academicJournals

Vol. 8(6), pp. 312-318, June 2014
DOI: 10.5897/AJEST2014.1727
Article Number: 7A06EE645954
ISSN 1996-0794

http://www.academicjournals.org/AJEST

African Journal of Environmental Science and Technology

Full Length Research Paper

Bahir Dar tannery effluent characterization and its impact on the head of Blue Nile River

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Received 1 May, 2014; Accepted 5 June, 2014

A study was conducted to characterize Bahir Dar tannery effluent and determine its impact on the head of Blue Nile River using selected physicochemical parameters. Samples were taken from the direct effluent stream and four sampling sites (one upstream and three downstream) were selected along the river to determine its impact on the river. Samples were collected from October to March, 2010/11. Temperature, pH, conductivity and total dissolved solids (TDS) were measured *in situ* using a combined meter. The samples for the rest physicochemical parameters were collected from the sites using the appropriate method. In the laboratory, BOD_5 and COD were measured according to standard methods. Total nitrogen, total phosphorous, chloride and sulphide, were determined with Hach nutrient analysis kits and a Hach spectrophotometer. Total suspended solids were determined photometrically. The heavy metal, chromium (as Cr total), was determined using atomic absorption spectrophotometry according to standard methods. The results show that the impact of the effluent from biological oxygen demand (BOD), chemical oxygen demand (COD), NH_3-N, total nitrogen, chlorides, sulphides and chromium was significant with concentrations of 342±52.5, 850.75±96.2, 288±75.8, 462.5±130, 1408.13±405.3, 16.05±3.04 and 3.54±0.55, respectively and most of the effluent characteristics were beyond the provisional discharge limit set out by the Ethiopian Environmental Protection Authority. Analysis of variance indicated that all the physicochemical parameters except temperature, pH and total phosphorous significantly varied among sampling sites ($p<0.05$); the reference or upstream site having lower value than downstream sites. The result shows the pollution load of the effluent on the river and the urgent need for measures to be taken.

Key words: Tannery effluent, physicochemical parameters, Blue Nile River.

INTRODUCTION

Industrial waste is the most common source of water pollution in the present day (Ogedengbe and Akinbile, 2004) and it increases every year because most countries are getting industrialized. Worldwide, it is estimated that the industry is responsible for dumping 300-400 million tons of heavy metals, solvents, toxic sludge, and other wastes into waters each year (UNEP, 2010). Thus, the environment is under increasing

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*Corresponding author. E-mail: assefawosnie@gmail.com pressure from wastes emanating from such industrial activities. As compared to other industries, leather tanning is one of the most polluting activities (Khan et al., 1999) as it consume huge amount of water in several stages, generating an enormous amount of liquid effluents (Farenzena et al., 2005) which are hazardous to the environment to which they are discharged.

Tannery wastewater is highly polluted in terms of biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), nitrogen, conductivity, sulphate, sulphide and chromium (Mondal et al., 2005) and in most developing countries tannery effluents are discharged directly into sewers or water bodies without treatment (Verheijen et al., 1996; Favazzi, 2002). The high BOD_5 content of the effluent will affect the survival of gill breathing animals of the receiving water body and high COD value indicate toxic state of the wastewater along with presence of biologically resistant organic substances. The high level of ammonia-N is toxic to aquatic organism and nitrogen may cause eutrophic condition. The high salinity and TDS of the effluent may result in physiologically stressful conditions for some species of aquatic organisms due to alterations in osmotic conditions. Studies show that increase in salinity causes shifts in biotic communities, limit biodiversity, exclude less tolerant species and cause acute or chronic effects at specific life stages. Changes in the ionic composition of water can also exclude some species while promoting population growth of others (Weber-Scannell and Duffy, 2007). The pollutants are poisonous to man and aquatic life resulting in food contamination.

In Ethiopia, although the use of leather and leather products goes back to prehistoric times, tanning hides and skins of animals into leather has been practiced as industrial activity since the last decades (EEPA, 2003). Presently, Ethiopia's leather industry is in the forefront of the leather sector development within the Eastern and Southern Africa region (UN, 2002). Currently, there are 20 operational tanneries that turnout wastes directly into the nearby water bodies like the other industrial activities. This makes industrial and chemical pollution to become the third major problem in the country and one of the great environmental concerns (Zinabu and Zerihun, 2002). This is becoming evident through the pollution of water bodies and human habitat in the major cities, rivers and lakes. Similarly, Bahir Dar Tannery is discharging its effluent into Blue Nile River. In view of the negative impact of this effluent on the environment, the present study aimed at determining the levels of physicochemical pollutants in effluent samples from the tannery and assessing its impact on Blue Nile River.

MATERIALS AND METHODS

Description of the study area

This study was conducted in Bahir Dar, the capital city of Amhara Region which is situated on the southern shore of Lake Tana, the source of Blue Nile (Abay) River. Bahir Dar Textile factory and Tannery are the most important industries in the city. Both the textile factory and the tannery discharged their effluent directly into the Blue Nile River. The downstream part of the river is used for domestic activities including drinking, irrigation and recreation (swimming and bathing). The use of the river in this way may lead to bioaccumulation of toxic pollutants like chromium which is hazardous to human beings as well as livestock.

Sampling

The study was conducted from October, 2010 to March, 2011. This time was selected to sample from both dry and wet periods so as to include possible seasonal effect. Direct physicochemical samples were taken from the effluent stream so as to compare with the country's discharge limit and four sampling sites (one upstream and three downstream) were established along the river length to assess the impact of the effluent on the river. One site directly below the source of pollution and two other sites at different intervals from the point of effluent discharge were chosen. The reference site was established directly above the effluent discharge where there is little disturbance. The sampling sites were designated as S_1 to S_4. The study area was mapped using Geographical Information System (GIS) using information obtained by Global Positioning System (GPS) (Figure 1).

Data collection

The physicochemical parameters include pH, temperature, BOD_5, COD, ammonia-nitrogen (NH_3-N), total nitrogen, total phosphorous, TDS, conductivity, total suspended solids (TSS), total chromium, chlorides and sulphides. These parameters were selected because they are considered to be deleterious on the receiving environment and they were included in the discharge limit. Temperature, pH, conductivity and TDS were measured *in situ* using combined pH/T°/TDS and conductivity meter. The sample for the rest physicochemical parameters were collected from the sites using a sampler which allows sampling from discrete depth and the sample was transferred into the storage bottle without agitation or aeration (Lind, 1979). Prior to sampling, the polyethylene bottle was cleaned with nitric acid and then washed and rinsed with distilled water. Then, the samples were taken to laboratory. In the laboratory, BOD_5 and COD were measured according to standard methods (APHA, 1998). Total nitrogen, total phosphorous, chloride, and sulphide, were determined with Hach nutrient analysis kits and a Hach spectrophotometer (DR010 Hach Co., Loveland, Colorado, USA). Total suspended solids were determined photometrically. The heavy metal chromium (as Cr total), was determined using atomic absorption spectrophotometer (Buck Scientific Model 210 VGP, USA) according to standard methods (APHA, 1998).

Data analysis

Descriptive statistics was used to analyze the physicochemical data. One-way ANOVA was used to compare the difference in physicochemical data among the sampling sites and means were separated using Tukey HSD.

RESULTS

The mean values for each parameter of the wastewater revealed that, most of them were beyond the standard provisional limit set by Ethiopian Environmental Protection Authority (EEPA, 2003) (Table 1).

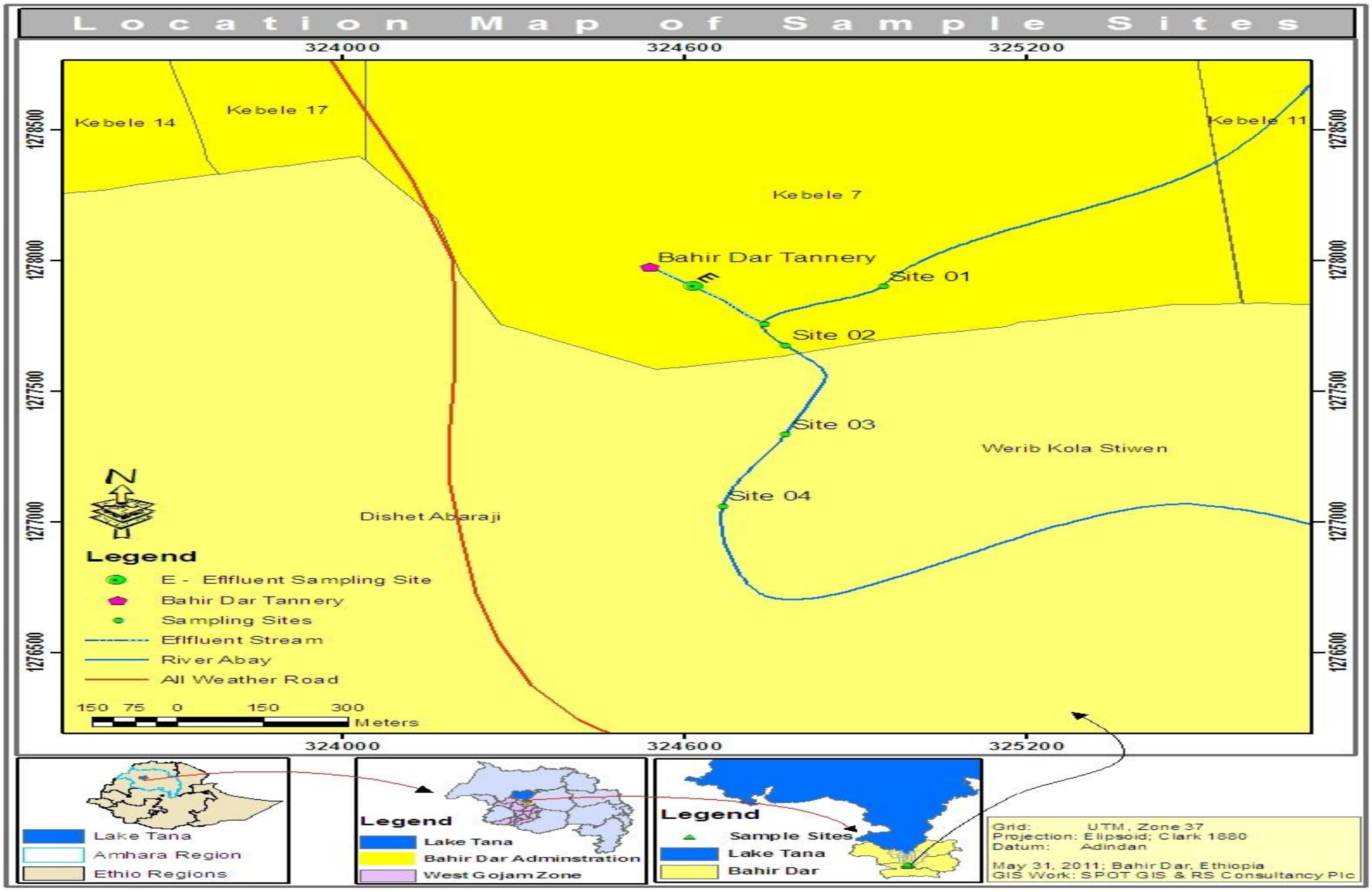

Figure 1. Map showing sampling sites on the effluent stream and along the Blue Nile River.

A detailed characterization of downstream water samples was also carried out to determine the pollution load of the effluent on Blue Nile River. The mean concentrations of pollutants and their variation along the sampling sites are presented in Table 2.

As shown in Table 2, the mean value of temperature and pH at downstream sites ranged from 20 to 24 and 7.13 to 7.15, respectively. Their value did not show significant variation among sampling sites ($F=2.22$, $p=0.16$, $R^2=0.69$ and $F=2.04$, $p=0.18$, $R^2=0.8$), respectively. The pollution profile for BOD$_5$ and COD along the downstream sites ranged from 34.9±9.05 to 73.4±13.2 mg/l and 107.3±26.7 to 206±32.6 mg/l, respectively. According to the ANOVA, the concentrations of these two parameters significantly varied among sampling sites ($F=20.1$, $P<0.0001$, $R^2=0.91$ and $F=26.23$, $P<0.001$, $R^2=0.93$), respectively. BOD$_5$ and COD values at the upstream site were significantly lower than the two downstream sites (S$_2$ and S$_3$). In addition, their concentrations at the last downstream site (S$_4$) were significantly lower than that of S$_2$, but there was no significant variation in their concentration between S$_3$ and S$_4$.

The levels of ammonia-N and total nitrogen in the water samples were in the range of 14.3±2.37 to 50±8.11 mg/l and 23±7.86 to 67.5±8.7 mg/l, respectively. Their values differed significantly among sampling sites ($F=26.81$, $P<0.0001$, $R^2 = 0.91$and $F=40.12$, $P<0.0001$, $R^2 = 0.94$), respectively. The upstream site had significantly lower concentration of ammonia-N than S$_2$ and S$_3$. But there was no significant difference in ammonia-N concentration between the last downstream site (S$_4$) and the upstream site.

Ammonia-N concentration at S$_4$ was also significantly lower than S$_2$, but there was no significant difference between S$_3$ and S$_4$. The concentration of total nitrogen significantly varied among all sampling sites; the upstream site having lower concentration (Table 2).

The level of phosphorous in the downstream water samples ranged from 5.3±0.98 to 6.5±1.1 mg/l while concentration of phosphorous at the reference site was 6.3±1.7 mg/l. This value did not show significant difference among sampling sites ($F=0.12$, $P=0.95$, $R^2 = 0.15$). Total dissolved solids, conductivity and TSS also vary in their values along the sites. Their values at

Table 1. Physicochemical characteristics of Bahir Dar Tannery effluent.

Physicochemical parameter	Mean ± SE	Range	Discharge Limit
Temperature (°C)	25.5 ± 2.2	20.3-30.5	40°C
pH	7.15 ± 0.09	7.13-7.16	6 - 9 pH units
BOD_5 (mg/l)	342 ± 52.5*	214-452	>90% Removal or 200 mg/l
COD (mg/l)	850.75 ± 96.2*	651-1023	500 mg/l
Total ammonia (as N) (mg/l)	228 ± 75.8*	96-420	30 mg/l
Total nitrogen (as N) (mg/l)	462.5 ± 130.8*	89-692	>80% Removal or 60 mg/l
Total phosphorus (as P) (mg/l)	11.5 ± 4.8*	1-24	>80% Removal or 10 mg/l
TDS (mg/l)	2003.25±74.5	1832-2193	-
Conductivity (µs/cm)	3953.25±150.3	3668-4374	-
TSS (mg/l)	339±68,6*	204-525	50 mg/l
Chromium (as total Cr) (mg/l)	3.535 ± 0.55*	1.98-4.51	2 mg/l
Chloride (as Cl) (mg/l)	1408.125 ± 405.3*	613.5-2517	1000 mg/l
Sulphide (as S) (mg/l)	16.05 ± 3.04	8.95-23.39	0.1 mg/l

*Means above the EEPA Discharge Limit.

Table 2. Variation in physicochemical characteristics at the sampling sites along the Blue Nile River (Temperature in °C, pH in pH units, conductivity in µs/cm and the rest in mg/l) in 2010/2011.

Site	pH	Temperature	BOD_5	COD	Ammonia-N	Total nitrogen
Upstream / Reference (S_1)	7.16^{a}	24.63^{a}	11.4^{c}	27.4^{c}	0.2^{c}	1.1^{d}
Just below the effluent discharge (S_2)	7.15^{a}	24.56^{a}	73.4^{a}	206.0^{a}	50.0^{a}	67.5^{a}
200 meters below S_1 (S_3)	7.13^{a}	20.93^{a}	55.0^{ab}	164.0^{ab}	32.0^{ab}	45.0^{b}
400 meters below S_1 (S_4)	7.14^{a}	23.18^{a}	34.9^{bc}	107.3^{b}	14.3^{bc}	23.0^{c}

Table 2. Contd.

Site	Total phosphorous	TDS	Conductivity	TSS	Chloride	Sulphide
Upstream / Reference (S_1)	6.3^{a}	150.2^{c}	307.0^{c}	41.0^{b}	34.0^{c}	0.03^{b}
Just below the effluent discharge (S_2)	6.0^{a}	1517.0^{a}	3051.0^{a}	222.0^{a}	299.6^{a}	0.55^{a}
200 m below S_1 (S_3)	5.3^{a}	1167.0^{ab}	2274.0b	157.5^{ab}	213.8^{b}	0.04^{b}
400 m below S_1 (S_4)	6.5^{a}	903.8^{b}	1793.7^{b}	108.8^{ab}	174.0^{b}	0.01^{b}

Means within a column followed by the same letter are not significantly different from each other according to Tukey HSD ($p<0.05$).

downstream sites ranged from 903.8±116.1 to 1517±196.8 mg/l, 1793.7±252.5 to 3051±397.2 µs/cm and 108.8±25.1 to 222±46 mg/l, respectively. The values of TDS significantly varied among sampling sites (F=51.18, P<0.0001, R^2=0.95). The upstream site had significantly lower TDS concentration than the three downstream sites. There was also significant difference between S_3 and S_4. Similarly, the values of conductivity showed significant difference among sampling sites (F=54.3, P<0.0001, R^2 =0.96). The upstream site had significantly lower value than all downstream sites and its values at S_3 and S_4 were also significantly lower than S_2. Total suspended solids concentration showed significant variation among sampling sites (F=6.09, P=0.02, R^2 =0.7); the upstream site having significantly lower value than the site just below the effluent discharge (Table 2).

The concentration of chromium at the two downstream sites was 0.165±0.11 (S_2) and 0.142±0.097 mg/l (S_3) while the concentration at the other downstream site (S_4) was not detected. Here, the concentration of Cr at the

Table 3. Literature on concentration of tannery effluents (pH in pH unit, Temperature in °C and the rest in mg/l).

Parameter	Present study	Literature	Reference	Discharge limit
Temperature	25.5	21.2±0.8	Seyoum et al., 2003	40
pH	7.15	4.74-8.66	Deepali et al., 2009	6-9
BOD_5	342	2982.5 840-1860 585-639 1425-1500	Seyoum Leta et al., 2003 Haydar et al., 2007 Akan et al., 2009 Deepali et al., 2009	>90% or 200 mg/l
COD	850.75	11123 1320-54000 2389-3784 1916-27810	Seyoum et al., 2003 Haydar et al., 2007 Seyoum et al., 2003 Deepali et al., 2009	500
NH_3-N	228	1330	Seyoum et al., 2003	30
Nitrogen	462.5	122.2	Seyoum et al., 2003	60 mg/l
Total phosphorous	11.5	16.65-19.93	Seyoum et al., 2003; Seyoum et al., 2003	10 mg/l
TDS	2003.25	42716.33	Deepali et al., 2009	-
TSS	339	3491.9-9485.33	Deepali et al., 2009	50
Total chromium	3.54	8-32.2	Seyoum et al., 2003; Akan et al., 2009	2 mg/l
Chlorides	1408.13	630.4-4313	Akan et al., 2009; Deepali et al., 2009	1000 mg/l
Sulphides	16.05	630.4	Seyoum et al., 2003	1 mg/l

reference site was not detected as that of S_4. Chloride and sulphide levels in the downstream samples varied between 174±66.46 to 299.6±98.13 mg/l and 0.008±0.002 to 0.55±0.23 mg/l, respectively. Chloride values at the downstream samples varied significantly among sampling sites (F=45.85, P<0.0001, R^2=0.95) with the reference site having significantly lower value than the downstream sites. Sulphides showed significant variation among sampling sites (F=26.1, P<0.0001, R^2=0.9). The site just below the effluent discharge had significantly higher value than the two downstream and the upstream sites (Table 2).

DISCUSSION

In this study, a detailed characterization of wastewater was carried out on Bahir Dar tannery effluent and the result showed that most of the parameters under investigation were high and well beyond the provisional standard limit set by EEPA (2003).

The values of temperature and pH in this study were within the discharge limit and below what Seyoum et al. (2003) and Deepali et al. (2009) reported (Table 3). The lower value of pH and temperature in this study might be due to variation in the sampling time of the day and the difference in production capacity of the tanneries. BOD_5 and COD mean values were above the discharge limit. But the values in this study were lower than what Seyoum et al. (2003), Haydar et al. (2007), Akan et al. (2009) and Deepali et al. (2009) reported (Table 3). These high levels of BOD_5 and COD values observed in the waste may be due to high amount of organic matter from various chemicals used during the processing of hides and skins. It has been reported that a significant part of chemicals used in the tanning process is not actually absorbed in the process and discharged into the environment (UNIDO, 1991), thereby increasing the levels of BOD_5 in the effluent. The high BOD_5 content of the effluent will affect the survival of gill breathing animals of the receiving water body and high COD value indicate toxic state of the wastewater along with presence of biologically resistant organic substances.

Ammonia-N and total nitrogen concentrations were above the discharge limit as shown in Seyoum et al. (2003) report. These high levels of ammonia-N and nitrogen might be attributed to several components in tannery effluent containing nitrogen as part of the chemical structure and the nitrogen contained in proteinaceous material of the skin (Bosnic et al., 2000). The high level of ammonia-N is toxic to aquatic organism and nitrogen may cause eutrophic condition. The mean phosphorous concentration of the effluent was somewhat similar to what Seyoum et al. (2003) and Akan et al. (2009) reported (Table 3) and showed little deviation from the discharge limit.

Total dissolved solids, conductivity and total suspended solids values in this study were found to be high. But Seyoum et al. (2003) and Deepali et al. (2009) reported values greater than the result of this study (Table 3). This deviation might be due to the variation in size and production capacity of the tanneries under investigation. The total dissolved solids may increase salinity of the water and thus may render it unfit for irrigation and other purposes for the immediate downstream users while the suspended impurities cause turbidity in the receiving system.

Chromium level in this study is 36 times higher than the discharge limit set out by EEPA (2003). Similarly, sulphide and chloride values were above the discharge limit. These high values observed in the effluent may be due to the chemicals used by tanneries. Studies (Table 3) reported higher values of these pollutants and this might be also due to the variation in size and production capacity of the tanneries under investigation. Generally, the result showed that the effluent is rich in organic pollutants, but relatively poor in phosphorous content.

The mean concentration of pollutants along Blue Nile River indicated that the concentration of the various pollutants decrease downstream from the point where the effluent joins the river to the last downstream site (S_4). This is attributed to the dilution capacity of the river, uptake of pollutants by the vegetation along the river gradient and some reactions that can change the pollutants to harmless ones, may take place as the water flows downstream from the point pollution source.

Even though there was no significant variation among sites, the mean temperature value of the upstream site was slightly higher than the last downstream sites and the slight variation might be due to the difference in the sampling time. The pH in all sites was more or less neutral. The result in this study slightly deviates from the work of Seyoum et al. (2003) (Table 3) and this might be due to the size of the river and its dilution capacity.

The concentration of BOD_5 and COD at S_2 is very much reduced by 76-79% from the direct effluent owing to the dilution capacity of the river. The concentrations at downstream sites were well beyond the reference site indicating the organic pollution load of the effluent on the river. This increase in BOD_5 and COD increases rates of biological or chemical decomposition leading to oxygen depletion which produce both acute (mortality) and chronic (reduced growth, fecundity and disease resistance) impacts on aquatic biota (Allison, 1996).

The concentration of NH_3-N and nitrogen at S_2 showed 78-85% reduction from the direct effluent value. This rapid reduction might be due to the size of the river. Seyoum et al. (2003) reported total NH_3-N and nitrogen reduction of 92-95 and 69% respectively (Table 3). The standard provisional limits for NH_3-N and N of tannery wastewater are 30 and 60 mg/l respectively. All the values at downstream sites were beyond the limit and the value at the reference site. This indicated that the tannery wastewater was responsible for these pollutants. The nitrogen in ammonia form is toxic to aquatic organisms. In the environment ammonia-nitrogen is oxidized rapidly to nitrate, creating demand and low dissolved oxygen in the water. Moreover, the high nitrogen may cause eutrophication problem (USEPA, 2008). Eutrophication reduces dissolved oxygen in water and alters stream habitat available for macroinvertebrates, fish eggs and fish both of which are critical for fish and other aquatic life. This may disrupt the ecological cycle of the stream so that certain biological communities experience severe mortality.

The phosphorous content in downstream samples was within the standard provisional limit set by EEPA (2003). Its concentration did not show significant difference between the sites. The reference site had almost similar phosphorous content as that of the downstream sites showing that the tannery effluent was not responsible for this pollutant. This might be due to the addition of municipal wastewater into the river above the reference site. So in this study, phosphorous does not give concern as severe pollutant from the tannery and may not cause eutrophication.

Total dissolved solids, conductivity and total suspended solids at S_2 showed a 25-34% reduction than the direct effluent value. As compared to the other parameters, the values of the above parameters showed slight reduction at downstream sites. This might be due to their initial high concentration which made the dilution process slower. The values at the downstream sites also significantly differ from the reference site indicating the increasing impact of the tannery effluent on downstream water bodies. Studies by Seyoum et al. (2003) and Birnesh (2007) reported the same result (Table 3). High concentrations of total dissolved solids forms a layer on the bottom of water course and covers natural fauna on which aquatic life depends. This can lead to localized depletion of oxygen supplies in the bottom waters. It also reduces light penetration and thus photosynthesis in the water. On the other hand, high conductivity indicates salinity increment in the receiving water. This may result in adverse ecological effects on aquatic biota (Lefebvre and Moletta, 2006).

Chromium concentration at S_2 showed a 95% decrease from the effluent and it was not detected at S_4. The level at the reference site also was not detected indicating the pollution at downstream sites originated from the effluent. Similarly, chloride and sulphide contents at S_2 showed dramatic reduction with 96-98% from the direct discharge owing to the dilution effect of the river. Chloride concentrations at S_2 were significantly higher than the reference and the other downstream sites. But all the downstream sites have values beyond the standard provisional limit set out by EEPA (2003). The values indicated that most of the concentration of chlorides and sulphides at downstream sites were the contribution of the tannery effluent. The presence of these ions increases the salinity of the receiving water body. The discharge of high salinity and TDS effluents into receiving system may result in physiologically stressful conditions for some species of aquatic organisms due to alterations in osmotic conditions. Studies show that increase in salinity causes shifts in biotic communities, limit biodiversity, exclude less tolerant species and cause acute or chronic effects at specific life stages. Changes in the ionic composition of water can also exclude some species while promoting population growth of others (Weber-Scannell and Duffy, 2007).

Conclusion

Even though tanning industries are very important for the country's economy and to improve standards of living of citizens, their waste is directly discharged into the nearby water body without treatment. Most of the physico-chemical parameters investigated in this study showed that almost all the effluent characteristics were above the provisional discharge limit set by the Environmental Protection Authority indicating the poor treatment mechanism employed by the tannery. Most of the physicochemical parameters along the river gradient were also high and beyond the discharge limit. This will create a problem for downstream users as they use it for domestic, agricultural and recreational value. So, this fact must regularly be brought to public awareness by using media or direct contact with the downstream users. The Environmental Protection Authority should also establish environmental protection laws which consider technical and financial capability of the industries so as to control industrial pollution. Not only establishment, the laws should also be enforced and environmental standards with their protocols should be followed with strict and continuous monitoring to safeguard the environment from heavy loads of pollutants and toxic substances.

Conflict of Interests

The author(s) have not declared any conflict of interests.

ACKNOWLEDGEMENTS

The authors thank Amhara National Regional State for financial support and Bahir Dar University for the provision of material and laboratory facilities.

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