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Changes in the Physichochemical Properties of Upper Awash River Caused by Effluents from Anmol product Ethiopia paper factory, Ginchi, Ethiopia.

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ABSTRACT

Pulp and paper industry effluents entering water body is considered as the major sources of pollutants in the environment. In this study physicochemical characteristics of the effluent from Anmol product Ethiopia recycled paper Industry and the receiving upper Awash River water quality were investigated from January to March 2015. A total of five composite samples, two of which were from the raw and treated effluents and the remains from upper Awash River water were collected and analyzed. The raw effluent consists of 470-2499.3 mg/L five days Biological Oxygen Demand (BOD5),2969-5848.6 mg/L Chemical Oxygen Demand (COD), 298-501.3 mg/L Total Suspended Solids (TSS), 1032-2333.3 mg/L Total Dissolved Solid (TDS) and pH varied from 3.24-10.66. Aerobic treatment of raw effluent attribute to insignificant reduction in TSS (112-532 mg/L), BOD5 (405-1314.6 mg/L) and COD (2304-3729 mg/L). However, TSS, TDS, total Nitrogen, total Phosphorus, Potassium, Chlorides and Sulphates were found higher after treatment. Copper, Iron and Zinc were found in small quantity in raw effluent and were not removed after treatment. The investigation across the river indicated the levels of some parameters decreased downstream of the River. However, most parameters such as TSS, TDS, BOD5, COD and total nitrogen were much higher than the maximum allowable limit prescribed by WHO even at downstream of the river. The dendrogram of the effluent quality parameters clearly indicate that this Industry does not meet the prescribed discharge limits and the River is highly polluted due to the discharge of effluents from ther Industry.

Keywords: Physicochemical characteristics; Effluent; Water quality; Pulp and paper industry

INTRODUCTION

Pulp and paper industry is considered as one of the major potential sources of pollution in the environment [1]. The process of paper making involve the use of large amounts of water, chemicals, additives and fillers depending on the type of paper to be produced and adopted manufacturing process, consequently discharging huge volume of black liquor containing undissolved substances including lignin and hemicellulose, toxic waste material like dimethyl sulphite and high COD to the environment [2-4]. Moreover, pollutants released from Pulp and Paper industry are rich in dissolved solids such as chloride and sulphate of Na, Ca and varying amounts of suspended organic materials [5]. The direct discharge of such effluents in aquatic system spoils fresh water ecosystems which results in series problems for aquatic life and for different uses of water [5,6].

In paper recycling industries, because of the color on old papers, bleaching the pulp with peroxides and ozone is not as efficient as using chlorine or chlorine dioxide; as a result the effluent usually contains a powerful oxidizing agent, chlorates [7]. The high organic content of pulping effluent coupled with chlorates from the bleaching process result in the production of highly toxic organic compounds such as chlorinated phenols, furans and aliphatic hydrocarbons [8]. Some members of these families are known to be toxic, mutagenic, persistent, bioaccumulating and are thought to cause harmful disturbances in biological systems and pose human health risk [9]. This urges the need to control the quality of the effluents.

In recent years, related to increasing industrialization and fast developmental activities in Ethiopia, the existing and newly established paper industries expected to fulfil the increasing demand of paper. These industries mainly use imported pulp and recycled paper for paper production. Among the newly established paper industries, Anmol recycled paper industry, which produces paper from recycled pulp, was established near upper Awash River, which is considered as a river heavily utilized by the local communities near the river and downstream of the river for different domestic and agricultural uses [10]. However, many externalities are associated with the river. The river found to contain high concentration of salts, organic wastes, and pathogenic organisms because of a number of industries and other antropogenic activities that release their wastes to the river [10].

The Awash River basin is divided into upper, middle and lower valleys, and Anmol recycled paper industry is discharging its insufficiently treated effluent directly in to upper Awash River valleys. Its effect can be easy recognized by the local community as the colour of the river was changed and fishes present in the river were slowly disappeared. Therefore, for any interventions assessing effluent physicochemical characteristics and their effects to the river water quality is needed.

A number of studies related to physicochemical characterization of pulp and paper industry effluents have been carried out in different countries to investigate the pollution load of pulp and paper effluents [3,9,11]. Their results confirmed that the effluent of pulp and paper industry was loaded with many pollutants in which the volume and characteristics of pollutants varied depending on the type of raw materials used, manufacturing process, the amount of water being used, and adopted treatment technology. For instance, BOD5 (306-408 mg/L), COD (1736-4357 mg/L), Cl- (43.5-347.6 mg/L), TDS(486-1380 mg/L) in effluents from Lalkuan paper factory, India. Relatively higher amounts of BOD5 (870 mg/L), COD (2000 mg/L), TS (2890 mg/L) were also determined in paper factory effluent in M. Bhilai, India [9,12]. Extremely higher BOD5 (2200 mg/L), COD (10,300 mg/L), TS (5950 mg/L) in Egyptian recycled paper industry effluents [13]. Moreover, Fazeli et al. found increased level of heavy metals in paddy crop field irrigated with paper industry effluent. However, in Ethiopia studies related to type, transport and effects of pollutants emanated from pulp and paper industry were not studied. Therefore, this study aimed at investigation of the physicochemical characteristics of effluent of Anmol product Ethiopia paper factory and its subsequent effect on level of the physicochemical properties of the receiving upper Awash River.

EXPERIMENTAL PROCEDURES

Description of the study area

Anmol product Ethiopia recycled paper factory was established in 2009 in Oromia region, Ethiopia. It is located 74 kms west of the capital city Addis Ababa, near upper Awash River and it covers over 13-hectare areas. The study area has an average annual temperature of 23.8°C and receives mean annual rainfall of 1172 mm. It is characterized by a bimodal rainfall pattern, during summer (July-September) and spring (April-May). The study area has an altitude of 3000 m a.s.l. with dry mid land (wayina daga) climatic condition. The area lies between 38°8'0"E to 38°9'0"E and 9°0'40"N to 9°1'50"N. At the study area, recently established Anmol product Ethiopia paper factory produces paper from used paper collected from different parts of the country as well as finished pulp imported from Indonesia. The paper mill uses a lot of water from two sedimentation sources pumped to the production area of the mill through plastic tubes and finally the effluent from the mill is passed through a plastic tube and pumped to a storage pond near the mill. The pulp collected from the storage pond is reused in the mill, whereas the effluent leaving the pond is directly discharged to the upper Awash River. The river originated from the central Ethiopian highlands of elevation 3000 m west of Addis Ababa and flowing northeast wards, crosses rift valley and finally entered in Lake Abe at an elevation of 250 m after covering a total distance of 1200 km.

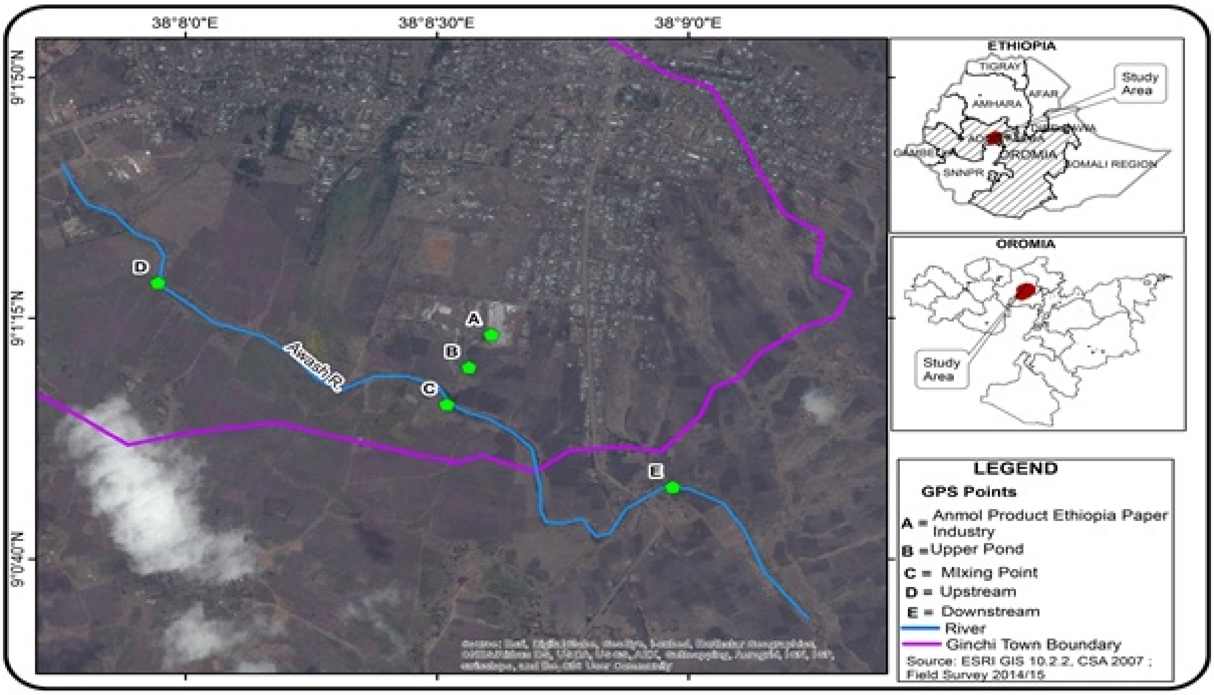

Figure1: Location maps of the study area and sampling site.

Sample collection

Effluent samples of the factory and water samples from Upper Awash River were collected from five different sampling sites, designated as site A, B, C, D, and E (Figure 1), with a total sample volume of 2 L from each sampling site. Effluent samples were collected when it pumped in to the factory oxidation pond located near the mill (A), and after the effluent leaving the pond (B). And water samples from the upper Awash River were collected at the point of discharge (C), at about 1 km upstream of the effluent entry point (D), and at a distance of 1 km downstream of the effluent entry point (E). Both the effluent and river water samples were 12 h and vertically well mixed composite samples collected in the month of January to March, 2015 of dry season in fifteen days interval using polyethylene plastic bottles. All the bottles were previously washed with detergent, 1M H2SO4 and rinsed with the water sample at the point of collection. Samples were transported to the laboratory within 2 hours, and refrigerated at 4°C. Prior to treatment, the samples were warmed to room temperature (21 to 25°C). In general, sample collection, preservation and storage were performed according to standard procedures recommended by American Public Health Association [14].

Chemicals and reagents

All the reagents and chemicals used in this study were analytical grade. Hydroxylamine buffer solution, disodium hydrogen phosphate pH=7.4 and borax pH=9.2, (BDH Chemicals Ltd. England), 0.25 N K2Cr2O7 solution (Breckland Scientific LTD), 0.25N ferrous ammonium sulfate and Ferroin indicator (Eurostar Scientific LTD),powder HgSO4 for the determination of chemical oxygen Demand, 8N NaOH, manganous sulphate, sodium iodide azide reagent, conc. H2SO4, 0.025N Na2S2O3 solution, starch indicator for biological oxygen demand determination, methyl red-Bromocresol mixed indicator, 40% NaOH, 2% boric acid, conc. HNO3, vanado molybdate, conc. HCl, H3PO4, H3BO3 buffer solution for the determination of total phosphorus, Copper sulphate and Potassium sulphate mixture for the determination of total nitrogen were all supplied by CDH Chemicals Ltd., England. Other chemicals and reagents used such as Calmagite indicator, 0.02N EDTA, for the determination of total hardness, Calver 2 calcium indicator for calcium determination, phenolphthalein indicator and methyl orange indicator and 0.02N H2SO4 solution for determination of total alkalinity, standard 0.014N silver nitrate solution and potassium chromate indicator for the determination of chlorides, SulfaVer 4 reagent for sulphate determination, Na2SO4 standard solution, powder sodium ascorbate, Zincon reagen and NH2OH.HCl solution for Zinc metal determination, Sodium meta bisulfite solution,diphenylcarbazide reagent, Phenanthroline reagent for total iron determination neocuproine reagent for copper metal determination, stock standard solutions containing 1000 mg/L, in 2% HNO3, of the metal Fe, Zn, and Cu were supplied by HACH Scientific LTD,USA. Distilled water was used for dilution of sample and metal standard solutions as well as for rinsing glassware and sample bottles.

Physicochemical analysis of effluent and river water samples

Anmol product Ethiopia recycled paper factory effluent samples and upper Awash River water samples collected from different locations were analyzed for the required parameters following the standard method [14] and the methods used for the analysis were summarized below:

Table 1: Required Parameters, Analytical Methods followed, and Equipment used.

Physico-chemical Parameters	**Analytical Methods**	**Equipments**
Turbidity	Turbidmetric	UV-Visible Spectrophotometer (HACH Scientific LTD 6305,USA)
Total Dissolved Solid (TDS)	Gravimetric	Drying oven (Digitheat, J.P.), digital analytical balance (Mettler Toledo, Model AB104,) Filter paper 70 µm pore, glass fiber filter (47 mm).
Total suspended solid (TSS)	Gravimetric	
pH	pH meter	pH meter (HI9023 microcomputer)
Eelectrical Cconductivity (EC)	Potentiometry	Conductivity meter (HI 8733)
Biological oxygen demand (BOD)	Winkler's iodometric	Biochemical Culture Box (SPX 250B, china)
Chemical oxygen demand (COD)	Dichromate closed reflux	Automat digester (B414,Switzerland)
Alkalinity	Titrimetric method	Burette (50 mL), Measuring cylinders, pipettes, Borosilicate volumetric flasks (25, 50 and 100 mL)
Bicarbonate (HCO3-)	Titrimetric method	
Carbonate (CO32-)	Titrimetric method	
Total Hardness	Titrimetric method	
Cl-	Silver Nitrate Titrimetric	
Total phosphorus (TP)	Colorimetric Methods	UV-Visible Spectrophotometer (T/70/T80, China)
Total Nitrogen (TN)	Kjeldahl Methods	Kjeldahl heating apparatus (K-355,)
Sulphate (SO4-)	Sulfaver (Turbidmetric)	UV-Visible Spectrophotometer (HACH Scientific LTD 6305,USA)
Na	Flame photometric	Flame photometer (Halseled-410)
K	Flame photometric	Flame photometer (Halseled-410)
Fe	Phenantholine method	UV-Visible Spectrophotometer (HACH Scientific LTD 6305,USA)
Cu	Neocuproine method	
Zn	Zincon Method	

Method validation

A blank was conducted using distilled water and reagents for the characterization of each physicochemical parameter. Samples were analyzed in triplicate and Calibration of the instrument was carried out with range of standard solution. For UV-Visible spectrophotometric and flame determination five working calibration standards were prepared by serial dilution of concentrated stock solution of each metal solution. A calibration curve of Absorbance Vs concentration was established for each metal and used for determination of metal concentration in the samples of effluent and river water

Statistical methods

Data on both effluent and river water physicochemical parameters were analyzed using one way ANOVA model using SPSS version 15.0 software, followed by the least square difference (Fischer LSD) test to compare means results of data obtained from physicochemical analysis of effluents and among the different sampling points of river water. The coefficient of correlation between some physicochemical parameters was calculated by Pearson correlation test at 0.05 and 0.01 significant levels and Hierarchical cluster analysis (HCA) was used to classify effluent and river water samples of the study area into different groups based on similarities in measured water quality parameters using R-software.

RESULTS AND DISCUSSION

Physicochemical Characteristics of Anmol product Ethiopia paper factory effluents. Mean values of the physichochemical characteristics of both raw and treated effluents in comparison with the [18] standard are shown in Table 1.

The pH of the effluent was oscillating between acidic and basic range, with value 3.23 and 10.7 for the raw and 3.4 and 10.3 for the treated effluent. The low pH values of effluents may be attributed to acidic digestion with salts of Sulphites (SO32-) during pulp production. The higher values of pH obtained confirmed the factory also uses NaOH liquor during digestion. The values obtained were not met both the national and the WHO permissible limits of pH 5-9 for the discharge of effluent into surface water.

Table 2: Mean values (n=3) of physiochemical characteristics of Anmol product Ethiopia paper factory effluents collected for two consecutive months (January to March, 2015) with standard discharge limits.
WHO[a] (2008) World Health Organization standard limit
EEPA[b] (2010) Ethiopian Environmental Protection Authority

Parameter	Condition	Min.	Max.	Mean ± SD	Discharge permissible limit	
					WHO[a]	EEPA[b]
BOD5 (mg/L)	Raw	470	2499.3	1176.84 ± 88.10	50	40
	Treated	405	1314.6	886.7 ± 63.01		
COD (mg/L)	Raw	2969	5848.6	4065.86 ± 301.30	250	120
	Treated	2304	3729.6	2947.2 ± 224.19		
TP(mg/L)	Raw	0.37	0.42	0.39 ± 0.004	2	-
	Treated	0.35	1.69	1.02 ± 0.03		
TN (mg/L)	Raw	7.79	20	13.89 ± 0.74	10	-
	Treated	12.41	12.8	12.6 ± 0.25		
Turbidity (NTU)	Raw	118.28	499.32	270.35 ± 11.09	5	5
	Treated	50.88	418.65	198.12 ± 7.24		
TS (mg/L)	Raw	1512	3432	2592.67 ± 297.99	1000	
	Treated	1230	2854	2197.33 ± 210.94		
TDS (mg/L)	Raw	1032	3134	2333.33 ± 312.67	1000	1000
	Treated	1118	2650	2092 ± 268.`9		
TSS (mg/L)	Raw	298	726	501.33 ± 62.67	200	100
	Treated	112	532	282.66 ± 28.44		
EC (µS/cm)	Raw	1576	4720	3198.67 ± 0.24	1000	1000
	Treated	1705	4020	2888.33 ± 0.36		
PH	Raw	3.23	10.66	6.83 ± 0.10	43348	5.5-9
	Treated	3.4	10.3	6.47 ± 0.12		
Na (mg/L)	Treated	140	900	556.67 ± 16.59	400	400

	Raw	130	800	493.33 ± 12.83		
K (mg/L)	Treated	2.9	12.1	6.57 ± 0.18	-	-
	Raw	2.1	11.6	8.23 ± 0.21		
Total	Raw	49.5	3335	1394.83 ± 58.5	-	-
Hardness (mg/L)	Treated	47.52	3036	1291.17 ± 65.84		
Ca (mg/L)	Raw	11.09	1150	483.03 ± 22.79	200	200
	Treated	8.71	1104	464.23 ± 16.63		
Mg (mg/L)	Raw	5.23	110.4	44.94 ± 1.38	150	150
	Treated	6.18	66.24	31.34 ± 0.95		
Alkalinity (mg/L)	Raw	ND	2000	1032.68 ± 64.62	-	-
	Treated	ND	1700	953.09 ± 57.18		
CO32- (mg/L)	Raw	ND	281	93.89 ± 5.08	-	-
	Treated	ND	389.42	129.81 ± 6.25		
HCO3- (mg/L)	Raw	ND	2440	1068.97 ± 71.04	-	-
	Treated	ND	2074	898.84 ± 58.33		
Chloride (mg/L)	Raw	186.22	3818.7	1454.98 ± 101.13	1000	750
	Treated	150.41	815.44	419.33 ± 25.22		
Sulphate (mg/L)	Raw	26.7	282.32	195.31 ± 12.76	-	-
	Treated	219.25	424.22	309.09 ± 14.85		
Fe (mg/L)	Raw	0.27	2.77	1.42 ± 0.02		
	Treated	0.18	1.67	1.003 ± 0.01		
Cu (mg/L)	Raw	ND	0.033	0.01 ± 0.0001	2	2
	Treated	ND	0.026	0.01 ± 0.0001		
Zn (mg/l)	Raw	ND	0.59	0.195 ± 0.002	10	6
	Treated	0.128	0.552	0.34 ± 0.004		

As shown in Table 2, Electrical conductivity levels of the factory effluents were considerably high, 1476-4720 µS/cm for raw effluents and 664 – 4020 µS/cm for treated effluents, indicated the presence of higher concentration of dissolved ions (Surumbar, 2010) .The mean conductivity values for both sampling points were higher than the National and WHO standard values of 1000 µS/cm for the discharge of effluents into river water.

Total Suspended Solid (TSS) concentrations were ranging from 298 to 726 mg/L for raw effluents and from 112 to 532 mg/L for treated effluent. The values were above the WHO standard of 200 mg/L for the discharge of effluents into surface water (Table 2). Such elevated value of TSS, in the factory effluents may be due to the presence of non dissolved substances including lignin and hemicelluloses, which are not biodegradable and contributed from raw material preparation, pulping, rinsing, bleaching and Paper making process (Ljungberg and Brannvall, 2011).

The value of Total Dissolved Solids (TDS) was ranging from 1032 to 3134 mg/L for raw effluents and 1118 to 2650 mg/L for treated effluents. Similarly, the value of Total Solids (TS) observed was ranging from 1512 to 3432 mg/L for raw effluents and 1230 to 2854 mg/L for treated effluents (Table 2). These values obtained for TDS and TS were above the National and WHO standard of 1000 mg/L for the discharge of effluents into surface water (Table 2).

Turbidity values were ranging from 118.28 to 499.32 NTU for raw effluents and 50.88 to 418.655 NTU for treated effluents (Table 2). The values obtained for turbidity in both sampling points were higher than National and WHO Standard of 5 NTU to discharge effluents into stream. This high turbidity of the effluents indicated the presence of various non-dissolved solid by-products during paper production process such as lignin and hemicelluloses (Surumbar, 2010).

The effluents have COD concentration 2969 to 5848.6 mg/L for raw effluents and 2304 to 3729.6 mg/L for treated effluent (Table 2). BOD5 concentration of the effluents obtained for the raw effluent was 470 to 2499.36 mg/L and for the treated effluents ranged between 405 to 1314.6 mg/L. The concentrations of BOD5 and COD in both sampling point were higher than the WHO values of 50 mg/L and 250 mg/L for the discharge of effluents into surface waters, respectively (Table 2). The BOD5 value was also higher than value reported by Jitendra and Surumbar, ranging from 306 to 408 mg/L of the pulp and paper mill effluent in India. However; the BOD5 and COD value in this study is comparable with the BOD5 value 2200 mg/L found by [13] for effluents released from digester of Egyptian recycled paper mill, and the COD values ranged from 1736 to 4357 mg/L for pulp and paper mill effluents from the factory in India as [9]. The high BOD5 and COD values of the Anmol product Ethiopia paper effluents suggest the presence of oxygen demanding organic pollutants at higher level and inorganic pollutants, such as Sulphides in which its oxidation also demand oxygen.

The BOD5/COD ratio is great importance for quantification of biodegradability of a contaminated effluent. A high ratio (>0.5) indicates good biodegradability [13]. A ratio less than 0.5 is considered as low and corresponds to low biodegradability of the organic material present in the effluents. In this study the mean BOD5/COD ratio of the effluent were 0.29 for raw effluent and 0.3 for treated effluent indicating that low biodegradable organic molecules are present in the effluents at higher level.

Total nitrogen (TN) and Total Phosphorus (TP) concentrations of Anmol product Ethiopia paper factory were ranged from 7.79 to 20 mg/L, 0.37 to 0.42 mg/L for the raw effluents and ranging from 12.41 to 12.80 mg/L, 0.35 to 1.69 mg/L for treated effluents, respectively. The values of TN recorded were higher than the permissible limit of 10 mg/L and TP was found below permissible limit 2 mg/L set by WHO. The discharge of such effluents with high nutrients may cause eutrophication, consequently lead to the death of aquatic life because of oxygen depletion of the receiving water bodies.

The sulfate concentration of the effluents was 26.1 to 282.32 mg/L for the raw effluent and 219.25 to 424.22 mg/L for treated effluent (Table 2). Higher concentration of sulfate was observed in the treated effluent, which might be due to the sulphite or sulfide in the effluent oxidized into sulfate in well aerate zone. The discharge of such effluents with high sulfate content into river stream might cause unpleasant odour in the receiving water body and toxic effect on the aquatic organism upon its reduction and depletion of oxygen in the water body during its oxidation by microorganisms [15]. On the other hand, as shown in Table 2, the concentrations of chloride (Cl-) observed during the study period were 186.22 to 3818.74 mg/L for the raw effluent and 150.41 to 815.44 mg/L for treated effluent, in which the chloride contents for raw effluent was significantly reduced downstream of the effluent from 3818.74 mg/L to 815.44 mg/L mainly as a result of reaction of chlorine with high organic content of pulping effluents to form highly toxic organic compounds such as chlorinated phenols, furans, aliphatic hydrocarbons and bio-accumulated [9]. However, the Chloride contents for raw and treated effluents were higher than WHO limit 600 mg/L (Table 2). This high values of chloride indicated either elemental chlorine or chlorine containing agents were used for bleaching purpose.

The total alkalinity value ranges from 1098.08 to 2000 mg/L for the raw effluent and from 280 to 1700 mg/L for the treated effluents determined for samples with pH value greater than 7. The total hardness of Anmol product Ethiopia paper effluents were ranging from 49.6 mg/L to 3335 mg/L for the raw effluents and ranging from 47.52 mg/L to 3036 mg/L for the treated effluents (Table 2). The values were above 150 mg/L and can be categorized as hard effluents [2].

The composition of metals in the raw effluents samples were ranging from, Na (140-900 mg/L), K (2.9-12.1 mg/L), Ca (11.09-1150 mg/L) and Mg (5.23-110.4 mg/L), and in the treated effluent Na (130-800 mg/L), K (2.1-11.6 mg/L), Ca (8.18-1104 mg/L) and Mg (6.18-66.24 mg/L) (Table 2). The result shows that Na and Ca concentrations in the raw and treated effluent are much higher than the National and WHO industrial discharging limit while the concentration of Mg was within limits.. The higher values of Ca and Na in the effluents may be due to caustic treatment during pulping or bleaching process of the raw material.

The ranges of values of heavy metals analyzed in the factory raw effluents were recorded as Fe (0.27-2.77 mg/L), Cu (0-0.033 mg/L) and Zn (0-0.59 mg/L) and for the treated effluent were Fe (0.18-1.67 mg/L), Cu (0.-0.026 mg/L) and Zn (0.128-0.552 mg/L) (Table 2). Iron was found comparatively higher in concentration compared to other heavy metals, which reflect toxic nature of the paper mill effluents [16]. However; the heavy metal contents of the effluents were within National and WHO industrial effluents discharge limit (Table 2).

Correlation analysis

The correlations among some selected physicochemical properties of raw Anmol product Ethiopia paper factory effluents are presented in Table 3. The results of the analyses for most parameters show the expected trends in effluent quality. BOD has significantly positively correlated with the parameters such as TN(r = 1), K(r = 0.96), TH(r = 0.98), Ca(r = 0.98) and HCO3-(r = 0.94). However, it has negative correlation with carbonates (r = -0.53), COD (r = - 0.58) Fe(r = -0.1) and Turbidity(r = -0.82). This indicate that changing in amount of TN, K, TH, Ca and bicarbonates have caused significant positive change in BOD value of these effluents. TS and TDS (r = 0.98) have significantly positive correlation with each other as well as with EC(r = 0.99), total alkalinity, sulphate, carbonate and bicarbonate. However, they were negatively correlated with chlorides, COD and Fe. This is pointed out that increase in TS and TDS led to an increment of BOD, EC and decrement in chlorides. This confirmed that degradation of both TS and TDS reduce the dissolved oxygen of the effluents which led to increase the BOD and freely moving ions in the effluents.

As shown in Table 4, total hardness has strong positive correlation with BOD(r = 0.98), Ca(r = 1), Mg(r = 1). However; it is negatively correlated with turbidity(r= -0.91), COD(r = -0.42), carbonate (r = -0.68). Moreover, chemical Oxygen Demand has a negative correlation with almost all parameters such as EC(r = - 0.94), TS(r = -0.98), TDS(r = -1), TH(r= -0.42), HCO3-(r = - 0.82), SO4-2(r = -0.99) but has positive correlation with turbidity (r = 0.01), chloride (r = 0.98) and Fe (r = 87). This implies, that the presence in a high value of conductivity, TS, TDS, and TH increases COD. In general, the correlation in treated effluent of Anmol product Ethiopia paper effluent in Table 4 follows similar trends to raw effluent with the exception of COD that shows positive correlation with sulfate (r = 0.78) and chlorides (r = 0.85).

Table 3: Correlation matrix (Pearson) of raw effluent.
*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 Level (2-tailed)

Parameter	BOD	COD	TN	Turb	TS	TDS	EC	PH	TH	Ca	Fe	Cl-	TA	CO32-	HCO3-	SO42-
BOD	1															
COD	-0.58	1														
TN	0.96	-0.77	1													
Turb	-0.82	0.01	-0.64	1												
TS	0.71	-0.98*	0.87	-0.19	1											
TDS	0.58	-1 **	0.77	-0.01	0.98*	1										
EC	0.81	-0.94	0.94	-0.34	0.99*	0.94*	1									
PH	-0.09	-0.76	0.18	0.64	0.63	0.76	0.5	1								
TH	0.98	-0.42	0.9	-0.91	0.58	0.42	0.7	-0.27	1							
Ca	0.98*	-0.41	0.89	-0.92	0.56	0.41	0.69	-0.28	1	1						
Fe	-0.1	0.87	-0.36	-0.48	-0.77	-0.87	-0.66	-0.98	0.08	0.1	1					
Cl-	0.43	0.98	-0.65	-0.16	-0.94	-0.98*	-0.87	-0.86	-0.26	-0.24	0.94*	1				
TA	0.81	-0.94	0.94*	-0.34	0.99*	0.94*	1 **	0.5	0.7	0.69	-0.66	-0.87	1			
CO32-	-0.53	-0.38	-0.29	0.92	0.21	0.38	0.06	0.89	-0.68	-0.69	-0.79	-0.54	0.06	1		
HCO3-	0.94*	-0.82	1**	-0.58	0.91	0.82	0.96*	0.26	0.86	0.85	-0.44	-0.71	0.96*	-0.21	1	
SO42-	0.45	-0.99*	0.67	0.14	0.95	0.99*	0.88	0.85	0.28	0.27	-0.93	-1**	0.88	0.52	0.73	1

Table 4: Correlation matrix (Pearson) of treated effluent.

Parameter	BOD	COD	Turb	TS	TDS	EC	pH	TH	Ca	Fe	Cl-	TA	CO32-	HCO3-	SO42-

BOD	1														
COD	-0.25	1													
Turb.	-0.82	-0.35	1												
TS	0.1	-0.99	0.49	1											
TDS	0.02	-0.96	0.59	0.99	1										
EC	0.37	-0.99	0.22	0.96	0.92	1									
pH	-0.73	-0.48	0.99	0.61	0.7	0.37	1								
TH	0.93	-0.6	-0.55	0.47	0.36	0.69	-0.42	1							
Ca	0.93	-0.6	-0.55	0.47	0.36	0.7	-0.41	1^{**}	1						
Fe	0.99^{*}	-0.18	-0.86	0.02	-0.1	0.3	-0.78	0.9	0.89	1					
Cl-	0.3	0.85	-0.79	-0.92	-0.96	-0.77	-0.87	-0.08	-0.08	0.37	1				
TA	0.21	-0.99^{*}	0.38	0.99	0.97	0.99	0.52	0.56	0.57	0.14	-0.87	1			
CO32-	-0.91	-0.17	0.98	0.32	0.43	0.04	0.94	-0.69	-0.69	-0.9	-0.7	0.21	1		
HCO3-	0.6	-0.92	-0.04	0.85	0.79	0.97	0.11	0.86	0.86	0.54	-0.6	0.91	-0.23	1	
SO42-	0.4	0.78	-0.85	-0.87	-0.92	-0.7	-0.92	0.03	0.03	0.47	0.99	-0.81	-0.74	-0.5	1

Cluster analysis

Hierarchical cluster analysis (HCA) was used in this study to classify water and effluent samples of the study area into different groups. The HCA is designed to group water samples based upon similarities in measured parameters. The squared Euclidian distance between values of parameters measured were used to calculate similarity among samples so that similar items can be agglomerated by using linkage methods, which can ultimately assist in the recognition of potentially meaningful patterns. Güler and others described hierarchical cluster analysis as "an efficient means to recognize groups of samples that have similar chemical and physical characteristics."

The dendrogram of hierarchical clustering (Figure 2) shows that there are two pairs of samples that are fairly close, ((C, E) and D), while the linkage distance between cluster (A, B) and others are far, indicating samples D and (C, E) are more similar to each other than the samples (A, B). This examination of the sample cluster groups indicated that differences in groups may be attributable to the distance from the source of industry effluents. Within each cluster the samples (C, E) or (A, B) have shown more similarity, indicating composition similarities in measured parameters. Whereas the least polluted sample taken from upstream of the discharging point (D) separate itself entirely from effluent samples (A, B), indicated effluents from industry contributed to the change in composition of river water samples taken from downstream of the River (C, E).

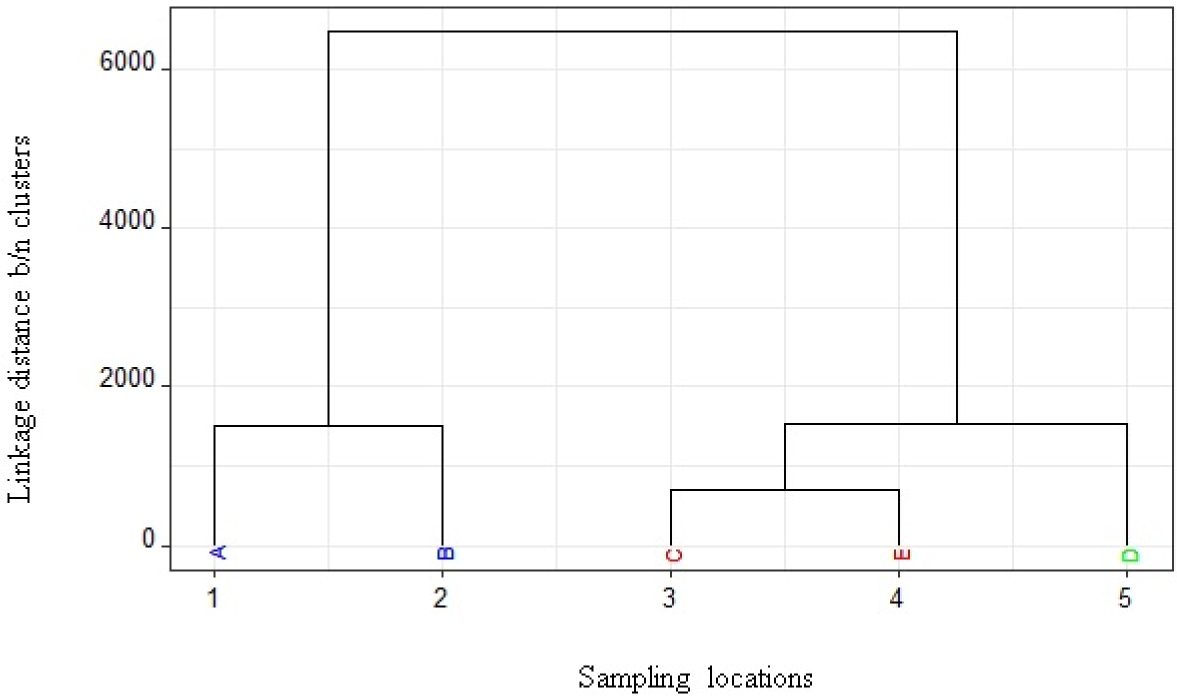

Figure2: Dendrogram of hierarchical clustering of water samples from upper Awash River and effluent samples of the factory.

Spatial variation on physicochemical characteristics of Upper Awash River water at the vicinity of Anmol product Ethiopia paper factory.

The variation in the physicochemical characteristics of upper Awash River water as a result of effluents discharged from Anmol product Ethiopia paper factory were investigated by considering three sampling sites as shown in Table 5. The values of the results were compared with the National standard [17] and [18]maximum permissible limits of river water.

Table 5: Average (n = 3) concentrations of selected physicochemical parameters of upper Awash River compared with river water maximum allowable standard concentrations.
[a]WHO (2008) World Health Organization standard limit.
[b]EEPA (2010) Ethiopian Environmental Protection Authority.

Parameter	Mean ± SD	Discharge point(C)		Maximum permissible concentration	
		Downstream(E)	Upstream(D)	EEPA[b]	WHO[a]
BOD(mg/L)	429.19 ± 27.64	65.48 ± 3.18	6.81 ± 0.089	10	10
COD(mg/L)	1066.7 ± 76.01	314.37 ± 19.80	7.53 ± 0.45	40	40
TP(mg/L)	1.04 ± 0.01	0.815 ± 0.005	0.78 ± 0.001	0.24	0.14
TN(mg/L)	9.06 ± 0.52	6.30 ± 0.18	2.40 ± 0.02		10
Turbidity(NTU)	198.12 ± 13.5	129.58 ± 9.6	22.51 ± 1.4	5	5
TS(mg/L)	1048.67 ± 118.1	804 ± 92.79	327.33 ± 34.4		
TDS(mg/L)	833.33 ± 68.77	663.3 ± 36.69	321 ± 13.57		500
TSS(mg/L)	215.33 ± 13.55	140.67 ± 10.43	33.33 ± 2.44	100	80
EC μS/cm	1247 ± 12.6	1028.33 ± 10.3	469.33 ± 8.2	300	300

pH	7.84 ± 0.43	7.23 ± 0.44	7.50 ± 0.21	6.5-8.5	6.5-8.5
Na(mg/L)	279 ± 0.68	161.33 ± 0.87	28.50 ± 0.07	200	200
K(mg/L)	3.467 ± 0.1	3.93 ± 0.08	2.1 ± 0.02	1.5	
TH(mg/L)	363.09 ± 30.8	345.08 ± 28.65	28.20 ± 1.5		500
Ca(mg/L)	118.33 ± 6.7	121.43 ± 5.12	74.62 ± 3.18	75	75
Mg(mg/L)	16.13 ± 0.92	9.96 ± 0.76	7.63 ± 0.49	50	50
Cl−(mg/L)	97.47 ± 4.76	50.10 ± 1.34	5.99 ± 0.27		600
T .Alkalinity	428.54 ± 29.42	353.01 ± 24.5	237.35 ± 16.2		
(mg/L)				200	200
CO32−(mg/L)	19.59 ± 0.62	29.39 ± 1.31	ND	ND	ND
HCO3−(mg/L)	482.80 ± 19.2	370.91 ± 17.34	289.6 ± 11.2	-	-
SO42−(mg/L)	56.3 ± 0.95	194.65 ± 1.84	4.89 ± 0.03	250	250
Cu(mg/L)	ND	0.005 ± 0.00	0.029 ± 0.00	2	1.5
Zn(mg/L)	0.065 ± 0.00	0.058 ± 0.00	0.089 ± 0.00	5	5
Fe(mg/L)	0.29 ± 0.001	0.38 ± 0. 001	0.13 ± 0.00	0.3	0.3

Chemical parameter classification by the use of hierarchical cluster analysis shown in Figure 3 clearly indicated correlation among measured parameters and the relative contribution of measured physicochemical parameters from the factory effluent on the river water composition.

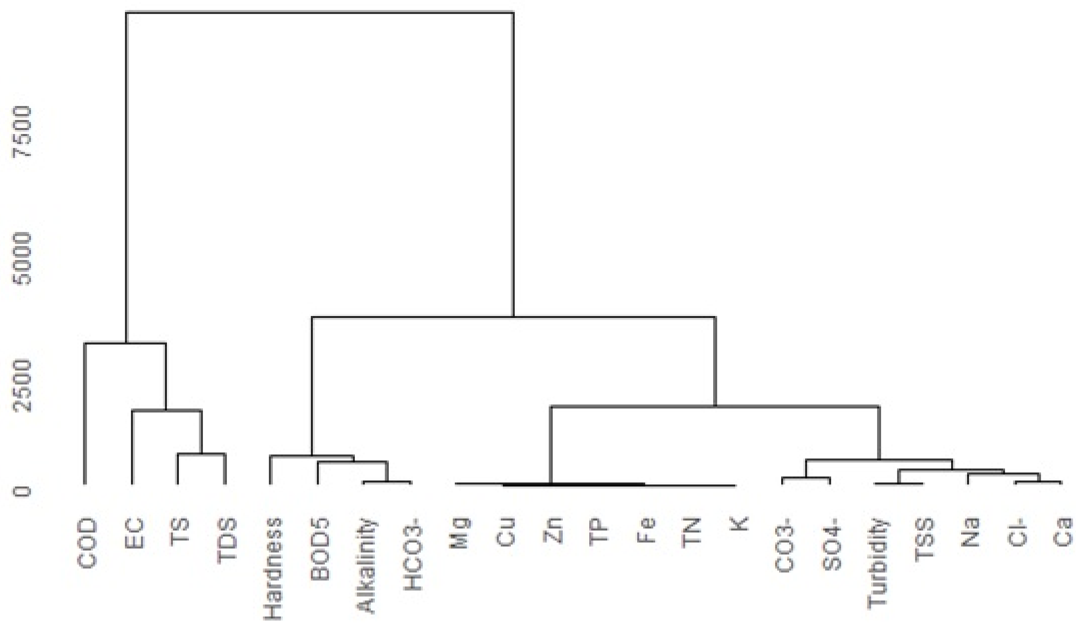

Figure 3: Dendrogram of hierarchical clustering of 22 water quality parameters.

The pH value of upstream sampling point was ranged from 7.05 to 7.91. This value was within the national maximum allowable concentration of river water standard limit of, 6.5-8.5. However; a slight increase in pH value 7.16 to 9.16 at discharge points and a slight drop 5.12 to 9.38 at the downstream were observed. This could be attributed to the addition of the Anmol paper industry effluents along with the eroded soil and trash materials added into the river and slight drop in pH value for the downstream is due to dilution. But this change is not serious still the pH values of the river remain within the national and WHO river water standard limit and may not cause an adverse effect on the survival of aquatic organisms.

The mean concentration of Total solids (TS) at sampling points C, E and D, of Awash River water samples were found 1048.67 ± 118.1, 804.00 ± 92.79, and 327.33 ± 34.4 mg/L respectively. The total solids at the discharging point were slightly higher and decreased downstream samples which have more total solids than upstream samples (Figure 4). The increment in the magnitude of TS at discharging point compared to at downstream and upstream values might be due to the influence of the Anmol paper industry effluents on the river.

The mean Total Suspended Solids (TSS) content in upper Awash River water at sampling points C, E and D were 215.33 ± 13.55, 140.67 ± 10.43, and 33.33 ± 2.44 mg/L respectively. The suspended solids at the discharging point were slightly higher than the other sampling points. Again the downstream samples have more suspended particles then upstream samples (Figure 6). The total suspended solid values obtained for the river at discharge and downstream point was higher than WHO recommended maximum concentration of 100 mg/L in surface water.

The upper Awash River water samples during this study have higher Total Dissolved Solids (TDS) at point C, (833.33 ± 68.77 mg/L) and the downstream samples have dissolved particles of 663.33 ± 36.69 mg/L which was higher than the value at upstream sampling point (321.00 ± 13.57 mg/L) (Figures 4 and 5). The total dissolved solid values obtained for the river at discharging point were higher than WHO maximum permissible concentration of 500 mg/L for surface water.

The mean turbidity values of upper Awash River water sample during the study period at sampling points C, E and D were 198.122 ± 13.5, 129.58 ± 9.6, 22.51 ± 1.4 NTU respectively (Table 5). The turbidity values obtained at all locations were higher than the national [17] and WHO standard limit of 5 NTU for river water. There were significant differences in values obtained at the effluent discharge point, in comparing with other sampling points D and E (Figure 6). The excessive turbidity, TSS, TS and TDS in upper Awash River water observed during this study associated with Anmol product Ethiopia paper effluent contamination which may reduce the aesthetic value of the river such as decrease in photosynthesis process and also associated with microbial contamination since turbidity prevents deep penetration of light in water [19].

The mean electrical conductivity of the upper Awash river water samples at effluent discharging point(C), downstream(E) and upstream(D), during this study period were 1247 ± 12.6, 1028.33 ± 10.3, and 469.33 ± 8.2 µS/cm respectively. The EC values obtained at all sampling points exceed national [17] and WHO maximum permissible limit (300 µS/cm), which indicates the river is polluted. The EC of discharging point sample were higher than downstream and upstream samples (Figure 4). The conductivity value at discharge and downstream point obtained in this study was attributed to the discharge of effluents from Anmol product Ethiopia paper into the river. Conductivity in water analysis is used to indicate the contents of dissolved solids in water because the concentration of ionic species determines the conduction of current in an electrolyte and it is unsafe to aquatic live when it is above the permissible limit [20].

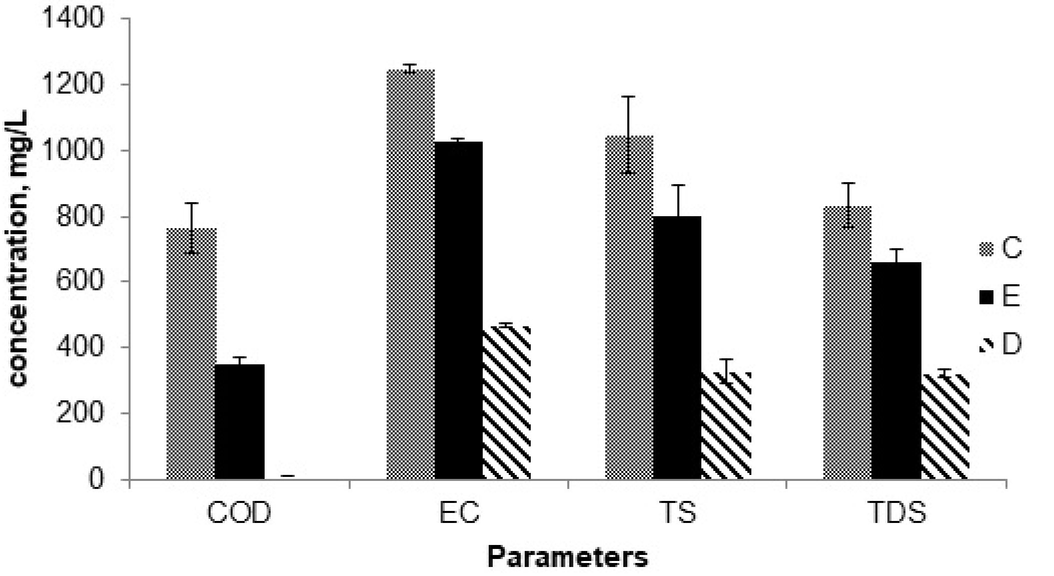

Figure 4: Trends of average concentrations of COD, EC, TS and TDS.

The BOD5 values measured at sampling points C, E and D, were 429.19 ± 27.64, 65.48 ± 3.18 and 6.81 ± 0.089 mg/L, and the mean COD values were 1066.73 ± 76.01, 314.37 ± 19.80, and 7.53 ± 0.45 mg/L respectively). The lowest values were recorded in the upstream and the highest values at the effluent discharging point (Table 5. This is attributed to the discharged of effluents containing high organic matter from Anmol product Ethiopia paper industries to the upper Awash river. The observed BOD5 and COD levels (Table 5) were also noticed to be above the national [17-20] and WHO maximum allowable concentration for undisturbed river which is less than 10 mg/L and 40 mg/L respectively. These high levels of BOD5 and COD could deplete the DO in the water system. The result indicated that the water bodies sampled were deteriorated due to continuous discharge of Anmol product Ethiopia paper factory effluents.

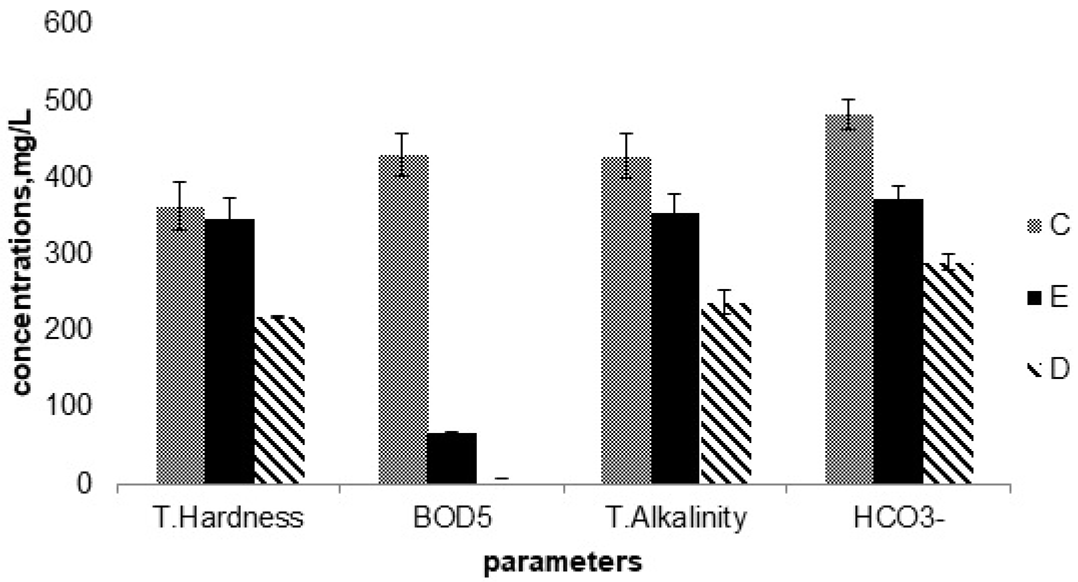

Figure 5: Trends of average concentrations of T. Hardness, BOD5, T. Alkalinity and HCO3-.

Total phosphorus: The sampling site at effluent discharging point (C) was the highest with mean total phosphorus load of 1.04 ± 0.01mg/L. The total phosphorus content in downstream and upstream of the river was also high with average concentration of 0.815 ± 0.005 and 0.78 ± 0.001 mg/L respectively (Table 5). The elevated TP levels in all sampling sites could possibly result from soap and detergent used by the nearby residents that use the river for bathing, nearby hotels that discharge their domestic effluents to the stream which drains the effluents to the upper river Awash. At discharging point and downstream the level of phosphorus was higher that might be due to the addition of effluents from Anmol product Ethiopia paper. The average total phosphorus levels recorded at each sampling site were in excess of 0.14 mg/L maximum allowable concentration WHO and can cause eutrophication.

Total nitrogen: The average concentrations of TN at sampling points C, E and D were 9.06 ± 0.52, 6.30 ± 0.18 and 2.40 ± 0.02 mg/L respectively. The higher concentrations of total nitrogen was observed at the effluent discharging point and followed by a decline at the downstream and the lowest concentration was registered at the upstream (Table 5). It is probably due to diffused sources of pollution entering into upper Awash River such as cow's dung and nearby latrines of the residential to the stream which drains the effluents to the river. The mean total nitrogen level recorded at effluent discharging point is in excess of 10 mg/L maximum allowable concentration WHO and can cause eutrophication.

The highest average concentrations of total alkalinity during this study period observed at effluent discharge point(C) (428.54 ± 29.42 mg/L) and followed by a decreased mean value at the downstream(E) (353.01 ± 24.5 mg/L) and the lowest concentration was registered at the upstream(D) (237.4 ± 16.22 mg/L). The total alkalinity values of the river at the three sampling points were in excess of 200 mg/L of national [17] and WHO maximum allowable concentration (Table 4.7) of surface water. The average bicarbonate content also shows similar trends. The lowest concentration of carbonate was observed at upstream sampling point (ND) but the highest value was obtained in downstream sampling point (29.39 ± 1.31 mg/L) (Table 5). This might be due to the dissolution of carbonate rocks in the river and the lower concentration of carbonate at effluent discharging point could be due to the acidic nature of the Anmol product Ethiopia paper effluent containing organic matters under aerated condition added to the river [2].

The mean concentrations of total hardness of upper Awash River water at sampling points C, E and D were found to be 363.09 ± 30.8, 345.08 ± 28.65 and 28.50 ± 1.5 mg/L (Table 5). The result indicates the total hardness of the river at effluent discharge point and downstream was above the WHO maximum allowable limit of 500 mg/L. Water of hardness level 50-100 mg/L is classified as moderately soft, 100-150 mg/L is slightly hard, while above this value is hard water [21]. Hence, upper Awash River water downstream of effluent discharge point categorized as very hard water. This might be due to the addition of effluents from Anmol product Ethiopia paper which have been accumulating much dissolved calcium and magnesium ions that could possibly cause hardness. An increase in hardness level adversely affects detergent performance which constitutes the major problem to people who rely on the surface water for cleaning purpose [22].

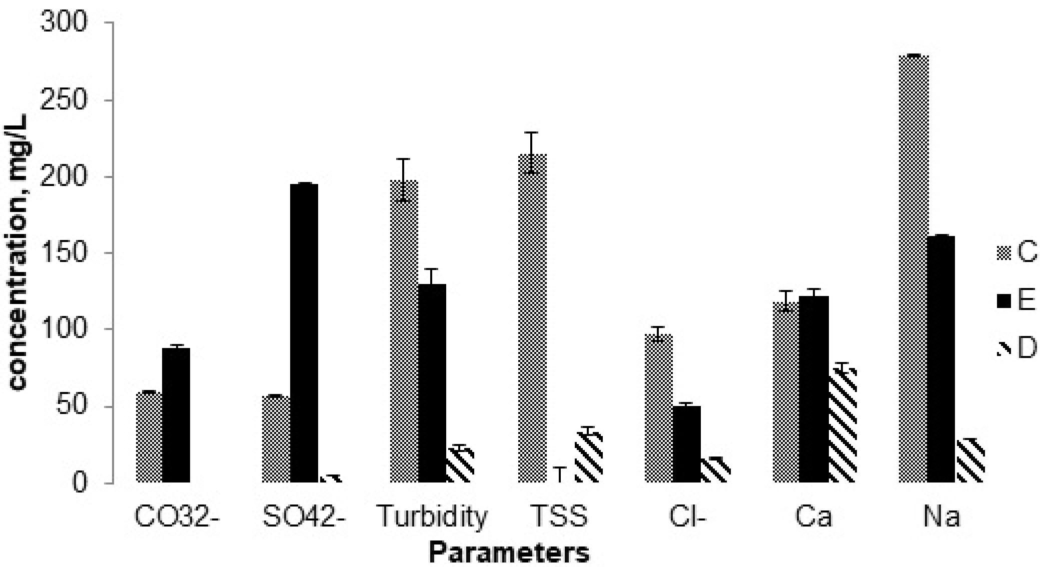

Figure 6: Tends of average concentrations of CO32-, SO42-, Turbidity, TSS, Cl-, Ca and Na.

Chloride (Cl-): The mean concentration of chloride at sampling points C, E and D sampling sites during this study period were found 97.47 ± 4.76, 50.10 ± 1.34 and 5.99 ± 0.27 mg/L respectively. The highest chloride concentration was found at discharging point which is attributed to the addition of effluent from Anmol product Ethiopia paper that contains chlorine compounds. Chlorides in water are not harmful to human and other animals until a concentration of 600 mg/L [18]. Above maximum safe chloride concentration limit was not recorded in all sampling points. However; effects may be worse when the pulp and paper effluents containing chlorine compounds are added to the river. This is because of the chlorine in the effluent coupled with high organic content of the effluents, results in the production of highly toxic organic compounds which are known to be toxic, persistent and bio accumulating and are thought to cause harmful disturbances in biological systems, and pose a human risk through long term exposure via drinking water and through bioaccumulation along with food chain [9,10].

The mean sulfate (SO42-) concentration at sampling points C, E and D of upper Awash River water sample were found 56.3 ± 0.95, 194.65 ± 1.84 and 4.89 ± 0.03 mg/L which were found unexpected trend. Apparently, more concentration of sulfate (SO42-) was obtained in downstream than any other sites. This result may be due to the high BOD5 and COD values at discharging point which decreases dissolved oxygen level of the river resulted in the subsequent reduction of sulfate to sulfide. In polluted waters the dissolved oxygen is very low and sulfate is readily reduced to sulfide causing noxious odors [15]. However; in the downstream concentration of sulfate was found increased probably due to the decrease in organic load because of more dilution resulted in the oxidation of sulfides to sulfate. The mean sulphate level of the river at discharging point and downstream were higher than the national EEPA and WHO maximum allowable limit of 250 mg/L.

The mean concentration of magnesium at sampling points C, E and D were 16.13 ± 0.92, 9.96 ± 0.76 and 7.63 ± 0.49 mg/L and the mean Ca concentrations were 118.33 ± 6.7, 121.43 ± 5.12 and 74.62 ± 3.18 mg/L respectively (Table 5). High concentrations of Mg and Ca were observed at effluent discharging point. The value decreases downstream and low value of Ca and Mg were recorded at upstream point. The presence of appreciable higher concentration of Ca was consistent with the level of hardness of the water observed during this study period. The concentrations of Ca at the three sampling sites were above the WHO maximum restriction limit of 75 mg/L of surface water while Mg was found below the recommended limit of 50 mg/L.

The mean concentration of sodium at sampling points C, E and D ,were 279 ± 0.68, 161.33 ± 0.87 and 28.50 ± 0.07 mg/L and potassium were 3.467 ± 0.1, 3.93 ± 0.08 and 2.1 ± 0.02 mg/L respectively (Table 5). Higher concentrations of K and Na were observed at effluent discharging point. The value decreases downstream and low value of K and Na were recorded at upstream point. The higher concentration of Na at discharging point indicates the effect of anmol product Ethiopia paper effluent with high content of Na probably from the caustic treatment during pulping or bleaching process of the raw material. The mean sodium level of the river at discharging point and downstream was above WHO 200 mg/L maximum allowable concentration while K was higher at all sampling sites than the national maximum allowable concentration of 1.5 mg/L of surface water.

The mean values of various heavy metals analyzed at sampling points C, E and D, were Fe(0.29 ± 0.001, 0.38 ± 0.001, 0.13 ± 0.00mg/L),Cu(ND, 0.005 ± 0.00, 0.029 ± 0.00 mg/L) and Zn (0.065 ± 0.00, 0.058 ± 0.00, 0.089 ± 0.00 mg/L) respectively (Table 5). The heavy metal concentrations in upper river Awash water samples at all sampling sites measured were within the national [17] and WHO except iron which was slightly higher at effluent discharge point and downstream sampling points which reflects the influence of the Anmol product Ethiopia paper effluents on the river.

CONCLUSION

Both raw and treated effluents of Anmol product Ethiopia paper factory were characterized by extremely high concentrations of organic matter (COD & BOD5), electrical conductivity, sulphates, TDS, TS, turbidity, Chlorides, Bicarbonate, total alkalinity, carbonates, Ca, Na, TN as well as strong hardness with pH value varies between strongly acidic and basic ranges. While, metals such as, K, Fe, Cu, Zn, and Mg were found in less amount in both raw and treated effluents of the factory which were also found within the national [17] and WHO industrial effluent discharge limits to surface water. However, the rest parameters were much higher than this discharge limits.The Selected physicochemical characteristics of the raw and treated effluents were not significantly differing during the study period for most of the parameters. The mean value variations of the parameters such as BOD5, COD, Turbidity, TS, TSS, TDS, EC, pH, Na, Mg, Ca, sulfate, carbonates and total alkalinity of raw and treated effluents were not significantly varied ($p > 0.05$). This reveals that the overall effluents treatment of the oxidation pond is not satisfactory rather it is used only as storage during day time which might expose organisms to toxic effects when discharged to the river bodies. Statistical analysis showed BOD5, COD, Ca, total hardness, Mg, TS, TDS, EC, total alkalinity, bicarbonate and chloride of the effluents were highly inter correlated. However; no significant association of turbidity was observed with COD and TDS while other parameters were moderately correlated.

The result also indicates that discharge of raw and inadequately treated effluents from the factory have considerable influences on the upper Awash River water quality. Higher concentration of physicochemical parameters like Turbidity, TS, TDS, EC, BOD,COD, total alkalinity, bicarbonates, total hardness, TN, chlorides, K, Fe, Ca, Mg and Na was observed at sampling site C (effluent discharge point). This is clearly due to the addition of Anmol product Ethiopia paper mill effluent which contains dissolved metal ions, organic materials and colloidal particles. The downstream samples have slightly higher value of parameters like Turbidity, TS, TDS, EC, BOD, COD, total alkalinity, bicarbonates, carbonate, total hardness, TN, chlorides, sulphates, K, Fe, Ca, Mg and Na. The concentration of sulfate was found increased in the downstream sampling point probably due to the decrease in organic load because of more dilution resulted in the oxidation of sulfides to sulfate.Similarly, the water sampled from Upper Awash river at the vicinity of Anmol product Ethiopia paper excluding pH, K, Mg, chloride, Cu, Zn, all the rest examined parameters at discharge and downstream sampling points were much higher than the Ethiopian Environmental Protection Authority [17] and WHO maximum allowable limit.

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