, $P<0.05$ for COD). These correlation between BOD, COD and DO suggest a similar cause. The correlation analysis of TDS versus BOD and COD gives a positive correlation ($r =0.9408$ & $r =0.8667$ respectively) showing that as TDS increase BOD and COD also increases. Theses correlation analysis shows that levels of TDS, BOD and COD are highly correlated with each other in sampling area during different climate change. Chromium levels are high (52.12±15.52 mgL^{-1}) in almost all sampling points with climate change. Tannery effluent with climate change shows highly adverse effect on river Ganga.

Key words: Tannery effluent, seasonal variation, season, river water, chromium

Introduction

Industrial effluents from leather tanneries discharged higher amount of metal especially chromium. These effluents released on river or canal as well as dump into ground water and lead to contamination of chromium due to accumulation, as results in this series of well there is higher chance of chromium exposure. It has been reported that only about 20% of the large number of chemicals used in the tanning process is absorbed by leather and the rest is released as waste (UNIDO 2005; Dikshit *et al*., 1989). The toxicity of chromium is the major problem for human health (Health and Welfare Canada 1980). 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 metals exceeding the toxic range in soils (Huq 1998). It is also reported that the wastes from the leather industry consist of tanned and untanned solids, waste waters (effluent) including the sludge and waste gases (Ogbonna *et al*., 1998).

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). The Common mineral elements such as Al, Fe, Ca, Na, K and Si are present in significant quantities in sludge and may also contain trace elements and heavy metals such as Cr, Cd, Pb, Hg, As, Cu, Ni, Zn, B, Se, Mo as well as N and P in both organic and inorganic forms (Akan *et al*., 2009; Ogbonna *et al*., 1998). Eventually the effluents and sludge from these tanneries are discharging onto land and into water bodies. The dissolved and suspended particles of the effluent would affect the quality of ground water, in addition to reduced clarity. There is also a great danger to man and livestock particularly from the high Cr content and it has been found to be toxic to humans at levels as low as 0.1 mg/L (UNIDO 2005). Hence, the need to monitor the heavy metal pollutant levels of these areas. Deepali and Gangwar (2010) have observed that the average chromium concentration 0.93 mgL^{-1} in ground water samples of tannery. The Ganga river, a major source of water for northern India and has been extensively survey for its physiochemical parameters (Saikia, 1988; Subramania *et al*., 1987; Ajmal *et al*., 1987). A different pattern observed for the distribution of heavy metals in sediments of the river Ganga (Jha *et al*., 1990; Ansari *et al*., 2000; Datta and Subramanian 1998; Ramesh *et al*., 2000; Singh, 2001). Analysis of upstream and downstream water and sediment revealed a significant increase in chromium level at Jajmau area of Kanpur showing unchecked release of untreated tannery effluent. This case study also shows the change in the magnitude of the physiochemical parameters of the water and sediments due to tannery pollution (Khwaja *et al*., 2001).

Although there are no enough evidences for impact of tannery effluent on ground/drinking water with reference to river water. The present study is, therefore focused to see the effect of tanneries on some very important source of drinking water such as borewell. The Ganga river in Jajmau area at Kanpur city is valuable source of irrigation and fishing, so in order to find current status of pollutants discharged from the various tanneries. Chemical criteria provide significant information about the present status of contaminant concentration on river water and ground water and their impact on blood chromium content with special reference to human health.

Materials and Methods

Samples and sampling sites: Samples were from Jajmau Industrial area, tanneries from these areas discharge their effluents into canals, which converge at a confluent point and flow into the river Ganga. Water samples were collected twice in every month during summer (March to June), monsoon (July to October) and winter (November to February) at three stations viz. upstream and downstream from the tannery effluent discharge point on the river Ganga. The locations of sampling area were selected as upstream and downstream at effluent point of tannery waste water which is situated at the Jajmau area. The sampling area-P3 was upstream (5 Km) at Jajmau and sampling area-R3 was downstream (5 Km) from the effluent discharge point in to river. These river are strategically located in the rapidly expanding northern region of Kanpur city and catering to a large population. In Jajmau area many tanneries are located and they discharging their effluents which converge at a confluent point and flow into the River Ganga. Water samples from these areas were collected and designated as upstream (P_1, P_2 and P_3; 1 Km, 2.5 Km and 5Km respectively) and downstream (R_1, R_2 and R_3; 1 Km, 2.5 Km and 5Km respectively). For River Ganga, water samples were collected at immediate point of effluent discharge from tannery into river Ganga (Q).

Determination of physico-chemical environmental parameters: Water temperature was measured by using a thermo-probe at the site of collection and recorded in a Celsius scale. The concentration of dissolved oxygen (DO) present in the water samples was estimated by Winkler method for measuring dissolved oxygen involves titrating a sample with a series of reagents. The samples were analysed for a number of physico-chemical parameters employing standard methods (APHA 2005). The parameters included colour, odour, temperature, pH, total hardness, total solids (TS), total dissolved solids (TDS), total solids (TS). The alkalinity described by Trivedi and Goel (1986) by titrating against sodium thiosulphate using as indicator. The biochemical oxygen demand (BOD), TDS and TS determination of the water sample in mg/l was carried out using the standard methods (APHA, 2005). The dissolved oxygen content was determined before and after incubation. Sample incubation was for 5 days at 20^0C in BOD bottle and BOD 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 148^0C, with back titration.

Determination of chromium content in water and sediment samples: This procedure measures only hexavalent chromium (cr^{6+}). Therefore, to determine total chromium convert all the chromium to the hexavalent state by oxidation with $KMnO_4$. The hexavalent chromium was determined colorimetrically by reaction with diphenylcarbazide in acid solution. In brief, digested the sample with a sulfuric-nitric acid mixture and then oxidize with $KMnO_4$ before reacting with the diphenylcarbazide. Each final solution determined by using standard colorimetric method (APHA 2005). Suitable volume of sample was taken, filtered through whatman (no. 42) filter paper and then acidified with concentrated HNO_3 to bring down the pH up to 2. 100 ml of sample was taken and added 5 ml concentrated HNO_3, and then digested in a closed chamber, within 30 minutes digestion was completed and make up the volume to 100 ml with distilled water. The Cr (VI) concentrations in samples were determined colorimetrically by using spectrophotometer at 540 nm by diphenyl carbazide (DPC) method (APHA 2005).

All sediment samples were oven dried at 80 to 100^OC, gentle crushed and sieved to collect < 60 ìm grain size. Sediment samples were digested by the addition of aqua regia (mixture of HCl and HNO_3, ratio 3:1) and 30% H_2O_2. The samples were heated over a hot plate at 90^OC for two hours. The volumes were adjusted to $100cm^3$ with distilled water. Blank solutions were handled as detailed for the samples. Determination of Cr was made directly on each final solution using Atomic Absorption Spectroscopy (AAS) as described by Floyd and Hezekiah (1997).

Results

The quality of water in the river system is seriously affected by pollutants which enter through besides other pollutants also contain high concentration drains that bring domestic as well as industrial effluents. Because of adsorption, hydrolysis and co-precipitation only a small portion of free metal ions stay dissolved in water and a large quantity of them get deposited in the sediment. The temperature of water varied between P (P1, P2 & P3) to R (R1, R2 & R3) and Q site. In all the seven sites a high temperature was recorded during summer, normal temperature in monsoon and lower temperature during winter, which is a normal feature of water bodies in this region (table 1). The pH of confluence point (Q) was significant ($P<0.05$) alkaline (7.9±0.13) during summer as compared to upstream point P3 (7.4±0.07) which may be due to dumping of tannery wastes, garbage and sewage water. The desirable limit of pH recommended by (Bureau of Indian Standards) BIS (1992) is 6.5-8.5.

The mean seasonal DO levels for samples analysed for point P3 to Q and R3 are as presented in figure 1. The confluence point, Q had significant decrease ($P<0.05$) in mean DO value 3.79±0.101 mgL^{-1} during summer as compared to mean DO value (4.41±0.27 mgL^{-1}) of upstream point P3 (5 km upstream from confluence point, Q) at Jajmau. The seasonal variation of mean DO value between upstream (P3) and downstream (R3) might be due to changes in volume of fresh water of River Ganga. The high levels of DO during monsoon season at upstream point P3 (P3; 7.56±0.44 mgL^{-1}) as compared to confluence point summer (Q; 3.79±0.10 mgL^{-1}), monsoon (Q; 6.76±0.13 mgL^{-1}) and winter (Q; 5.91±0.228 mgL^{-1}) might be attributed to dilution of the effluent and sewage by rain water (figure 1a).

The mean BOD levels for samples analysed for upstream to Q and downstream are shown in figure 2. The mean concentrations of BOD for point P1 to P3 ranged from 18.77±0.496 to 31.142±2.01 mgL^{-1} for summer, 32.38±0.402 to 30.89±0.461 mgL^{-1} monsoon season, 23.65±1.115 to 16.58±0.535 mgL^{-1} during winter as compared to confluence point Q, during summer 41.07±1.268 mgL^{-1}, monsoon 34.12±1.577 mgL^{-1} and winter 36.69±1.409 mgL^{-1}. BOD level shows that significant increase ($P<0.05$) during summer at confluence point Q, as compared to upstream point (P3) (figure 2a). While the COD level for upstream point (P1 to P3) ranged from 118.12±0.688 to 119.44±0.485 mgL^{-1} for summer, 124.07±0.558 to 125.44±1.17 mgL^{-1} monsoon season, 138.45±0.620 to 156.78±0.774 mgL^{-1} for winter season (figure 3). The concentration of COD at confluence point Q, was 115.49±1.0 mgL^{-1} during summer, 123.06±1.12 mgL^{-1} for monsoon and 127.81±0.615 mgL^{-1} for winter as compared to upstream point.

Observation shows that significant relationship between Biochemical oxygen demand (BOD), Dissolve oxygen (DO) and Chemical oxygen demand (COD) during summer. The correlation coefficient as shown in figure 4 and 5 revealed a significant negative correlation showing that as BOD and COD increases in values DO decreases with correlation of $r = -0.944$ ($t = 6.978$, $P<0.05$ for BOD) and $r = -0.970$ ($t = 9.696$, $P<0.05$ for COD). These correlation between BOD, COD and DO suggest a similar cause.

The seasonal mean TDS level for samples analyzed for points upstream (P1, P2 & P3), confluence point Q and downstream

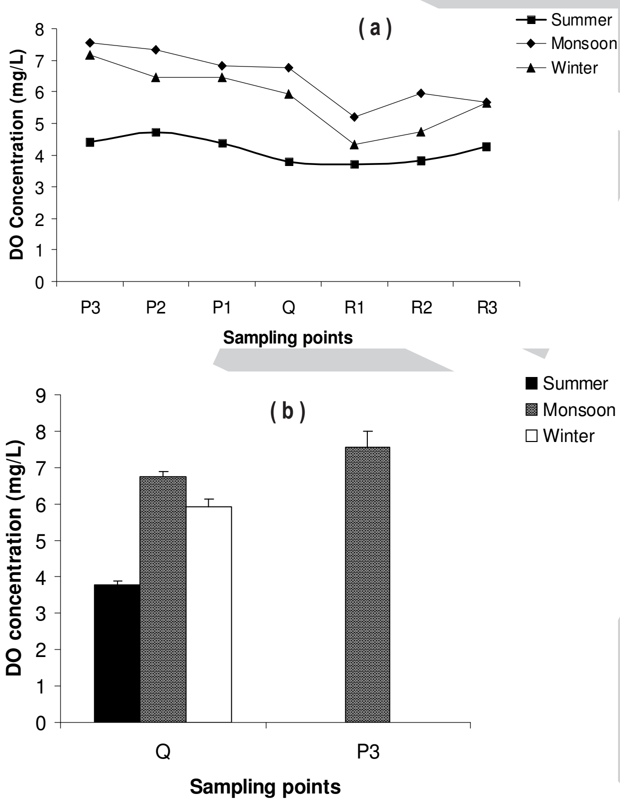

Fig. 1(a): The level of DO (mgL^{-1}) for water samples at different points of river Ganga with seasonal variation **(b)** The high level of DO (mgL^{-1}) confluence point Q, during monsoon season as compared to upstream point P3. Statistical significance is given in comparison to control $^{*}P<0.05$

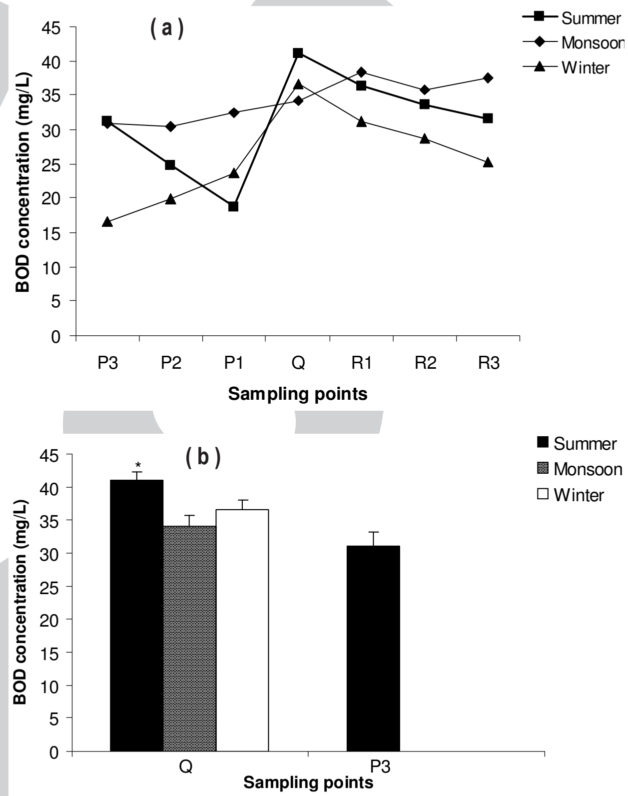

Fig. 2(a): Seasonal variation of BOD level (mgL^{-1}) for water samples at different points of river Ganga, **(b)** The high level of BOD (mgL^{-1}) at confluence point Q, during summer as compared to upstream point P3. Statistical significance is given in comparison to control $^{*}P<0.05$

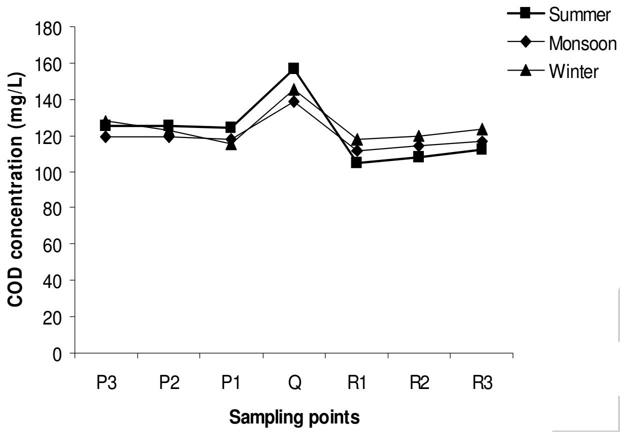

Fig. 3: Seasonal variation of COD level (mgL^{-1}) for water samples at different points of river Ganga

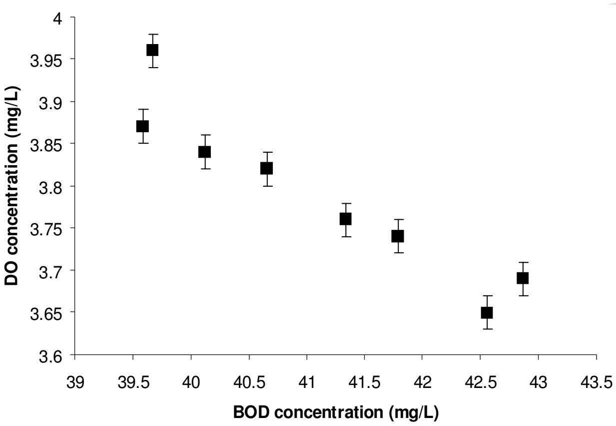

Fig. 4: The correlation coefficient between DO level and BOD concentration at confluence point Q, during summer (r = -0.944, t= 6.978 & *P<0.05)

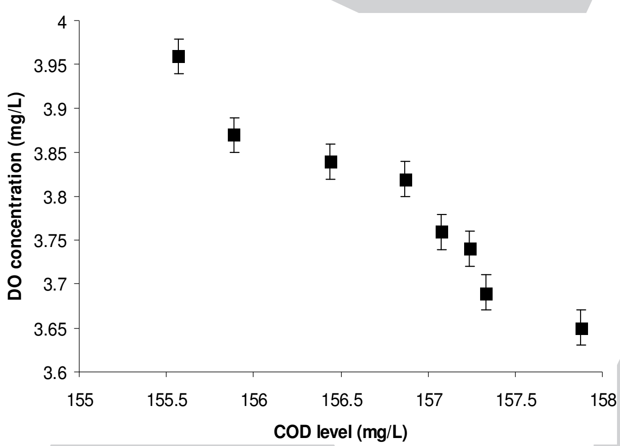

Fig. 5: The correlation coefficient between DO level and COD concentration at confluence point Q, during summer (r = -0.970, t= 9.696 & *P<0.05)

(R1, R2 and R3) are as presented in figure 6. Total dissolved solid (TDS) value was higher at the confluent point (Q) and fluctuates between 381.37±70.39 to 417.25±4.33 to 371.25±14.22 mgL^{-1} during summer, monsoon and winter respectively. This

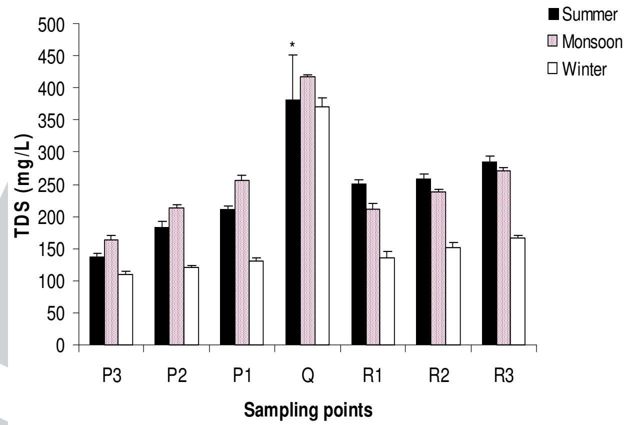

Fig. 6: Mean seasonal variations of Total dissolved solids (mgL^{-1}) in water samples at different points of river Ganga

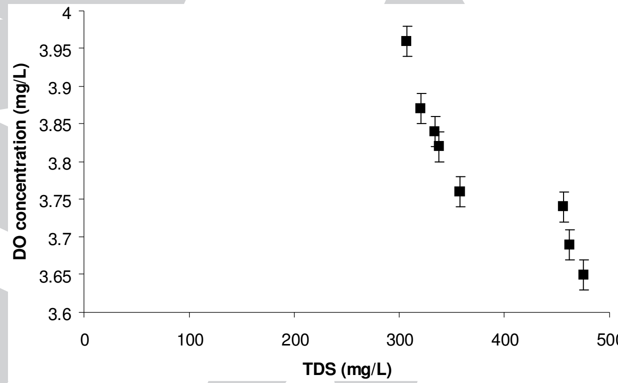

Fig. 7: Correlation analysis between TDS level (mgL^{-1}) and DO concentration (r = 0.909, t= 5.318 & *P < 0.05)

observation revealed that a significant increase (P<0.05) in TDS value between upstream point P3 (5 km form confluence point, Q) and confluence point Q during summer. The relationship between mean dissolved oxygen (DO) and total dissolved solid (TDS) at the confluence point Q, during summer gives an inverse correlation (r = -0.909, t= 5.318 & P<0.05) showing that as TDS increases in values DO decreases. The TDS values were noted to be high corresponding to low DO values (figure 7). The correlation analysis of TDS versus BOD and COD gives a positive correlation (r=0.9408 & r=0.8667 respectively) showing that as TDS increase BOD and COD also increases (figure 8a & 8b). Theses correlation analysis shows that levels of TDS, BOD and COD are highly correlated with each other in sampling area. The observation of mean value of TS (total solids) shows no significant variation at upstream, downstream and confluence point Q, during summer, monsoon and winter (figure 9).

The mean seasonal variations of chromium concentration in upstream (P1, P2 and P3), confluence point (Q) and down stream (R1, R2 and R3) sample points are represented as figure 10. The concentration of all the metals especially chromium (Cr) were higher at the confluence point (Q) and decrease toward down stream (R1, R2 and R3) throughout the sampling season summer, monsoon and winter. The mean concentrations of total chromium in samples, for confluence point (Q) were 52.12±15.52 mgL^{-1}, 34.05±19.2 mgL^{-1} and 45.5±4.0 mgL^{-1} during summer, monsoon and winter respectively. Figure 11 shows the mean concentrations of heavy metals in sediment samples at upstream point (P1, P2 & P3), confluence point (Q) and down stream point (R1, R2 & R3) during summer, monsoon and winter. The mean value of chromium at confluence point, Q during summer was (51.12±14.13 mgL^{-1}) significant ($P<0.05$) as compared to control (upstream point P3).

The mean concentration of heavy metals in ground water samples for confluence point (Q) were 52.12±15.52 mgL^{-1} for Cr, 1.103±0.23 mgL^{-1} for Pb and 0.13±0.08 mgL^{-1} for As during summer, while both Pb and As found as very low concentration during monsoon and winter. The level of Pb in monsoon and winter were 0.43±0.57 mgL^{-1} and 0.71±0.31 mgL^{-1} respectively, while mean concentration of As were 0.06±0.06 mgL^{-1} and 0.06±0.01 mgL^{-1} during monsoon and winter respectively. These observations revealed that Pb and As found as very low concentration at confluence point, Q (figure 12).

Discussion

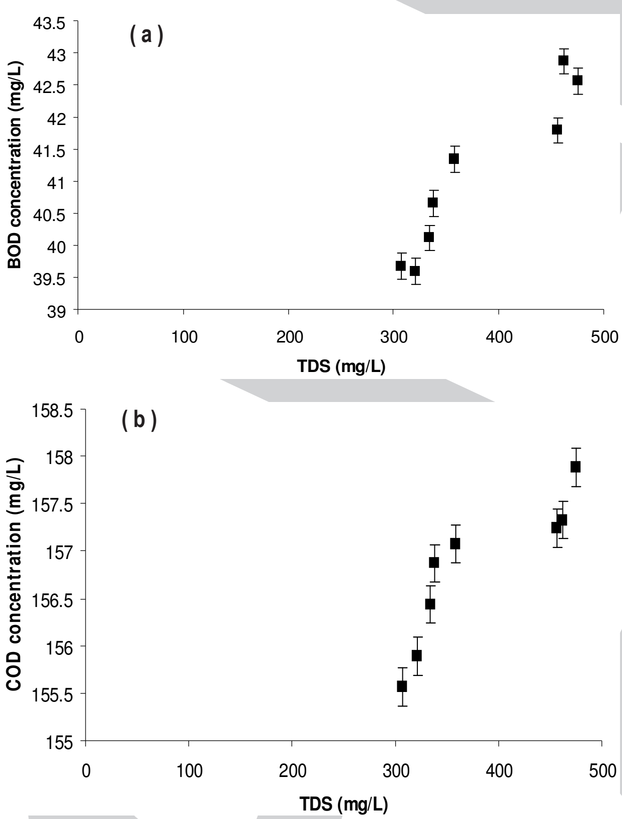

Fig. 8(a): A significant positive correlation between TDS level (mgL^{-1}) and BOD concentration (mgL^{-1}) (r=0.9408, t= 6.706 & *$P < 0.05$), **(b)** A significant positive correlation between TDS level (mgL^{-1}) and COD concentration (mgL^{-1}) (r=0.8667, t= 4.22 & *$P < 0.05$)

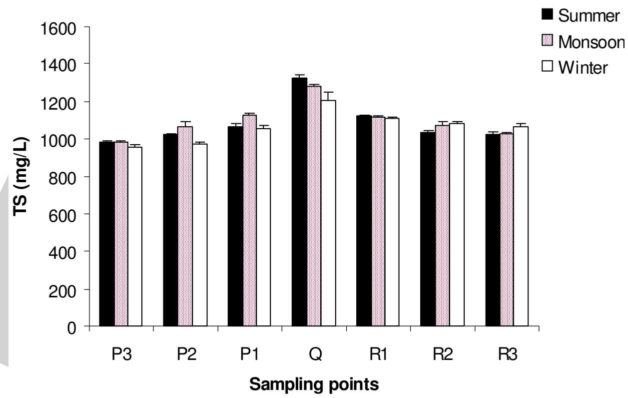

Fig. 9: Mean seasonal variations of Total solids (mg/L) in water samples at different points of river Ganga

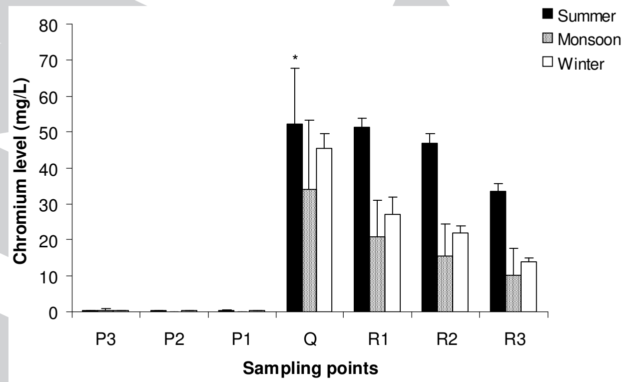

Fig. 10: Mean±SD value of chromium concentration (mg/L) in water samples at different points of river Ganga. Statistical significance is given in comparison to upstream point *$P<0.05$

Chromium is an essential element for humans, and daily ingestion of 0.5g to 2g is required for adults, though daily requirement for chromium is under discussion (Janus, 1990; Gunton, 2001). The excess effects of chromium are leads to growth retardation, damage to kidney and liver and cancer (Frisbie, 2002). Water samples were collected from the Ganga River during Summer, Monsoon & Winter and tested for physical qualities and chemical contents. The important water quality parameters, such as temperature, pH, DO, BOD, COD, TDS, TS and heavy metals such as chromium, lead and arsenic were analyzed at seven points.

Excess alkalinity gives a bitter taste to water. Maximum alkalinity values were registered during summer at Site R_1 and Site R_3, Where as at Site Q, it was during monsoon. The higher alkalinity in itself is harmful to human beings, but still it delimits the water for domestic uses. A significant higher alkalinity during summer due to excess evaporation of water and dumping of tanneries wastes. Maximum alkalinity values were registered during summer at downstream (R1 to R3) and site Q. The significant higher alkalinity of water in itself is harmful to human beings and livestock, but still it delimits the water for domestic and agricultural uses.

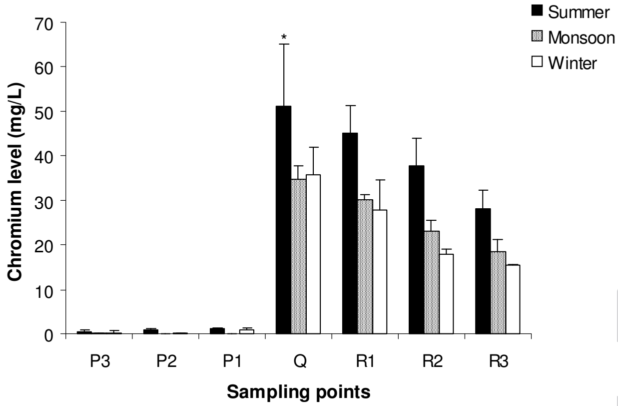

Fig. 11: Mean±SD value of chromium concentration (mgL^{-1}) in sediment samples at different points of river Ganga. Statistical significance is given in comparison to upstream point *P<0.05

Fig. 12: Comparison between heavy metal concentrations (mgL^{-1}) in water samples at different sampling points with seasonal variation

Heavy metal concentration (mg/L)

Table - 1: Mean values of physico-chemical features of water of river Ganga during summer, monsoon and winter. ([a]Distance from confluence point, Q)

Physico-chemical characteristics	Season	[a]Upstream			Confluence Point (Q)	[a]Downstream		
		P3 (5 km)	P2 (2.5 km)	P1 (1 km)		R1 (1 km)	R2 (2.5 km)	R3 (5 km)
Air temperature(°C)	Summer	28.8±4.6	29.2±4.8	29.3±5.2	29.2±4.8	29.2±5	29±4.7	28.7±4.3
	Monsoon	26.8±3	26.7±3	26.6±3	30.7±1.77	28.1±4.2	27.4±3.6	27.6±3.9
	Winter	15.6±4.2	15.9±4.3	16±4.8	16.1±4.5	16.3±4.6	16.1±4.2	15.7±4.1
Water temperature(°C)	Summer	26.7±4.7	26.9±4.9	27.1±4.6	28±5.4	27.2±4.6	27.4±4.8	26.8±4.4
	Monsoon	26.1±3.1	25.9±3	26.1±3.1	30.2±1.2	26.4±2.8	26.3±2.8	26.3±2.9
	Winter	14.7±4.2	15.1±4	15±4.3	15.6±4.2	15.2±4.1	15.3±3.9	14.8±4.1
pH	Summer	7.4±0.07	7.4±0.27	7.5±0.31	7.9±0.13*	7.6±0.26	7.6±0.2	7.6±0.23
	Monsoon	7±0.18	7.1±0.18	7±0.15	7±0.17	7.1±0.16	6.9±0.33	7±0.13
	Winter	7±0.17	7±0.16	7.1±0.12	7.1±0.21	7±0.45	7±0.45	6.9±0.45

* Statistical significance is given in comparison to upstream point P3 (P<0.05) during summer

In the case of dissolve oxygen, standard for sustaining aquatic life is 4 mgL^{-1}, whereas for drinking purposes it is 6 mgL^{-1}. While in the case of biochemical oxygen demand (BOD), standard for drinking purpose is 0.2mgL^{-1}, which is exceeded to a great extent as shown by the mean values (41.07±1.26 mgL^{-1}) during summer at site Q. The decrease value of dissolved oxygen in river water at confluence point Q, when compared with the upstream point (P3) might be due to influx of untreated effluents of tanneries into the river water, and high levels of DO during the monsoon and winter season might be attributed to the dilution of the tanneries effluent by rain water and due to lower temperature it is possible that pollutant load may be high but has less adverse effect. The low values of DO (3.79±0.101 mgL^{-1}) during summer at site Q, revealed that the lower oxygen carrying capacity in warmer (temp 28±5.4 ^{O}C) water and increased microbial growth due to high temperature. The lower values of DO observed may also be due to the nature of untreated tanneries effluent discharge into the river water that require the high demand on the DO thereby reducing the levels of dissolved oxygen. BOD and COD values were higher at the confluence point Q, during all season but it slightly fluctuating during upstream and downstream points. The BOD and COD value at confluence point Q, during all season show the highest value, which indicate high organic load. The high value of BOD and COD at confluence point Q might be due to influx of untreated effluent from tanneries which contain higher organic matter into the river, while the decrease in values of upstream point might be attributed to dilution factor due to immense volumes of fresh or rain water. The high and low value of BOD and COD during summer and monsoon season due to reduction in the volume of water and the addition of both organic and inorganic substances from tanneries, while the dilution of effluent by fresh water reduce the BOD and COD level (Akan *et al.*, 2009). The BOD and COD levels recorded in the entire sampling points were higher in the EU guidelines (for BOD 3-6 mgL^{-1} and 200 mgL^{-1} for COD) for the protection of fisheries and aquatic life and for domestic water supply (Chapman, 1996). The curve between TDS versus BOD, COD shows a significant positive correlation that as TDS increases BOD and COD also increase. Theses correlation analysis revealed that the levels of TDS, BOD and COD are affected by same activities with in sampling area. While the correlation analysis between TDS and DO showing a significant negative correlation as TDS increases with corresponding to low DO values. These findings are resembles with the reported value that low DO usually depicts a high TDS values (Ademoroti, 1996). The seasonal variation found in the concentrations of heavy metals between upstream and downstream points. The higher levels of heavy metals during the summer period affected by the same reason, reduction in the volume of water and addition of tanneries effluent, while the low level of theses metals during the monsoon season might be caused by dilution of effluent by fresh water. The levels of Chromium in sediment samples during summer were almost equal to the concentration of chromium in ground water samples at confluence point, Q. These facts also confirm that sediment could act as sink for a wide range of contaminant including heavy metals from various sources (Stephan *et al*., 2001).

Chromium toxicity is frequently the result of long term low level exposure to pollutants common in our environment: air, water, food and numerous consumer products (ATSDR, 1994; Haq *et al*., 2009). Exposure to chromium is associated with many chronic diseases such as dermatitis, ulcers and perforation of the nasal septum and respiratory illness as well as increased lung and nasal cancer (Kornhauser *et al*., 2002; Angerer *et al*., 1987; Lin and Tai, 1994; Stern and Bragt, 1993). Recent research has found that even low levels of chromium, lead, mercury, cadmium, aluminum and arsenic can cause a wide variety of health problems (Rodrigues and Formosos, 2005) and long time exposure leads to immunomodulation (Katiyar *et al*., 2008, 2009). The toxicity of chromium is usually cumulative in nature. In this case, chromium contaminated water utilized by local populatio,n residing in tanneries affected area. The individuals residing in these areas are very prone to infectious diseases such as skin lesions, respiratory problem and indigestion. Approximately 4.67d to develop some awareness to avoid chromium contaminated water.

Conclusion

The diminishing quality of water seriously delimits its use for human consumption and for aquatic life. Therefore, the continuous and periodical monitoring of water quality is necessary so that appropriate preventive and remedial measures can be undertaken. The observations revealed that, climate change has positive effect to tanneries pollution, although river water is certainly unfit for domestic and irrigation purposes without any form of treatment. Tanneries pollution generally accelerates to cause greater deterioration. So few years from now, serious water quality deterioration could take place, which will serious threat to aquatic and human life.

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