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Chapter

Evaluation and Quantification of Anionic Surfactant in the Gomti River at Lucknow City, India

Vinay Kumar, Pokhraj Sahu, Pramod K. Singh, Nishi K. Shukla, Devendra P. Mishra and Markandeya

Abstract

In this paper, an attempt has been made to check the level of surfactants particularly in drinking water, which can lead to toxicity in human body system. In this study, a total of 10 locations were selected to enumerate the concentration of surfactants and other physicochemical parameters with metals in the flowing water of river during pre-monsoon 2019. Analyzed result showed that the concentration of surfactants was significantly high and other parameters were also high. It was also found that river at the vicinity of town areas or midstream in the Lucknow city contained high amount of an anionic surfactants due to the nonpoint sources generated by human activities, low concentration was found in upstream, and average concentration was found in downstream, showing natural degradation of surfactants. The values of other parameters were higher than the prescribed limit, which is the serious problem for human being.

Keywords: the river water, detergent, surfactant, sodium dodecyl sulfate, heavy metals

1. Introduction

Water resources have been the most exploited natural system, since man-made and other activity play a negative role on the earth. The pollutants coming as a waste to the water bodies are likely to create nuisance by way of physical, chemical and biological appearance and this contaminated water is also harmful for human utilities. In the last few decades, the significant deteriorations in water and sediment quality throughout the world are as a result of the extensive population growth also increased industrialization with urbanization which increased the demand of river water [1]. Overall, river water is a major source of fresh water. The establishments of industries in river escort are highly responsible to pollute fresh water; it is a global issue that has no respect for National or International boundaries. The Gomti River is considered to originate from a lake "Fulhar Jheel" in the Pilibhit town in Uttar Pradesh, one of the major tributary of the Ganga. The river flows through different district before meeting the Ganga river in Kaithi, Ghazipur bordering Varanasi (at an elevation of 61 m). The distance of Gomti River is 15 km in the Lucknow city and receives improper treated wastewater from point sources such

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as defense, milk dairy, vegetable, oil, carbon etc. Fifty non-point sources are also discharging wastewater into the river Gomti about 250 MLD from Ghaila bridge upstream to Shaheed Path downstream while three drains Nagaria, Sarkata and Pata were discharged there wastewater without any proper treatment from Daulatganj sewage treatment plant. Three main sources contributed maximum surface water pollution are wastewater discharge from household activity, agriculture practice and from various industries that entire source contribute to detergent in their water. Detergents play a crucial role toward increasing pollution load originated from various sources that come from agriculture runoff in the form of herbicides, residential areas in the form of household detergent and insecticides and from certain industries.

"Detergent" applies to all the products containing soap, surfactant or any substance intended for cleaning and washing process. The uses of detergent have in different forms such as powder, liquid, bar, molded piece and in the form of cake. Several studies reported that the problem of detergents in the river water is growing rapidly in various countries presented in **Table 1**.

River name	Detergent concentration (g m ⁻³) Reference
Gomti River (India)	0.1005–0.2758	Present study
Melez Stream (Turkey)	0.01–6.93	[2]
Gediz River (Turkey)	0.023–4.48	[3]
Yuvarlak Stream (Turkey)	0.12	[4]
Bakırçay River (Turkey)	0.01–0.29	[5]
Küçük Menderes River (Turkey)	0–0.93	[6]
Halifax Harbour River (Canada)	0.001–0.2	[7]
England Rivers	0.007–0.173	[8]
England Rivers	0.012–0.08q	[9]
Tama River (Japan)	0.035–0.219	[10]
Hyogo River (Japan)	0.004–2.5	[11]
Tsurumi River (Japan)	0.01–0.29	[12]
Sumida River (Japan)	0.005–0.01	[13]
Saar River (Europe)	0.01–0.09	[14]
Teshiro River (Japan)	0.01–0.27	[15]
Teganuma River (Japan)	0.019–1.4	[16]
Yodo River (Japan)	0.043–0.089	[17]
Miami River (America)	< 0.05	[18]
Oohori River (Japan)	0.5–1.6	[19]
Mississippi River (America)	0.01–0.3	[20]
Litheos River (Mediterranean)	0.1	[21]
Yorkshire River (England)	0.05–0.25	[22]
Laguna Bay (Filipinler)	0.002–0.102	[23]
Itter River (Germany)	0.007–0.011	[24]
Gediz River	0.084–5.592	[25]

Table 1.

Comparison of detergent concentrations in water of different rivers.

However, surfactant; any organic substance has surface-active properties due to hydrophilic and hydrophobic groups with capable of reducing surface tension of water which forming water-air interface and make a emulsions at water solid interface. The surfactants are also responsible not only for causing foam in rivers and creating procedural problem during wastewater treatment but also responsible for reduction of water quality [26]. Surfactants are classified in several category as anionic, cationic, non-anionic and zwitter ionic or amphoteric surfactant by their ionic activity (special nature) in water [27], if the head of an ionic surfactant carries a positive charge called cationic surfactant, head carries negative charge called anionic surfactant, center attach with both positive and negative charge called amphoteric or zwitter surfactant and the hydrophobic part bonded with oxygen-containing hydrophilic groups (without charge) in non-ionic surfactant. The non-anionic and anionic surfactant is used in laundry detergent due to their high cleaning efficiency as compare to cationic surfactant. The anionic surfactants are carrying negative charge at their head, the negative compound is group of alkyl sulfates and another compound is also using in phosphate and carboxylates. The natural soaps have poor ability in hard water and production of soaps was uneconomic because of lacking of food and oil, after First World War competition of soap industry increase with food and oil industry. German Scientists experimented with synthetic detergent and developed second-grade detergent by using alkyl-naphthalene sulfate. In 1930s the petroleum industries growing rapidly and refineries waste converted into long alkenes chain then reached with benzene and sulfuric acid and developed alkylbenzene sulfonate after neutralization with sodium hydroxide. The alkylbenzene sulfonate has become one of the best laundry detergents and their sale increased a thousand fold as compare to soap. In 1950s, river beginning to foam due to over exploiting of the detergent in Europe and America while the concentration of detergent in potable water of 32 ppb American city during 1959 found 15 to 34 ppb [23]. The Legal action was followed by German Detergent Act of 1962. The United Kingdom passed legal requirement mandatory of laboratory test for bio-degradation of anionic surfactant in 1973. The alkylbenzene sulfonate have replaced with linear alkylbenzene sulfonate (LAS) due to high biodegradability. LAS is a group of anionic surfactant that is found in drinking water, as well as in domestic and industrial wastewaters in bulk form than any other groups because of their ease and low cost [28–30]. They have also adverse effects on aquatic species at 0.005 LAS/L and may cause histological degradation in fish species [31, 32]. They can further induce severe damage to vital organs, even hematological, hormonal and enzyme disturbances, growth and development of the plankton constituents [33, 34], as well as toxic to aquatic life at ≤ 0.025 LAS/L. The alkyl sulfates as sodium dodecyl sulfate (SDS) have found economic and safe ingredient using in food processing (USEPA) and it also called sodium lauryl sulfate. Sodium dodecyl sulfate is less negative effect and inexpensive as compare to LAS so it is using huge after 1980s.

Water quality assessment and seasonal variations in physicochemical parameters of the Gomti River were studied by several researchers [35–40] but still, the Gomti River water study about surfactants level was not studied. The present investigation reveals the level of detergents in the Gomti River which generates base line data and help to government and policy maker.

2. Materials and methods

2.1 Study area

The Gomti River is one of the major tributaries of the Ganga, situated 26.8°N, 80.9°E in Lucknow city after 250 km flowing river from the origin point. The river

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Sample code	Sampling location	Latitude	Longitude (north)	Distance (km)
W/S-1	Ghaila bridge	25°30.58′ 7	8°44.74′	1.5
W/S-2	Gau Ghat	25°29.43′	78°46.54	1.8
W/S-3	Kudiya Ghat	25°30.99′	78°46.71′	1.8
W/S-4	Daliganj Bridge	25°32.25′	78°47.20′	3.0
W/S-5	Hanuman Setu	25°32.25′	78°44.27	3.4
W/S-6	Khatu Shyam	25°32.09′	78°47.14	3.7
W/S-7	Nisatganj Bridge	25°30.56′	78°43.09′	4.1
W/S-8	Gomti Barraj	25°27.56′	78°46.44′	5.1
W/S-9	Dilkusha Garden	25°28.78′	78°42.89′	6.3
W/S-10	Shaheed Path	25°27.90′	78°39.09′	7.9

Table 2.

Description and geographical position of sampling sites in the Gomti River.

serves as one of the major source of drinking water for the Lucknow city and the population of about more than 4.5 million helped by the river in a different way. The study area covers 10 different locations presented in **Table 2**. In this study, selected total 10 reasonable locations in the Lucknow city being an over loaded of pollutants source in stream and identified the levels of toxic heavy metals and other characteristics.

2.2 Criteria for the river water sampling

Sampling stations were selected considering the population load, demographical distribution of river and sources of wastewater. One of the main goals of this study is to collect the samples that are representative of the site conditions, so that an accurate assessment can be made with a minimum number of samples. Predetermined sampling protocols have been chosen for the present investigation. Two pre-washed polythene bottles having 1 and 2 L capacities with stopper were used for the samples collection as per CPCB guideline and store for further analyses.

2.3 Method used for the river water quality assessment

In this study essential physicochemical parameters were recorded during premonsoon 2019 and analyzed in the laboratory according to standard procedures [41]. Various physicochemical parameters like temperature, pH, turbidity, total dissolved solids (TDS), total suspended solids (TSS), total hardness, biochemical oxygen demand (BOD), dissolved oxygen (DO), carbon dioxide (CO₂), electrical conductivity (EC), chloride, sulfate, nitrate, phosphate, total alkalinity, chemical oxygen demand (COD), fluoride (F^-), cadmium (Cd), iron (Fe), lead (Pb), chromium (Cr), copper (Cu), manganese (Mn), cobalt (Co), nickel (Ni) and zinc (Zn) were analyzed.

2.4 Determination of anionic surfactant through methylene blue active substances method (MBAS)

The sample 20 mL was transferred into a 40 mL vial (vial A) equipped with a screw cap and teflon liner. The alkaline buffer (2 mL), neutral methylene blue

Metals	Wave length (nm)	Detection limit (ppm)	h) Sensitivity (ppm) -0.009	
Cd	228.8	0.004		
Pb	217.0	0.1	0.06	
Cr	357.9	0.03	0.05	
Cu	324.7	0.01	0.025	
Ni	232.0	0.09	0.04	
Zn	213.9	0.005	0.008	
Fe	248.3	0.05	0.05	
Mn	279.5	0.15	0.02	

Operating condition of atomic absorption spectrophotometer (AAS).

solution (1 mL) followed by chloroform (5 mL), were added to vial A in successive order. The vial was tightly closed using a holed screw-cap and teflon liner before being vigorously shaken for 2 min using a vortex mixer. After being shaken, the screw-cap was loosen to release the pressure inside and awaited the phase to separate. Once the two phases were separated, a Pasteur pipette was used to transfer the bottom (chloroform) layer into the new vial (vial B) that contained ultra-pure water (22 mL) and acid methylene blue solution (1 mL). Vial B was then shaken using a vortex mixer for 2 min. The cap was then loosened for few seconds and re-tightened. After the chloroform had completely separated from the water (after 2 min), the chloroform layer was collected using a Pasteur pipette and placed in a 10 mm quartz cell. The absorbance of the chloroform phase was measured by using a UV spectrometer at a wavelength of 650 nm. The concentration of anionic surfactants as MBAS is calculated from the calibration curve established with appropriate reference material such as sodium dodecyl sulfate (SDS) (0.05, 0.1, 0.5, 1.0, 1.5 and 2.0 μ M).

2.5 Quality assurance and quality control

Appropriate quality assurance and procedures were followed to ensure the reliability and reproducibility of the results. Glassware were dipped in chromic acid for overnight and washed 2–3 times with de-ionized water before use. Analytical grade standard chemicals and reagent blanks were used during analyses to check chemical impurities and other environmental contaminations. Always, freshly prepared solutions were standardized against primary standard for actual strength. Triplicate samples were analyzed to check precision of the analytical method and instrument. For elemental analysis, certified reference material (CRM) multi element standard solution IV (CertiPUR® 1.11355.0100 Lot. No. HC081563, Merck) were used and the operating condition are given in **Table 3**.

3. Result and discussion

The river is characterized by sluggish flow throughout the year, except during the monsoon season, when heavy rainfall causes a manifold increase in the runoff causing more turbid of water. The summaries of result for physicochemical and heavy metals are presented in **Figures 1–3**.

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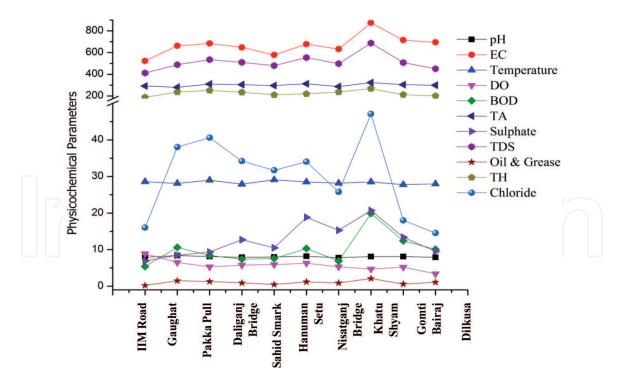


Figure 1.

Graphical representation of physicochemical parameters in the Gomti River water [in mg/L except pH and EC $(\mu S/cm)$].

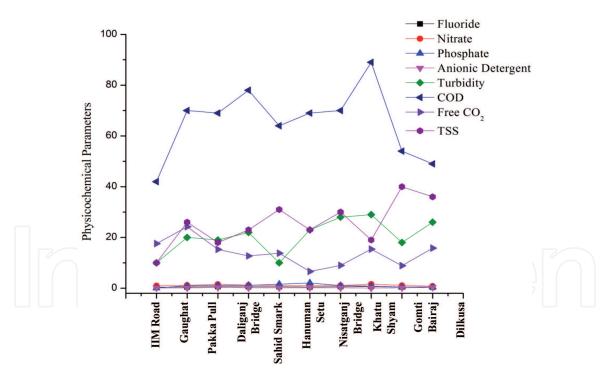


Figure 2.

Graphical representation of physicochemical parameters in the Gomti River water (in mg/L).

3.1 Physical parameter in the Gomti River water

Electrical conductivity varied from 523 to 874 μ S/cm and it depended upon the presence of cations and anions, mobility, valence and temperature of water which was a good measure of total amount of salt present in water. Spot temperature were measured in the ranged from 27.8 to 29.1°C (**Figure 1**). Temperature is one of the critical and influencing physical parameter of water quality because it influences the

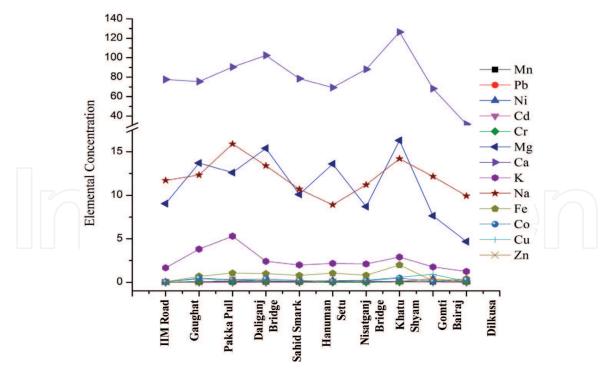


Figure 3. *Graphical representation of trace elements in the Gomti River water (in mg/L).*

aquatic life by altering the dissolve oxygen (DO) and other concentration in the water making oxygen less available for respiration and metabolic activity of aquatic organisms [42, 43]. Turbidity was measured by the Turbidity meter and average value is recorded between minimum 10.0 NTU at IIM Road and maximum 29.0 NTU at Gomti Barraj. Obtained turbidity was very high in all the studied locations and found above the prescribed limits by BIS (10500-2012) [44]. Comparatively high turbidity in Gomti Barraj may be due to the mixing of large amount of sewage water, disposal ash and organic pollutants from the surrounding locality. The increase in turbidity by organic pollutants resulting eutrophication of water bodies which consequently diminish the light transmission into water and thus gradually condense overall productivity.

The average value of TSS in river was recorded 25.6 mg/L, which was well within the standard limit (150 mg/L) prescribed by WHO in terms of inland surface water. The amount of total dissolve solids (TDS) in water indicates salinity of water and may also be used as an indicator for rapid plankton growth and sewage contamination. In this study average TDS value is measured value were ranged from 412 to 687 mg/L at IIM Road (**Figure 1**).

The lowest and highest values of Hardness were observed 188.0 mg/L at IIM road and 268.0 mg/L at Gomti Barraj location. Hardness is caused due to presence of cations like Ca⁺², Mg⁺², Fe⁺³ etc. This is the property of water to precipitate soap by formation of complex with calcium, magnesium present on water. The calcium and magnesium are exists in surface and ground water mainly as carbonates and bicarbonates. River water contributed calcium as due to higher proportion of calcium in the surrounding rocks and soils which is essential for plant precipitation of lime, bone building etc. The main source of magnesium is sewage inflows and minerals generate from soil erosion and are important for enzyme activation, growth of chlorophyll and phytoplankton [45]. In the present study calcium content were found to 126 mg/L and magnesium 11.18 to 16.30 mg/L. The lowest values of calcium and magnesium were observed 31.62 and 4.68 mg/L at Dilkusha, while highest 126.3 and 16.3 mg/L at Khatu Shyam location respectively.

3.2 Chemical parameters in the Gomti River water

The pH value of all the studied water samples is measured by digital pH meter and average pH is recorded between 7.8 and 8.4 which was found very approximate to the high limit (6.5 to 8.5) prescribed by the BIS (10500-2012) [44]. As per measurement, pH values were found lowest (7.8) in Khatu Shyam location and highest (8.4) found in Gau Ghat location (**Figure 2**). pH that maintains the acidic or alkaline property is a vital characteristic of any aquatic ecosystem since all the biochemical activities and retention of physicochemical attributed to the water are greatly depend on pH of the surrounding water [46]. It also prevails in biological and physicochemical attributes of surrounding water.

DO was measured between 3.4 and 8.9 mg/L whereas the highest concentration at IIM Road was found and lowest concentration at Dilkusha. The aquatic life distressed when DO levels drop from 4 to 2 mg/L [47] and as DO level falls undesirable changes in odor, taste and color reduce the usefulness of water [43]. Biochemical oxygen demand (BOD) is also an important parameter of water quality which measures the quantity of oxygen consumption by microorganisms during decomposition of organic matter present in the water. BOD of the water river was measured by using method APHA 5210. For drinking purpose, BOD of water should be zero. High BOD than the prescribed value was found in the studied river where the minimum average value was found 5.4 mg/L at IIM Road and highest was found in 19.9 mg/L at Gomti Barraj (**Figure 2**). The alkalinity express the buffering capacity of the water which appreciably maintain the pH by absorbing access H⁺ ions and protects the water body from pH fluctuation. Whereas carbonates and bicarbonates associated with sodium and potassium contribute only alkalinity not hardness because of incapability of sodium and potassium to form complex with electron donor ligands. In this study, lowest and highest alkalinity was found to be 280.0 mg/L at Gau Ghat and Gomti Barraj respectively whereas the average value of alkalinity was found to be 300.8 mg/L. The alkalinity values were found higher than the prescribed limit by IS-10500, 2012 standard. The average value of potassium was recorded 2.53 mg/L were ranged from 1.24 mg/L at Dilkusha to 5.30 mg/L at Pakka Pul. In this study, the Sodium content is measured between 8.90 and 15.90 mg/L whereas the highest concentration at Pakka Pul is found and lowest concentration at Hanuman Setu. In this study, the oil and grease was observed between 0.6 and 2.1 mg/L, whereas the highest concentration at Khatu Shyam, while lowest concentration at Gomti Barraj. The chemical oxygen demand (COD) was analyzed by using open reflex digestion method and COD varied from 42.0 to 89.0 mg/L with an average value was 13 mg/L. The maximum value of COD was found to be 89.0 mg/L at Khatu Sham station. Mixing and accumulation of sewage discharges from nonpoint sources resulted high COD at this location. The Hanuman Setu and Gau Ghat are contributing lowest and highest value of CO₂ concentrations were 6.6 to 24.2 mg/L respectively and the average values was found to be 13.9 mg/L. The activity of the microorganisms increase due to organic load of water results the increase the level of CO_2 in river water.

Chloride is not harmful to humans but high concentration of chloride increase the corrosive property of water. The chloride content was within permissible limit as prescribed by BIS and average values were recorded as lowest and highest (14.5 to 47.1 mg/L) at Shaheed Smarak and Gomti Barraj, whereas the average values of chloride was 30.0 mg/L. The value of sulfate were recorded between 6.9 and 20.7 mg/L. Comparatively lowest and highest amount of sulfate was recorded at IIM Road (6.9 mg/L) and at Gomti Barraj (20.7 mg/L), which is might be due to discharge of municipality sewage and dumping of domestic waste into the lakes. The average value of nitrate and phosphate were found 1.20 and 1.0 mg/L respectively (**Figure 2**). High level of nitrates is found in rural areas because of extensive application of nitrogenous fertilizers in agriculture. In urban areas sewage water rich in nitrates contaminate surface water thus increases the nitrate amount [48].

3.3 Anionic surfactant level in the Gomti River water

Detergents make our cloth brighter or whiter by emitting blue light after absorbing UV light. In this study, the anionic surfactant is measured between 0.1005 and 0.2758 mg/L whereas the highest concentration was analyzed at Pakka Pul and lowest concentration at Khatu Shyam station. The average value (0.1832 mg/L) was found within the prescribed standard of Indian standard, while the value were exceed in Pakka Pul, Daliganj Bridge and Dilkusha sampling station, at this location the activity of washer man is higher to washing the cloths that can creating the emerging level of anionic detergent (Figure 2). Different type of detergent are using for cleaning of cloth such as Surf Excel, Active Wheel, Ariel, Tide Nirma, Saheli, Ghari, Rin Supreme and Fena in the powder form and many others in liquid form. This washing substance made up with many different chemical components such as surfactants, enzyme, bleaches, optical brightness, perfume, color and builders, and anti-redeposition agent and filter. They are dissolved in water and react with dirt and remove from cloth and other materials. The discharging of that wastewater into the river water without proper treatment created serious issue such as foaming, decreasing light penetration into different depth of the river making aerobic zone, eutrophication and several eco-toxic effects on aquatic animals. The concentration of anionic surfactant from 1 to 20 mg/L showed LC50 in fish [49, 50]. Koç and Güven [51] studied the single and progressive dose of 12.5 to 35.0 mg/L in Oncorhynchus mykiss. Many researchers have shown that activated carbon is an effective adsorbent for treating water with high concentrations of organic compounds [44]. Various biotechnological techniques have recently described an important group of bio surfactants using lipases or enzymes that can reduce environmental load of detergent products as the chemicals used in conventional methods; they are biodegradable and non-toxic, and also leave no harmful residues [52].

3.4 Heavy metals in the Gomti River water

The Gomti River receives industrial as well as domestic waste from various drains in the city. The analyzed concentration of Mn, Pb, Ni, Cd, Cr, Fe, Co, Cu and Zn were represented in **Figure 3** and the average value were found to be 0.045, 0.057, 0.134, 0.007, 0.036, 0.792, 0.250, 0.303, and 0.110 mg/L respectively.

The results were found that Cd and Pb in higher amount which is very toxic for environment as well as aquatic ecosystem. The level of Mn, Fe, Co, Cu and Zn were higher in Khatu Shyam. Higher concentration of metal in water and sediment could be due to the industrial/agricultural/domestic runoff coming into the river. The maximum concentration of Pb, Ni, Cd and Cr were observed at Gomti Barraj. Intake of excessive concentration of heavy metals can pose carcinogenic effect on human and water quality assessment is necessary where the water using as a drinking purpose because of human actives creating huge quantities of wastes that can cause environmental pollution. The concretions of As, Cu, Fe and Cd in the Gomti River water were 0.029 to 0.079, 0.0145 to 0.061, 0.077 to 1.685 and 0.0144 to 0.0244 mg/L respectively. Kumar et al. [53] also found the similar result in the Gomti River. Industrialization and urbanization is growing rapidly with population and untreated waste disposal also increased due to mismanagement and overload wastes discharges from household into aquatic system [54]. That untreated wastewater and sewage loaded with heavy metals and organic compound into the water stream.

4. Conclusions

River is an important for every human being. History showed that major civilization was developed on the bank of river. But due to modern civilization, increased in population and changing lifestyle of human, the quality and quantity of river is gradually reduced. The present study concluded that the level of total alkalinity, total dissolved solid, total hardness, turbidity, Pb, Ni, Cd, Ca, Fe and Cu was found beyond the acceptable limits of drinking water quality standard. The level of anionic detergent in drinking water is 0.2 mg/L recommended by Indian government but the value of anionic surfactant were exceed in Pakka Pul, Daliganj Bridge and Dilkusha sampling point. The emerging level of water pollution caused due to continuously discharging of improper and untreated sewage and wastewater. This study strongly recommended to awareness is need to people of this city and good operation practice to operator of STP.

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Conflict of interest

There is no conflict of interest.

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