

# **RESEARCH PAPER**

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# Water quality assessment of Shizaka streams, Tehsil Shewa, North Waziristan agency, FATA, Pakistan

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# Abstract

The present study was conducted on Shizaka Stream and Ghorghori Stream (Both are commonly called Shizaka Streams), Tehsil Shewa, North Waziristan Agency, FATA, Pakistan, to assess the water quality of these streams by studying their Physico-chemical parameters. This study was carried out from February to May 2016. Water quality is the study of chemical, physical and biological contents of water. Fish production depends upon the quality of water. Regular supervision of water quality is very important for aquaculture purposes. Various digital kits and chemical methods were used for assessment of these physico-chemical parameters. Water samples were collected for analysis on monthly basis from Shizaka Streams (Shizaka Stream and Ghorghori Stream). The mean Physico-chemical parameter's values recorded for four months were: pH 7.137, Temperature 23.2°C, Dissolved Oxygen 7.325mg/l, Electrical Conductivity 195.74  $\mu$ mhos/cm, Total Hardness 260.62mg/l, Total Alkalinity 252.055mg/l, Salinity 0.137mg/l, Total Dissolved Solids 196.43mg/l, Total Suspended Solvents 81.657mg/l, Sulphates 206mg/l, Ammonia 0.75mg/l, Free CO<sub>2</sub> 4.707mg/l, Nitrate 0.085mg/l, Magnesium 35.75mg/l and Calcium 138.375mg/l. The values of all the measured parameters except Magnesium and Total Suspended Solids were in the permissible range as described by the United States Public Health standards suggested for surface water in 1976 and World Health Organization. The study was made with the purpose to know the suitability of these streams for fish survival and prospects of aquaculture in the area.

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#### Introduction

Water quality is the study of chemical, physical and biological contents of water. Variability in water quality is in association with seasons and geographic areas (Lawson, 2011). It is the degree of fitness of water for the basic needs of various aquatic species and or requirements of mankind (Johnson et al., 1997). Liquid crystals of water are also found adjacent to hydrophilic surfaces (Jan et al., 2014). Scientifically, it is also called dihydrogen monoxide, although this term is rarely used (Barmer and Scott, 2011). About 3/4 of the earth is covered by water where 96.5% from oceans, 1.7% groundwater, 1.7% glaciers and ice caps, a very small amount in large aquatic areas and 0.001% as vapours, precipitations and clouds in air. In addition, freshwater contribute only 2.5% to the total water on planet earth while the rest are in ice and groundwater. Freshwater bodies like rivers, lakes contain about 0.3% and living organisms as well as manufactured products cover only 0.003% of the total freshwater (Gleick, 1993).

Water is extremely important and crucial for all kinds of living organisms. A very small portion of water (33400m<sup>3</sup>) out of total earth's water (1011 million Km) is accessible for drinking, agriculture, domestic and industrial consumption. While the remaining is enclosed in ocean, glaciers and underground. Day by day increasing population and industrialization has led to an alarming demand of water supply. Moreover, industrial pollutants, domestic sewage and synthetic chemicals are the main causes of pollution of such less amount of water. Owing to these pollutants, aquatic life as well as human being face a lot of diseases. Therefore, supply of water with good physico-chemical parameters is of prime importance for the welfare of human being (Darra, 1993).

One of the major problems human is facing in 21th century is the quality and quantity of water. In near future, it seems that climate change will greatly intensify these problems thereby creating serious consequences like elevation of water temperature, melting of glaciers and aggravation of water cycles, possibly leading to floods and droughts.

Poor sanitation directly related to lack of drinking clean water which nowadays adversely affects large percentage of human population in the world. Additionally, it also results in disturbance of food chain by exposing to toxicants/ pathogen (i.e. irrigation with polluted water and bioaccumulation of heavy metals by aquatic life), recreation (swimming in polluted surface water) (Jan et al., 2014). Due to contamination, trophic status of the water bodies can change and make them improper for aquaculture. Some biological or physicochemical factors may result in stress and badly affect the fish reproduction and growth (Iwama et al., 2000). The physical and biochemical conditions such as pH, temperature, turbidity, conductivity, total hardness of water, phosphates, oxygen, nitrate, carbon dioxide, chloride and heavy metals are important (Boyd, 1982; Boyd and Gross, 2000). Therefore, proper monitoring and management of physicochemical water quality parameters of rivers and streams is very crucial in reference to culturing and survival of fish.

In Pakistan especially Khyber Pakhtunkhwa, various studies have been carried out on water quality parameters and its impact on human and aquatic life i.e. Yousafzai *et al.* (2013), Korai *et al.* (2008), Jan *et al.* (2014) and Nazir *et al.* (2015). Therefore, the present study was conducted to study;

- The effects of different water quality parameters on the fish life in these Streams.
- The water quality parameters and their comparison with standard values.
- Make aware the people of the area about the importance of aquatic life

#### Materials and methods

#### Sampling Area

North Waziristan Agency (NWA) is the mountainous region situated in the Northwest of Pakistan. The latitude and longitude of NWA are 330 o'o" North and 700 o'o" East, respectively. Tehsil Shewa, a part of NWA having latitude and longitude of 33.253310 North and 70.494160 East respectively, is situated on the eastern side of NWA. The research area Shizaka where the two streams are present, have latitude and



longitude of 33.252627 North and 70.623229 East,

respectively.

Fig. 1. Map showing the study area (Shizaka Streams).

#### Water Quality Parameters Estimation

For the assessment of physico-chemical parameters, water samples were taken every month from both the streams, in triplicate, for four months (February to May 2016). Water samples were collected in clean, disinfected plastic bottles. Before collection, the plastic bottles were washed properly and then samples were collected from the depth of about 2cm to 5cm below the water surface in order to take better samples. The following parameters were studied.

#### Water Temperature

Water temperature was measured on the spot by using water temperature thermometer (Digital thermometer CE). The scale of thermometer was brought to the environmental temperature. After this it was kept in the stream water for 1.5-2 minutes for temperature measurement. This process was repeated three times and then the mean value was noted.

#### Water pH

pH of the water sample was measured using pH meter (LT Lutron WA-2015, Bench type real time datalogger).

The pH meter was switched on and calibrated against the standard buffer of pH 4.0 and pH 7.0. After calibration 25ml water sample was taken in a beaker and the probe of pH meter was dipped into it. The reading on the display was noted down.

#### Total Salinity and Electric Conductivity (EC)

Salinity and Electrical conductivity were measured by the conductivity meter (HI 8033, HANNA Instruments). The probe of conductivity meter was cleaned with tissue paper or piece of cloth and then the meter was turned on. The probe was dipped in the water and the reading was noted down from the digital display.

#### Total Dissolved Solids (TDS)

The quantity TDS was measured by the following formula.

TDS (mg/l) = EC of sample  $\times$  0.64

#### Dissolved Oxygen (DO)

Dissolved oxygen of the water was measured on the spot. The DO meter (Lutron WA 2015) was calibrated with 0% and 100% DO standard solution respectively.

The probe was putted into the water sample and the reading was confirmed.

#### Total Hardness (T. H)

25ml of water sample was taken and then added 1-3ml of pH-10 buffer solution to it. Few drops of Eriochrome Black-T (EBT) were added as indicator. After this it was titrated against 0.01N solution of Ethylenediamine tetra acetic acid (EDTA) until reddish colour changed to bluish purple. The amount of EDTA used was noted.

Formula =  $\frac{\text{Vol. of EDTA used} \times \text{Normality of EDTA } (0.01) \times \text{mol.wt of CaCO}_3 (100) \times 1000}{\text{Volume of water sample } (25\text{ml})}$ 

#### Free Carbon Dioxide

25ml of water sample was taken in a beaker. 5-7 drops of phenolphthalein indicator were added to it. This was titrated against 0.02 N solution of NaOH until the colour changed to pink. The volume of NaOH used was recorded and multiplied by 10.

#### Total Alkalinity

The total alkalinity was determined using the protocol described by APHA (1995) at the departmental laboratory.

#### Total Suspended Solids (TSS)

TSS was measured by "filtration method". Initially dry filter paper was weighted  $(W_1)$  on physical balance.

The apparatus was set for filtration. 50ml of water sample was filtered out. After filtration, the filter paper was weighted (W<sub>2</sub>).

W1= weight of filter paper before filtration W2= weight of filter paper after filtration TSS (mg/l) = W<sub>2</sub>- W<sub>1</sub>

#### Calcium Hardness

25ml of water sample was taken and added with 1-2ml buffer pH-10 solution. After that, 1-2ml Murices Oxides was added as an indicator. It was titrated against 0.01 N solution of EDTA until the reddish colour changed to bluish purple. The volume of EDTA used was noted.

Calcium hardness =  $\frac{\text{EDTA used} \times \text{Normality of EDTA } (0.01) \times \text{Mol.Wt of CaCO}_3 \times 1000}{\text{Volume of water sample } (25\text{ml})}$ 

#### Magnesium Hardness

Magnesium hardness was measured by subtracting Calcium hardness from total hardness.

Mg. Hardness (mg/l) = T.H – Calcium Hardness

#### Ammonia

Ammonia was measured using Hach DR/2000 Spectrophotometer. 25ml water sample was taken. Using pipette filter and pipette added 1.0ml Rochelle salts-PVA reagent to each cylinder and inverted several times to mix. Then added 1.0ml Nessler reagent and shaked the sample. The spectrophotometer was turned on at programme-3 until small display showed 425nm wavelength. The zero was pressed and showed ammonia.

The blank was removed from cell holder and placed in the prepared sample. The ammonia (mg/l) was noted.

# Sulphates

Sulphates were measured using Hach DR/2000 Spectrophotometer. One spoon Sulpha Ver 4 Sulphate reagent powder pillow (BaCl<sub>2</sub>) was added to 25ml sample and inverted for mixing. Due to the presence of sulphates, a white turbidity appeared. It was allowed for at least five minutes to develop fully. Another sample cell was filled with 25ml water and placed a cell holder into it. The light shield was closed. Sulphate meter scale was inserted into sulphate meter and adjust wavelength dial to 450nm. 6-8-0 programme was pressed and showed 450nm wavelength. Read/ enter was pressed which showed zero mg/l SO<sub>4</sub>. Prepared sample was taken and putted it in cell holder and SO<sub>4</sub> value was noted.

#### Nitrates

For estimation of nitrates concentration, Jan et al. (2014) was followed.

### Results

The results of the present study listed in Tables 1-3. The mean values of physico-chemical parameters recorded for four months were; pH 7.137, DO 7.325mg/l, Temperature 23.2°C, EC 195.74 µmhos/cm, TH 260.62mg/l, TA 252.055mg/l, Salinity 0.137mg/l, TDS 196.43mg/l, TSS 81.657mg/l, SO<sub>4</sub> 206mg/l, NH<sub>3</sub> 0.75mg/l, Free CO<sub>2</sub> 4.707mg/l, Nitrate 0.085mg/l, Mg++ 35.75mg/l and Ca++ 138.375mg/l. The values of all the measured parameters except Magnesium and Total Suspended Solids were in the range of the limits suggested by the United States Public Health standards suggested for surface water in 1976.

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Parameters	Feb.	March	April	May	Mean	Standard values *
pH	7.0	6.9	7.2	7.0	7.025	6.5-9.0
DO (mg/L)	7.4	7.6	7.1	6.9	7.25	5.0
Temp (°C)	23.0	22.7	23.8	24.1	23.4	16-40
EC (µmhos/cm)	204.32	223.07	128	180.61	184	100
TH (mg/L)	320	280	240	180	255	10-400
TA (mg/L)	232	160	260	200	213	10-400
Salinity (mg/L)	0.2	0.31	0.1	0.09	0.175	0.001-0.5
TDS (mg/L)	190	260.64	205.11	172	206.93	<400
TSS (mg/L)	88.40	93.02	112	60	88.35	<80
$SO_4(mg/L)$	25	245	232	122	213.25	250
$NH_3(mg/L)$	0.52	0.58	1.08	0.94	0.78	1.5
$CO_2(mg/L)$	3.8	4.2	3.4	5.3	4.175	10-15
Nitrate (mg/L)	0.12	0.05	0.10	0.09	0.09	0.1
$Mg^{++}(mg/L)$	58	38	33	44	43.25	<15
Ca++ (mg/L)	144	142	128	96	127.5	4-160
*I : :						

Limits suggested by the United States Public Health standards and World health Organization for surface water.

Table 2.	Physico-chemical	parameters of	Ghorghori Stream	n.

Parameters	Feb.	March	April	May	Mean	Standard values*
pH (mg/L)	7.5	7.0	7.2	7.3	7.25	6.5-9.0
DO(mg/L)	7.8	7.6	7.0	7.2	7.4	5.0
Temp (°C)	21.7	22.	23.9	24.0	23.0	16-40
EC (µmhos/cm)	197	202.32	211.61	219.02	207.48	100
TH (mg/L)	290	305	200	270	266.25	10-400
TA (mg/L)	310	276	295.46	283	291.11	10-400
Salinity (mg/L)	0.12	0.03	0.26	0.004	0.10	0.001-0.5
TDS (mg/L)	142.11	213	229.68	159	185.94	<400
TSS (mg/L)	74.22	53.64	91.01	81	74.96	<80
$SO_4 (mg/L)$	216	200	246	133	198.75	250
$NH_3(mg/L)$	0.37	0.58	1.0	0.94	0.72	1.5
$CO_2 (mg/L)$	4.8	5.2	5.06	5.9	5.24	10-15
Nitrate (mg/L)	0.003	0.18	0.04	0.11	0.08	0.1
$Mg^{++}(mg/L)$	30	21	35	27	28.25	<15
$Ca^{++}(mg/L)$	144	166	115	172	149.25	4-160

\*Limits suggested by the United States Public Health Standards and World Health Organization for surface water.

Table 3.	Mean	Physico-	chemical	Parameter	rs of Shizal	ta Streams.

Parameters	Mean (Shizaka Stream)	Mean (Ghorghori Stream)	Overall Mean
pН	7.025	7.25	7.137
DO (mg/L)	7.25	7.4	7.325
Temp (°C)	23.4	23.0	23.2
EC (μmhos/cm)	184	207.48	195.74
TH (mg/L)	255	266.25	260.62
TA (mg/L)	213	291.11	252.055
Salinity (mg/L)	0.175	0.10	0.137
TDS (mg/L)	206.93	185.94	196.43
TSS (mg/L)	88.355	74.96	81.657
SO4 (mg/L)	213.25	198.75	206
$NH_3$ (mg/L)	0.78	0.72	0.75
CO2 (mg/L)	4.175	5.24	4.707
Nitrate (mg/L)	0.09	0.08	0.085
Mg++(mg/L)	43.25	28.25	35.75

# 160 | Ahmad and Hasan

# Ca++(mg/L) 127.5 149.25 138.375 Discussion (Table 1 & 2). These values are normal values in the second values of the second values of

The results of the water quality parameters recorded show that all the parameters are in permissible range except EC and Mg which proves to be beneficial not only for Ichthyofauna, but all the aquatic organisms present in the area. All these parameters recorded play vital role in survival of fish and affect its diversity.

Temperature of water has a great effect on migration and distribution of fishes (Yousafzai *et al.*, 2013). Freshwater fish species are exothermic in nature that physiologically cannot normalise their body temperature (Moyle and Cech, 2004). Temperature range of 25-32°C is good while below 16°C and above 40°C is lethal for fish (Ali, 1999). However, range of water temperature varies for different species and it depends upon the cold, semi-cold and warm category.

Temperature may affect the limnological factors like gases solubility, water stratification and metabolic activities of aquatic life. Water temperature of these streams ranged from 21-24.1°C (Table 1 &2). The present recorded values for water temperature fall within the permissible range.

Water having pH equal to 7.0 is termed as pure/neutral water while that having pH above or below 7.0 called Alkaline or Acidic water respectively. pH 6.5 to 9.0 is very productive for fish survival ad growth while pH above 9.5 is unfavourable for fish growth; pH 11 is lethal for fishes. pH range of 7.5-8.5 is ideal for fish. Mostly natural water has pH of 6.0 to 9.0 (Ali, 1999). In case of aquaculture, pH of the standard water quality is 6.5-8.0 (Meade, 1989).

High photosynthetic activity results fluctuations in pH values because during daytime photosynthetic activity increases phytoplankton's consumption of carbon dioxide and release of carbonates which will lower the pH of the surrounding water making it acidic. In addition, during night time release of carbon dioxide occurs which elevates the pH level. Recorded pH of these streams ranged from 6.9-7.5 (Table 1 & 2). These values are normal values in accordance with the standard values.

Dissolved oxygen is as vital for fish survival as water temperature. Diffusion plays a key role to enter oxygen from atmosphere into the water column and in addition, photosynthetic activity results in oxygen production (Kalff, 2000; Stickney, 2000). Fast flowing water has high range of dissolved oxygen than stagnant water. In addition, more dissolution of oxygen occurs in cold water as compared to warm water. Quantity of Oxygen is inversely proportional to temperature. It is very important for respiration of plants and animals in the water.

In the presence of nutrients and proper sunlight, its production also takes place in the plants during photosynthesis (Muhammad et al., 2016). Moreover, 3-12mg/l of DO would enhance the growth and survival of fish (Boyd, 1979). It is difficult to determine its requirements of aquatic animals because it rapidly changes by various factors. As it is inversely proportional to temperature, high temperature will greatly reduce oxygen dissolution that may have bad effects on the development of fish eggs, which might lead to disturbance in species abundance, dominancy, age structure, etc. Dissolved oxygen in the present study was 7.0-7.8mg/l (Table 1 & 2). The recorded DO level falls within the permissible range and is very productive for fish growth.

Electrical Conductivity means the ability of water to conduct electricity depending upon the number of free ions and minerals salts of  $Ca^{+2}$ ,  $Mg^{+2}$ , Na, etc present in water. The range of electrical conductivity for freshwater is 100-1000µS/cm but may exceed in case of water pollution or large amount of land runoff (Chapman, 1997).

Electrical conductivity is directly proportional to water temperature. Due to its non-specific nature, it can be measured for establishing pollution zone. Electrical conductivity in the present study ranged from 128-223µmhos/cm (Table 1 & 2). The recorded EC value are out of the acceptable range. High EC may create high osmotic pressure around the roots of aquatic plants which prevent efficient water absorption by the plants resulting in poor and stunted growth of plants.

Total Hardness is a general term that used when dissolved minerals of Calcium, Magnesium, Manganese, etc., are present in water. The water hardness is very important in distribution of animals (Yousafzai *et al.*, 2013).

Presence of multivalent cations represents the hardness of water. Calcium and Magnesium commonly found in hard water (Weingartner, 2006). Hardness due to calcium and magnesium is called calcium hardness and magnesium hardness respectively while hardness due to both is called total hardness (Wurts and Durborow, 1992). Total hardness ranged from 180 to 320 mg/ during this study (Table 1 & 2). The recorded T.H of Shizaka and Ghorghori Streams falls within the acceptable range as suggested by the USPH standards for surface water in 1976 that is 10-400.

Alkalinity includes all those substances in water, which resist changes in pH on the addition of acids. As normal range of alkalinity makes the water neutralize so in case of lower alkalinity, the water becomes acidic which is not good for fish physiological activities and health. Therefore, normal value of alkalinity is very crucial for fish. Alkalinity of 10-400ppm is a standard range (Meade, 1989). For an aquaculture pond, total alkalinity ranging from 20-200mg/l is good (Muhammad *et al.*, 2016). The range of total alkalinity in the present study was 160-310mg/l (Table 1 & 2). The current recorded values of the parameters fall within the tolerable range.

Salinity is usually defined as the total amount of the salts or dissolved inorganic ions in the water. The freshwater life can tolerate the salinity of slight increase as freshwater has less than 01 ppt range of salinity. Brackish water is usually defined as the water that has a salinity range of more than 01 ppt. Freshwater have average salinity of 0.065 ppt (for soft water) and up to 0.30 ppt (for hard water) (Ali, 1999). The standard value for salinity suggested by the

USPH for surface water in 1976 is 0.001-0.5 ppt. The salinity ranged from 0.004-0.31mg/l in the current study (Table 1 & 2).

Total Dissolved Solid (TDS) refers to the weight of total amount of materials dissolved in water. TDS in water are the dissolved organic and inorganic substances like carbonates, bicarbonates, sulphates, phosphates, sodium, potassium, magnesium, chloride etc., in water. The recommended standard values of total dissolved solids for fish range <400ppm (Meade, 1989). Range of Total Dissolved Solids was 142-260mg/l (Table 1 & 2) in our study. These recorded values fall within the recommended standard value (<400ppm) for fishes [12] and USPH in 1976.

Total Suspended Solids (TSS) is the measurement of the floating suspended particles in the water. TSS results in an ultimate increase in turbidity of water and decreases transparency of water and penetration of sunlight. The high particulate matters can clog the fish gills. Total Suspended Solids ranged from 53-93mg/l (Table 1 & 2). The recorded values of physicochemical parameter of Shizaka Stream and Ghorghori Stream exceeded the limits in some months while in some these fall within the permissible range.

 $Mg^{+2}$  plays a key role in muscle's contraction and nervous impulsion. It is also present in coenzymes (Yousafzai *et al.*, 2013). The present study showed the range from 21-58mg/l (Table 1 & 2). The reported magnesium hardness exceeded the limits of standard for aquaculture. Too much  $Mg^{+2}$  does not affect the growth and production of plants directly. Rather it can cause deficiencies of other nutrients like Ca<sup>+2</sup> and K<sup>+</sup> which may have bad effect on the health of aquatic plants.

Water containing less than 10mg/l calcium are usually oligotrophic and that containing more than 25mg/l are eutrophic (Cambell and Wildberger, 2001). Boyd (1998) reported a range from 75-150mg/l of calcium hardness for freshwater aquaculture. In the present study, calcium ranged from 96-172mg/l (Table 1 & 2). In case of Shizaka Stream, calcium range fall within acceptable range while that of Ghorghori Stream, the reported range of second and fourth months is slightly above the standard limits compared with (Boyd, 1998) and USPH in 1976. According to APHA (1995), the tolerable limits of free  $CO_2$  for fish production are those that do not exceed 10mg/l. High concentration of carbon dioxide along with low DO are harmful for fish. More than 20ppm of free  $CO_2$  is considered lethal (Ali,1999). The observed range of free  $CO_2$  was 3.4-5.9mg/l (Table 1 & 2) in the current study. These values are in acceptance range.

Nitrate is soluble in water and a source of water. Normal amount of nitrate is used as fertilizer and is better for aquatic plants and nitrogen-fixing bacteria like *Nitrosomonas* and *Nitrobacter*. The standard value for nitrate is 0.1mg/l suggested by the USPH for surface water in 1976. The recorded range was 0.003-0.18mg/l (Table 1 & 2) with calculated mean (Table 3). The recorded values for nitrate fall within the normal range.

Sulphates are necessary for plant growth and important in protein metabolism. Aquatic fauna flourish well at concentration less than 50mg/l of water sulphate ions. Water containing less than 5mg/l of sulphates will not support the growth of algae. The standard value for sulphates is 250mg/l suggested by the USPH for surface water in 1976. The total range in the current study was 122-254mg/l (Table 1 & 2). These values are in permissible range but reached to the high limits. High concentration of sulphates affects the health of aquatic animals by causing gastrointestinal diseases. Moreover, it also makes the water unpleasant.

Ammonia is the main nitrogenous waste product and a major by-product of protein metabolism. Ammonia causes stress and damages gills and other tissues even in small amounts. Fish exposed to low levels of ammonia over time are more susceptible to bacterial infections, have poor growth and will not tolerate routine handling as well. We determined the concentration of ammonia in both streams which ranged from 0.37-1.08mg/l (Table 1 & 2). The recorded values are in acceptable range as described by USPH. Our results showed that most of the studied physicochemical parameters were in the normal range as described by various scientists in previous studies (Table 3). However, few parameters like Mg and EC exceeded the normal range while TSS and sulphates showed the peak values. The reason might be the entrance of wastes from houses. Moreover, majority of the population living on the banks of both the streams are shepherds having hundreds of goats and sheep. As a result, large quantity of animal's manure may be added to the stream water resulting enhanced concentration of some ions. If the animal's manure is not properly monitored, it will cause more water pollution leading to the increased level of various physico-chemical parameters in near future. It can badly affect the distribution and survival of the flora and fauna of both the streams. In addition, awareness campaign about the management of wastes from houses may reduce the chances of pollution.

#### **Conclusions and Recommendations**

It is concluded that although most of the recorded parameters are within permissible limits, but some have shown values above normal or peak values which shows that deterioration has been started and water bodies has started showing pollution stress.

It is suggested that people living on the banks of the streams should be made aware by arranging seminars and using electronic media about the conservation of these streams. State laws for environmental conservation should strictly be implemented. It is further suggested that domestic waste should be properly disposed off to stop more damage to the water in these streams.

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