

The Pollution Status of Awash River Basin (Ethiopia) Using Descriptive Statistical Techniques

Yosef Abebe Yimer^{1,*}, Abraha Geberkidan²

¹Water Quality Expert, Awash Basin Authority (AwBA), Adama, Ethiopia

²Departement of Chemistry, College of Natural & Computational Science, Mekelle University, Mekelle, Ethiopia

*Corresponding author: abayosef501@gmail.com

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Abstract The aim of this study is to assess the current status of the Awash River. The study was designed using 12 sampling stations for three consecutive months from December-2016 to February-2017. Samples were taken for physicochemical analysis from the main river and tributaries. All parameters have been analyzed using standard methods. High level of EC, TDS, NO_3^- , NH_3 , Cl^- , SO_4^{2-} , Cr^{+6} , DO, COD and BOD were recorded in station S04. Accordingly, EC in station S04, S07 and S09; nitrate in S02 and S04; chloride in S04 and S09; Na and alkalinity in S07, S09, S10, S11 and S12 exceeded the standard guideline limit of WHO and FAO. Some irrigation water quality parameters such as EC, %Na, SAR, RSC, HCO_3^- , and Cl^- concentration showed a progressive increase from station S10 to S12. Based on this investigation, it is concluded that the discharge of industrial, domestic, and agricultural effluents together with the expansion of Lake Beseka has strongly degraded the quality of Awash River at the study area. Untreated industrial wastes and unregulated lake water have caused significant pollution in the Awash River system and mitigation measures are required to restore good water quality.

Keywords: water quality, degradation, untreated waste disposal, effluents and Awash River

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1. Introduction

The river Awash sometimes called river's mother starts upstream of Addis Ababa and terminates at the Lake Abbie on the Ethiopian-Djibouti Border. Ethiopia is the second most populous country in Africa and has a total area of 1.13 million square kilometers; out of which one-tenth (1/10) of the catchment is covered by Awash Basin. It is the 4th and 7th important basin by mass and by volume, respectively. In this basin, various activities were taking place such as; urbanization, industrialization, small and large-scale agricultures. In addition to these, the key economic sectors such as sugar, textiles, floriculture, agro-processing, slaughterhouses, tanning, leather products, and others are located in the Awash Basin. Therefore, it is a home to the country's industrial and agricultural development sector. It is used as a source of water supply for towns like Awash, Adama, for the pastoral peoples Afar Region, and acts as a source of hydropower for energy supply to Ethiopia, driving industry, water supplies, irrigation, livestock watering and waste-disposal [1,2,3].

The water quality in the watershed is directly affected by vegetative cover, agricultural, and other land management practices [4]. In Ethiopia, the water quality problem of rivers is apparent. Awash River (AR) leads in the extent of impairment due to its service as a sink for a

basin-wide, urban industrial and rural waste [5]. Many industrial activities cause the production of waste residuals [6] and the basin is highly vulnerable to industrial and domestic waste discharges, with the resulting degradation of the river [7]. Wastes dumped in open space, valley and other places eventually end up to rivers during runoff [8].

Aquifers in and around the city of Addis Ababa are showing signs of increasing contamination by chemicals including nitrate and also there is an increasing concentration of heavy metal pollution, coliform and pathogen pollution in the water of Aba-Samuel reservoir and its tributaries; little and big Akaki Rivers [9,10]. The Akaki River is the most polluted river due to it being surrounded by industries and overcrowded and slammed areas [11]. The Akaki and Modjo Rivers are the major tributaries of AR. They are vulnerable to industrial and domestic wastes and are also used as a liquid waste disposal [11]. Their water qualities have surpassed the permissible limits set by National Environmental Quality Standards [9,10,11,12]. The final destination of the polluted water that drained from Akaki, Kebena, and other tributaries are entered into Aba -Samuel reservoir and then into AR.

According to Water Quality Sanitation report (2011), over 2 million tons of sewage and other effluents drain into the World's Water [13]. Recent studies indicate that in Ethiopia, human activities such as land use and modification, urbanization, human settlement, industrialization, modern agricultural and other practices associated with

rapid population growth are the major water quality degrading factors [5,12,14]. In addition to these; natural or man-made phenomena such as the increased water level of the highly saline LB also degrade the quality of AR and this has resulted in high degradation plus it has and human wellbeing impacts [15]. Thus improving water quality is a vital requirement for better public health, productivity, and economic prosperity [16].

The overall objective of the present study is to assess the current status of the Awash River Basin and degree of pollution on the surface water quality of AR using various physicochemical water quality parameters such as pH, EC, TS, TH, TDS, Turbidity, Mg^{2+} , Ca^{2+} , Na^+ , K^+ , Cl^- , F^- , SO_4^{2-} , PO_4^{3-} , HCO_3^- , CO_3^{2-} , NO_3^- , NO_2^- , NH_3 , Alkalinity, DO, BOD, COD, and some toxic metals Cr, Mn, Fe, Cu, and Zn in the study area.

1.1. Description of the Study Area

The Awash River basin lies between $7^{\circ} 52' 22''$ to $12^{\circ} 08' 24''$ North and $37^{\circ} 56' 24''$ to $43^{\circ} 17' 24''$ East. The basin is located at the heart of the rift valley at an altitude ranging from 2500 m asl at Worqe Mountain in the south of the basin and 250 m asl at the north furthest side of Lake Abbe, and covers a distance of 1250 km [17,18]. The total catchment area of the basin is 113,467 km² and distributed in 5 regional state and 2 city administrations. It is the most intensively utilized river basin and also the only basin irrigation water pricing is practiced [19]. In which there are about 34.4 million estimated livestock population and has 199,234 hectares of suitable land for irrigation. Based on Awash basin master plan report, currently the population of the basin is estimated to be reach 18.6 million with a distribution of 50.65 % in Oromia, 19.78 % in Amhara, 16.34 % in Addis Ababa,

5.35 % in Afar, 4.96 % in Ethio-Somalia, 2.8 % in Dire Dawa and 0.84 % in SNNP [20].

Out of the total length of the river, the study area covers half of the length (i.e 625 km) and 37.6 % of the catchment area and also consists about 62.68 % of the basin human population. AR is fed by several major tributaries; including the Akaki, Modjo, Kesseme, Awadi, Arso, Ataye, Borkena, Cheleka, Mile, and Logiya Rivers. It is characterized in a wide range of Agro-climatic zone namely from partly "Dega" to dominantly "Berha". The study was conducted in the Awash River basin namely, upstream Koka, Awash-Awash and Awash- Halidebi sub-basins.

1.2. Map of the Study Area

Sampling sites were selected based on accessibility, pollution load, presence of disturbing influences availability of stable stream bed, safety and security in 3 sub basins in Awash basin.

2. Materials and Methods

2.1. Methods of Data Collection

As seen in Figure 1, water samples were collected from 12 sample stations; the main river, Koka dam, Lake Beseka and tributaries once a month from December 2016 to February 2017 for three consecutive months, for the analysis of physicochemical and metals analysis such as pH, EC, TS, TDS, TH, Turbidity, Mg^{2+} , Ca^{2+} , Na^+ , K^+ , Cl^- , F^- , SO_4^{2-} , PO_4^{3-} , HCO_3^- , CO_3^{2-} , NO_3^- , NO_2^- , NH_3 , DO, BOD, COD, alkalinity, and some toxic metals Cr^{+6} , Mn, Fe, Cu, Zn, and other irrigation water quality parameters (WQP), such as B, SAR, %Na, RSC, and so on were used.

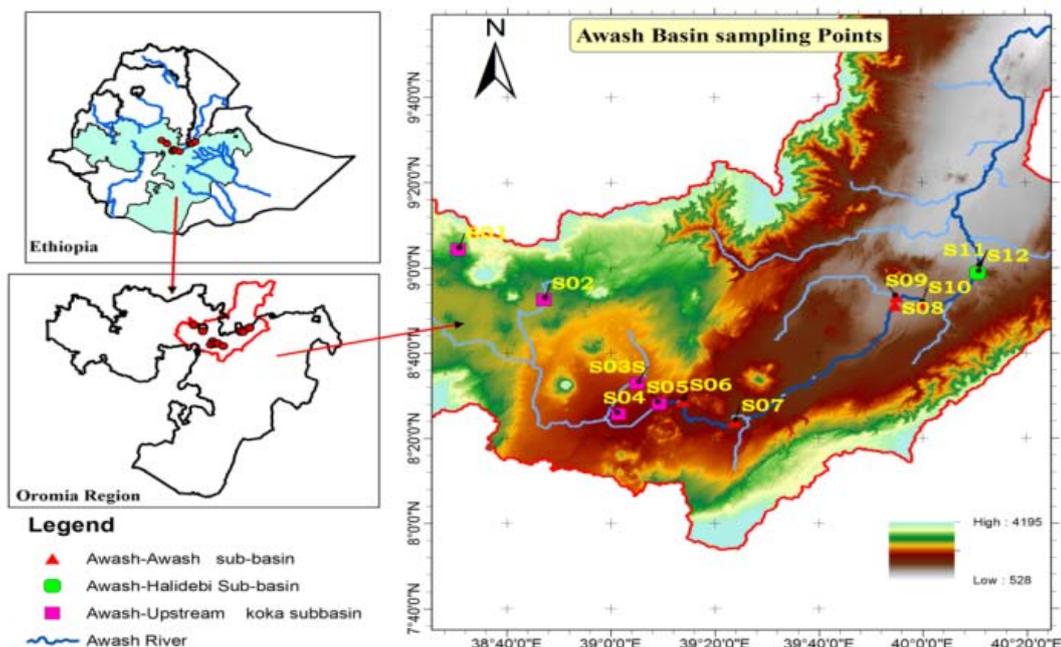


Figure 1. Location Map of the study area and sampling sites (N.B: The sites: S01RAH=Awash River @ Holeta base line, S02RAT=Akaki River @ Trunesh Bejing Hospital, S03RZR= Awash River @ Zeway Road, S04RMD=Modjo River downstream of factory, S05LKD=Lake Koka @ Koka Dam, S06RWB=Awash River @ Wonji bridge, S07SHS=Soddere Hot Spring, S08RBB=Awash River before Beseka mix, S09LBC= Lake Beseka @ Canal, S10RAB=Awash River after Beseka mix, S11RWS= Awash River @ Awash 7 & S12RMS= Awash RIVER @ Melka Sedi.)

2.2. Sample Collection and Sampling Precautions

The representative water sample was taken following the standard procedures using polyethylene plastic bags [21]. Accordingly, a river water sample was taken using grab sampling techniques from 12 stations. In the case of sampling the researcher cared and rinsed the sample bottles repeatedly with the sample water before taking to prevent any cross-contamination from previous samples and then collected about 1.5 liters of water sample from the sample stations for most physicochemical and heavy metals analysis, the researcher accounted and leaved an air space equivalent to approximately 1 % of the container volume to allow for thermal expansion during transport. To detect unauthorized tampering with samples up to the time of analysis, sample containers were sealed using self-adhesive paper, which includes sample Id, time and date of sampling, water type, and collector name. Delivered samples were stored at 4°C refrigerator at the specified temperature until the analysis is taken.

Table 1. Parameters and Instruments

Parameters & Symbols	Instruments / Apparatus
Temperature	SX 713 Cond/TDS/Sal/Res meter
TDS, Salinity, Conductivity	5 Series Portable con/TDS/Salinity meter
pH	Z-WAG-WE 30020 pH/Temperature
Turbidity	Turbidometer PT 0900914363/ Spectrophotometer
TH	Titration with 0.05 N EDTA
Mg ²⁺ , Ca ²⁺	Titration with 0.05 N EDTA
Na ⁺ , K ⁺	Flame Photometer
Fluoride, F ⁻	Spectrophotometer HACH
Chloride, Cl ⁻	Titration using 0.014 N AgNO ₃ Argentometric
Alkalinity	Titration with 0.01 N H ₂ SO ₄
Bicarbonate, HCO ₃ ⁻	Titration with 0.01 N H ₂ SO ₄
Carbonate, CO ₃ ²⁻	Titration with 0.01 N H ₂ SO ₄
Ammonia, NH ₃	Spectrophotometer Hach Company
Nitrate, NO ₃ ⁻	Spectrophotometer Hach Company
Nitrite, NO ₂ ⁻	Spectrophotometer Hach Company
Sulphate, SO ₄ ²⁻	Spectrophotometer Hach Company
Phosphate, PO ₄ ³⁻	Spectrophotometer Hach Company
Mn, Fe	Spectrophotometer Hach Company
Zn, Cr,	Photometer 7100/ Spectrophotometer
Cu, B	Photometer 7100/ Spectrophotometer
DO	Azide modification Water proof Hand-held DO 300 meter
BOD	Azide modification Water proof Hand-held DO 300 meter
COD	APHA 5220B. Open Reflux Methods

2.3. Chemicals and Reagents

During the study, chemicals like Buffer solutions (pH 7 and 4) were used to calibrate the instrument in pH determination, 0.01M KCl, to calibrate EC meter, 0.02N H₂SO₄ and bromo cresol-methyl red or phenolphthalein indicator for alkalinity, 0.02N EDTA and Maniver-2 for total hardness, 8N NaOH or KOH, 0.02N EDTA and Caliver-2 for calcium, potassium chromate indicator and 0.014M AgNO₃ for chloride, (Nitriver-6 and Nitriver-3) and Nitriver-3 in cadmium reduction and diazotization method for nitrate and nitrite, respectively, Sulfaver-4 for sulfate, SPADNS reagent for fluoride, Nessler indicator

for ammonia, Phosver-3 reagent for phosphate, Ferrover-3 for iron, citrate buffer and sodiumperiodate reagent for manganese, coppercol no.1 and coppercol no.2 tablet for copper, zinc-dechlor and zinc tablet for zinc, and chromicol no.1 and chromicol no.2 for chromium test. Alkali iodide azide reagent for BOD test, a sulfuric acid reagent for COD test were used to determine of the above-listed water quality parameters and various types of reagents and chemicals such as nitric acid and formaldehyde were also used for preservative of BOD, COD, etc during laboratory investigation.

2.4. Analytical Procedures and Analysis

On-site Analysis and precautions: The analysis and determination of some parameters such as Temperature, TDS and/or EC, and pH were analyzed on-site using portable or field instrument test kits like SX 713 Cond/TDS/Sal/Res meter or 5 Series portable Con/TDS/Salinity meter, and Z-WAG-WE 30020 pH/Temp meter (Table 2). The samples were transported to a laboratory as soon as possible for physicochemical and heavy metal analysis [22].

Laboratory Analysis and procedures: The partial physicochemical and some heavy toxic metals analysis were carried on for 28 water quality parameters. The water sample analysis was done as per the standard methods listed under Table 1 for the examination of water and wastewater manual [23] adopted by the Ethiopian Construction Design and Supervision Works Corporation (ECDSWC). Most physicochemical water sample parameters were carried out in accordance to the standard methods for analysis of AOAC and APHA methods [22,23].

2.5. Methods of Data Validation and Analysis

Data validation is a key activity to check the reliability of collected data for completeness, reasonableness, and elimination of errors. Therefore, the researcher validated the raw data using data validation method. The raw data obtained from water samples were checked and validated. Ionic balance error was calculated, the error in the ionic valance for majority of the samples were within 5%. Finally, the results were analyzed by descriptive and multivariate analysis using statistical software SPSS version 16.0 and Microsoft office excel and also results of water analysis were analyzed by comparing against WHO, FAO and other national and international Standards (Table 4). The output Table 5 delivers correlations between each of variables and associated significance tests. ANOVA at 95% & 99% level of significance were used to compare the quality of water among all sites (Table 3).

3. Results

3.1. The Surface Water Quality Analysis for Drinking Use

I. The pH

pH values varied from a minimum of 6.02 ± 0.0 at S01 and a maximum of 9.39±0.15 at S09. Some stations like

S03, S09, and S10 have beyond the limits of WHO (2011). However, the pH value at station S09 changed abruptly from 9.39 dropped in station S10, S11, and S12 to 8.57, 8.47, and 8.29 units, respectively. The statistical analysis showed that there is a significant difference between the 12 sampling sites. When pH exceeds from allowable limits of WHO it may affect water as well as land.

II. EC and TDS

EC has recorded a minimum, 77 $\mu\text{S}/\text{cm}$ at S01 and maximum $3,373 \pm 227.5 \mu\text{S}/\text{cm}$ at S09 which is 43 times greater than the baseline station. Based on their composition ions responsible for EC, different surface waters in the study area have different EC values. The mean EC value of station S04, S07, and S09 were $(1,769.7 \pm 807.7)$, $(2,176.7 \pm 70)$ and $(3,373.3 \pm 227.5) \mu\text{S}/\text{cm}$, respectively, and which are above the standard limits of WHO. Awash after LB station S09 shows at some extent the high amount of ionic concentrations than the remaining main course sites.

All identified sampling stations with high EC values harmoniously showed high TDS values as seen in Figure 2. Freshwater has a TDS from 0 to 1,000 mg/L; slightly saline water from 1,000 to 3,000 mg/L; and moderately saline water from 3,000 to 10,000 mg/L. Highest TDS value revealed in station S09 and lowest TDS seen in station S01. Based on this classification, Station S09 was categorized under slightly saline water. Generally, three sampling sites S04, S07, and S09 showed high TDS and EC values above the standard guideline limits of WHO.

III. Turbidity and TS

The lowest turbidity was observed in station S07 (1 NTU). Whereas, the highest turbidity was seen in station

S01 (3,700 NTU) due to the presence of suspended particles which come from erosion, runoff, discharges and so on. The experimental findings at 95 % confidence level also showed no significant difference between sampling stations. In the present study, the mean values for TS at 12 stations varies from $371 \pm 41 \text{ mg}/\text{L}$ at S06 to $3752 \text{ mg}/\text{L}$ at S01. Due to the presence of suspended and settle-able solids eroded, the water becomes more turbid and thus a considerably high value of TS was observed. Arguably soil erosion is a large contributor of solid in surface water, agricultural runoff, industrial wastes and effluent from industries.

IV. Sodium and Potassium

As seen in Figure 3 the concentration of Na, excessively high value was recorded in LB that was 39.39 meq/L and followed in station S07 about 25.65 meq/L. With regard to LB, the value of Sodium ion in station S08 was 19 times lesser than station S09 and which definitely contributed to the rising concentration of Na at station S10. It also further affects the rest two downstream stations. More consumption of sodium may cause hypertension, congenital heart diseases and kidney problems [24].

The recorded values for K for all studied sites are higher than the permissible limits of WHO, (2011) that is 12 mg/L. The lowest mean concentration of potassium was recorded in station S05 that is $14.23 \pm 1.66 \text{ mg}/\text{L}$. In contrary, the highest value of K was obtained in S09 $83.67 \pm 5.69 \text{ mg}/\text{L}$ which is 7 times greater than the standard limit of WHO. Eight stations have mean values between $15.10 \pm 2.10 \text{ mg}/\text{L}$ to $42.0 \pm 6.06 \text{ mg}/\text{L}$ and the remaining two stations S04 and S07 have $59.83 \pm 10.89 \text{ mg}/\text{L}$ and $72.0 \pm 11.14 \text{ mg}/\text{L}$, respectively.

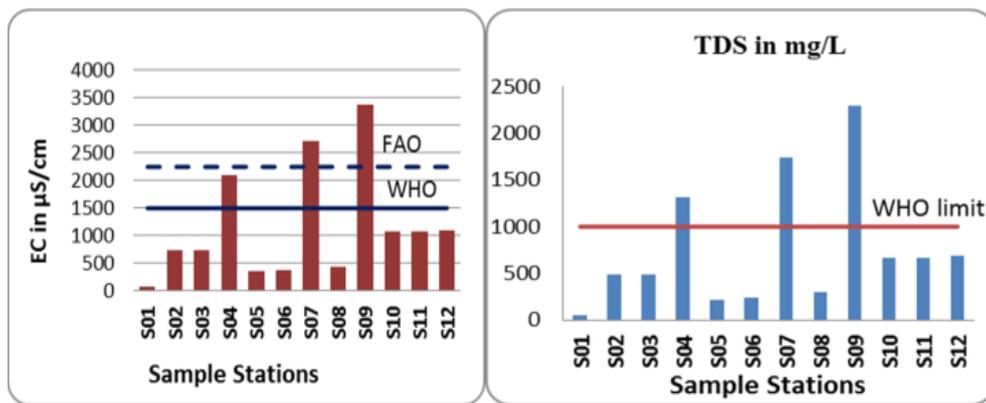


Figure 2. Electrical Conductivity and total Dissolved Solids

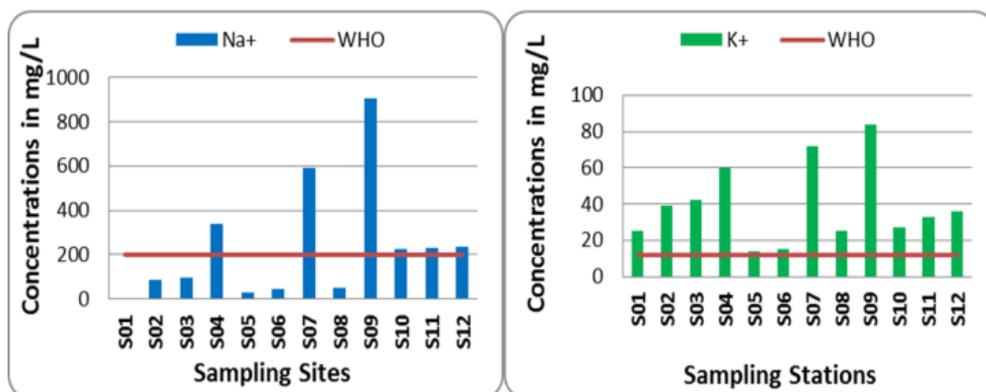


Figure 3. The Concentration of Sodium and Potassium with respect to WHO standards

V. Magnesium, Calcium and TH

The highest mean concentrations of Mg^{2+} and Ca^{2+} were recorded in the same station S04RMD 16.8 ± 8.02 mg/L and 68.8 ± 13.67 mg/L, respectively. Whereas, the lowest values of Mg^{2+} and Ca^{2+} were seen at station S09 1.28 ± 0.55 mg/L and 5.87 ± 0.92 mg/L, respectively. All sampling stations showed below the standard guideline of WHO that is 75 mg/L. Some evidence showed the incidence of heart disease is reduced in areas served by a public water supply with a high degree of hardness, the primary constituent of which is calcium so that the presence of this element in a water supply is beneficial to health [25].

Hardness value in the study area varied between 53.04 mg/L (S01) to 242 ± 69.7 mg/L (S04). Water that has a hardness less than 61 mg/L is considered as soft (S01 & S09); 61 to 120 mg/L, moderately hard water (S05, S06, S07, S10, S11 & S12); 121 to 180 mg/L, hard water (S02, S03 & S08); and more than 180 mg/L, very hard water (station S04) [26]. This Station (S04) showed higher concentrations of hardness than the standard guidelines limit of WHO that is 300 mg/L. Exceeding the permissible limits of hardness might cause poor leathering with soap, deterioration of the quality of clothes, scale formation and skin irritation [27]. TH showed high positive relationships with Ca ($r = 0.95$ at $p < 0.05$), Mg ($r = 0.696$ at $p < 0.05$).

VI. Carbonate, Bicarbonate and Alkalinity

As shown in Table 2, the value of pH in stations S02, S04, S06, and S08 were less than 8, equivalently the concentration of carbonate was almost traced in all identified stations. The standard guidelines of WHO for carbonate was still objectionable. The highest recorded concentration of HCO_3^- was seen in station S07 1341.37 ± 42.8 mg/L, followed a high concentration in S09, 1007.14 ± 212.5 mg/L and in station S04 (597.78 ± 215.19 mg/L). In contrary, the lowest concentration of bicarbonates was recorded in S01 that is 41.48 mg/L.

This study find that alkalinity is positively correlated with EC ($r = 0.942$, $p < 0.01$). The highest concentration of bicarbonate might be from industrial wastes, sewage, because of various carbonate rocks like limestone, dolomite, magnesites from which dissolution takes place with the participation of carbon dioxide. All sampling points except station S01 (34.0 mg/L) showed a high alkalinity values than the prescribed limit by WHO (100 mg/L). A high alkalinity in S09 may be due to the presence of high concentration of carbonates, bicarbonates, and sometimes due to the existence of silicates, and phosphates rock.

VII. Fluoride and Chloride

In all stations, fluoride concentrations varied from 1.31 ± 0.04 mg/L (S04) to 31.03 ± 28.59 mg/L (S09). Except for station S04, all the rest stations have high concentrations of fluoride than the WHO limits. When its concentration is higher in drinking water than the WHO limits (1.5 mg/L), it causes dental fluorosis. Surprisingly the toxicity level of fluoride in Lake Beseka or station S09 was too high (31 ± 0.04 mg/L) followed 15.75 ± 13.94 mg/L fluoride concentration recorded in S07. The highest concentration of chloride was obtained in station S09 that is 269.88 ± 54.21 mg/L and it might be the process of leaching of minerals, from rock, saline deposits, from

irrigation drainage, sewage, wastewater from industries etc. Sewage is such a rich source of Cl⁻. A high chloride results may indicate pollution water by sewage effluents [25]. The concentration of Cl⁻ is high in station S04 due to excess load of industries untreated waste water.

IX. Nitrate, Nitrite and Ammonia (NO_2^- , NO_3^- , & NH_3)

In the present study nitrate (NO_3^-), nitrite (NO_2^-) and ammonia (NH_3) were recorded beyond the limits of WHO at station S04. The highest concentration of nitrate, NO_3^- was seen at station S04 215.13 ± 181.99 mg/L, which is four times greater than the standard limits of WHO (50 mg/L) and followed station S02 52.63 ± 7.45 mg/L. All the rest stations including Lake Beseka and Soddire hot spring even showed below the limits of WHO. Highest concentrations of NO_3^- observed in S04 might be due to industrial discharge, municipal wastewater from Modjo town, fertilizers from floriculture, etc.

A high content of nitrite, NO_2^- was observed only in station S04 that is 4.89 ± 4.59 mg/L above the standard limits of WHO (2011). In most surface water sampled stations, the concentration of NH_3 was greater than the standard guidelines of WHO. Yet, the extreme concentration of NH_3 was seen in S04, which is an indicator of the existence of possible bacteria, sewage and animal waste pollution. Low concentration of NH_3 was seen in S02, S03, S05, S06, and S07.

X. Sulfate and Phosphate (SO_4^{2-} and PO_4^{3-})

Findings revealed that the concentrations of SO_4^{2-} in all sampled stations are generally below the standard limits of WHO (250 mg/L). However, the lowest mean value of sulfate was recorded at S05 (22.26 ± 6.37 mg/L) and highest concentration at station S09 (222.7 ± 70.3 mg/L). This may be due to various sedimentary rocks (gypsum) and anhydride or human economic activities. The mean concentration of orthophosphate ranges between 0.133 ± 0.03 mg/L in S07 (lowest) and 1.5 ± 0.85 mg/L in S04 (Highest), and PO_4^{3-} is may be due to extensive uses of phosphate based detergents for cleaning purposes, agricultural drainage, industrial waste.

XI. DO, BOD and COD Concentrations in Selected Station

All sampling sites revealed DO below 3 mg/L (ranged from 0 to 2.5 mg/L) which is very stressful to most aquatic organisms and may result in death through suffocations. Above 5 mg/L of DO for most marine plants and animals have enough oxygen to survive [28]. If DO level is below 3 mg/L the water called hypoxic (organisms may die). If all oxygen is used up below 0.5 mg/L like station S04 the water is called anoxic (Organisms die) and station S02 & S03 were obtained less than 2mg/L DO, such type of water exposure to less than 2 mg/L for one to four days may kill most of the biota in a system [29,30]. This idea is supported by Source to Tap and Back project, DO can range between 0-18 mg/L but in most natural water systems 5-6 mg/L to diverse aquatic populations, 9-10 mg/L is a very good for aquatic life generally higher DO reading indicates better water quality. For instance, the concentration of DO in S04 was nil (Figure 4). It might be due to the presence of excess organic matter like dead algae and untreated industrial waste, and the toxicity of the combined effects of chemical and heavy metals [31].

Table 2. The mean and Standard Deviation (M ± SD, n =33) of Physicochemical Water Parameters in 3 sub basins (from Dec. 2016 - Feb 2017)

Physico-chemical Parameters	Sampling sites						
	S01RAH	S02RAT	S03RZB	S04RMD	S05LKD	S06RWB	S07SHS
	M	M ± SD	M ± SD	M ± SD	M ± SD	M ± SD	M ± SD
pH	6.0200 ¹	7.19 ± 0.594 _{a,g}	8.68±0.14 _{b,e,h}	7.54±0.47 _{a,c,d,f,i}	8.42±0.25 _{b,c,e,i}	8.40±0.18 _{b,d,e,i}	7.95± 0.12 _{a,b,i}
EC -µS/cm	77.0000 ¹	731.50± 24.749 _a	740.33±111.10 _a	1769.68±837.74 _b	350.67±33.2 _a	364.0±15.10 _a	2716.67±70.24 _c
TDS - mg/L	50 ¹	482 ±28.28 _{a,e}	488±42.76 _{a,e}	1319±97.68 _b	220±19.08 _a	242±19.08 _a	1735±288.15 _c
Na ⁺ - mg/L	4.6000 ¹	87.50 ±9.19 _{a,b}	93.33±4.73 _{a,b}	338.33±86.22 _{a,c}	30.83±2.75 _b	43.17±10.25 _{b,d}	590.0± 255.15 _c
K ⁺ - mg/L	25.0000 ¹	38.65±3.75 _{a,b}	42.0±6.06 _{a,e,g,h}	59.83±10.89 _{a,c}	14.23±1.66 _b	15.10±2.10 _{b,d}	72.0± 11.14 _c
Ca ²⁺ - mg/L	11.4200 ¹	64.34±6.31 _{a,c}	60.80±20.80 _{a,c}	68.80±13.67 _a	30.13±7.43 _{b,d}	31.73± 2.01 _{b,d}	22.13±6.99 _{b,d}
Mg ²⁺ - mg/L	5.8800 ¹	1.62±0.43 _a	10.24±6.74 _{a,b}	16.80±8.02 _b	8.48±1.47 _{a,b}	7.20±3 _{a,b}	9.76±6.26 _{a,b}
NO ₃ ⁻ -mg/L		52.63±7.45 _{a,c,d,e,f,g,h,i,j,k}	11.90±7.93 _{a,b}	215.13±181.99 _c	1.40±0.56 _{b,d}	2.32±1.08 _{b,f}	.62±0.04 _{b,e}
Cl ⁻ - mg/L	10.6900 ¹	43.36±6.0 _{a,d,e,f}	66.53±17.6 _{a,d,e,f}	238.24±97.52 _{b,g}	20.67±3.36 _{a,c}	17.47±1.30 _{c,e}	154.2±10.61 _{b,d,h,i,j}
SO ₄ ²⁻ -mg/L	42.7600 ¹	30.31±8.05 _a	33.59±9.62 _a	106.97±50.22 _{a,b}	22.26±6.37 _a	25.45±7.74 _a	153.60±22.17 _{b,c,d,e,f}
HCO ₃ ⁻ - mg/L	41.4800 ¹	343.03±34.18 _{a,c,d,f,g}	228.64±27.28 _{a,b}	597.78±215.19 _c	172.62±64.0 _{b,d}	99.32±34.87 _{b,f}	1341.37±42.83 _e
CO ₃ ²⁻ - mg/L	.0000 ¹	5.60±7.92 _a	45.87±23.18 _a	0.0± 0.0 _a	31.33±19.68 _a	32.57±22.25 _a	0.0±0.0 _a
F ⁻ - mg/L	-----	1.56±0.48 _a	1.75±1.08 _a	1.31±0.04 _a	1.52±0.39 _a	2.97 ± 2.67 _a	15.75±13.94 _a
Alka. - mg/L	34.0000 ¹	225.68±50.46 _{a,d,e,f}	263.86±54.07 _{a,b}	489.99±176.39 _b	140.81±9.60 _a	152.94±11.61 _a	1099.49±35.11 _c
TH - mg/L	53.04 ¹	167.50±17.68 _{a,b,h,i}	194.67±47.38 _{a,b}	242.0± 69.66 _a	110.67±24.68 _{b,f}	109.33± 12.86 _{b,d,f}	96.0±38.57 _{b,c,f}
Turb. - mg/L	3700 ¹	211 _a ± 124	104 _a ±55	42 _a ±13	334 _a ± 326	127 _a ± 41	1 _a ± 1
TS - mg/L	3752 ¹	623 _{a,c,d,f,g} ± 191	595 _{a,b} ±74	1363 _{c,e,i,j,k} ± 89	644 _{b,d} ± 563	371 _{b,f} ± 41	1737 _{e,h} ± 289
NO ₂ ⁻ - mg/L	.0040 ¹	.083 _{a,c,d,e,f,g,h,i,j,k} ± .011	.0727 _{a,b} ±.0509	4.8923 _c ± 4.5977	.0367 _{b,d} ±.0396	.0167 _{b,f} ± .0121	.0100 _{b,e} ± .0017
PO ₄ ³⁻ - mg/L	-----	2.4550 _a ±.5445	1.2067 _a ±.9667	1.5 _a ±.85	.1833 _a ± .1168	.9867 _a ± 1.3800	.1333 _a ±.0306
NH ₃ - mg/L	1.4200 ¹	.3100 _a ±.1414	.6067 _a ±.2237	20.04 _a ±19.04	.5133 _a ±.2627	.8367 _a ±.2875	.2733 _a ±.0208
Physico- chemical Parameters	Sampling sites						
	S08RBB	S09LBC	S10RAB	S11RWS	S12RMS		
	M ± SD	M ± SD	M ± SD	M ± SD	M ± SD	M ± SD	
pH	7.17±0.05 _a	9.39±0.15 _c	8.57± 0.08 _{b,e,j}	8.47±0.10 _{b,e,f,j}	8.29±0.70 _{g,h,i,j}		
EC - mg/L	439.33±26.87 _a	3373.33± 227.45 _c	1082.0±181.5 _{a,b}	1076.33± 130.57 _{a,b}	1100.67±117.01 _{a,b}		
TDS - mg/L	296±12.17 _{a,e}	2295±179.02 _d	661±136.61 _e	668± 120.45 _{e,f}	693±87.96 _{c,g}		
Na ⁺ - mg/L	47.67±1.76 _{b,e}	906.67±106.93 _f	225.67±54.99 _{a,b}	230.83± 36.43 _{a,b}	233.33±22.55 _{a,b}		
K ⁺ - mg/L	25.27±5.51 _{b,e}	83.67±5.69 _{c,f}	27.20±17.85 _{b,g}	32.67± 4.04 _{b,h}	36.33±3.06 _{a,b}		
Ca ²⁺ - mg/L	38.40±4.23 _{b,c}	5.87±0.92 _d	30.13±2.01 _{b,d}	24.0± 3.20 _{b,d}	21.60±8.35 _{b,d}		
Mg ²⁺ - mg/L	7.52±2.16 _{a,b}	1.28±0.55 _a	6.08±1.39 _{a,b}	7.2000 _{a,b}	8.00±1.54 _{a,b}		
NO ₃ ⁻ - mg/L	1.42±0.74 _{b,g}	1.3±0.63 _{b,h}	1.89± 0.61 _{b,i}	1.99± 1.54 _{b,j}	1.89±1.08 _{b,k}		
Cl ⁻ - mg/L	20.60±2.54 _{c,f}	269.88±54.21 _g	72.2±2.59 _{a,e,f,h}	73.95± 5.13 _{a,e,f,i}	82.01±5.70 _{a,e,f,j}		
SO ₄ ²⁻ - mg/L	26.67±7.69 _a	222.75±70.33 _c	59.99±19.92 _{a,d}	82.05± 11.86 _{a,e}	65.39±25.49 _{a,f}		
HCO ₃ ⁻ - mg/L	235.18±27.43 _{b,g}	1007.14±212.50 _h	368.03±14.91 _{a,c,d,f,g}	356.06±57.7 _{a,c,d,f,g}	346.78±81.12 _{a,c,d,f,g}		
CO ₃ ²⁻ - mg/L	0.0± 0.0 _a	272.21±48.47 _b	59.28±14.65 _a	54.77± 12.11 _a	61.37±12.91 _a		
F ⁻ - mg/L	2.84±2.86 _a	31.03±28.59 _a	3.33±0.24 _a	2.98± 0.67 _a	3.71±0.72 _a		
Alka.- mg/L	192.77±22.48 _{a,d,e,f}	1279.13±109.87 _c	400.46±26.72 _{b,d}	383.13± 49.59 _{b,e}	386.53±45.92 _{b,f}		
TH - mg/L	127.33±15.53 _{b,e,h,i}	20.00±4.00 _f	100.67±10.26 _{b,f,g}	90.00±15.62 _{f,h}	87.33±27.15 _{f,i}		
Tur. -- mg/L	172 _a ± 16	33 _a ± 10	133 _a ± 42	146 _a ± 41	132 _a ± 13		
TS - mg/L	471 _{b,g} ± 8	2332 _h ± 170	797 _{a,d,f,g,i} ± 122	818 _{a,d,f,g,j} ± 118	829 _{a,d,f,g,k} ± 96		
NO ₂ ⁻ - mg/L	.0240 _{b,g} ± .0104	.0247 _{b,h} ± 0.0139	.0260 _{a,i} ± .0060	.0273 _{b,j} ± .0059	.0310 _{b,k} ± .0108		
PO ₄ ³⁻ - mg/L	.2367 _a ±.2994	.6667 _a ±.5740	.2467 _a ±.1115	.2833 _a ±.1656	.3433 _a ±.1474		
NH ₃ - mg/L	1.3667 _a ± 1.2928	1.0100 _a ±.9456	1.3200 _a ± 1.0278	1.8167 _a ± 2.0645	1.5933 _a ± 1.6945		

Note: The analytical results were statistically significant at $p < 0.05$, values represent means of physicochemical parameters describing the water quality in the study area. **Note:** Values with the same letter of superscripts are not significantly different at $p < 0.05$. Cells with no subscript are not included in the test. Tests assume equal variances.

1. This category is not used in comparisons because the sum of case weights is less than two.
2. This category is not used in comparisons because there are no other valid categories to compare.
3. Tests are adjusted for all pairwise comparisons within a row of each innermost sub-table using the Bonferroni correction

Table 3. Pearson Correlations and Significance Test

		pH	EC	TS	TDS	Turb.	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NO ₃ ⁻	NO ₂ ⁻	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	HCO ₃ ⁻	CO ₃ ²⁻	F ⁻	NH ₃	Alk.	TH	
pH	Pearson Corr.	1																				
	Sig. (2-tailed)																					
EC	Pearson Corr.	.405*	1																			
	Sig. (2-tailed)	.019																				
TS	Pearson Corr.	-.066	.585**	1																		
	Sig. (2-tailed)	.714	.000																			
TDS	Pearson Corr.	.360*	.972**	.609**	1																	
	Sig. (2-tailed)	.039	.000	.000																		
Turb.	Pearson Corr.	-.455**	-.305	.569**	-.305	1																
	Sig. (2-tailed)	.008	.084	.001	.084																	
Na ⁺	Pearson Corr.	.426*	.946**	.627**	.972**	-.256	1															
	Sig. (2-tailed)	.014	.000	.000	.000	.151																
K ⁺	Pearson Corr.	.230	.901**	.596**	.911**	-.227	.854**	1														
	Sig. (2-tailed)	.199	.000	.000	.000	.203	.000															
Ca ²⁺	Pearson Corr.	-.336	-.274	-.400*	-.271	-.197	-.404*	-.067	1													
	Sig. (2-tailed)	.056	.123	.021	.127	.272	.020	.709														
Mg ²⁺	Pearson Corr.	-.147	-.005	-.130	-.077	-.079	-.213	.014	.446**	1												
	Sig. (2-tailed)	.415	.977	.471	.670	.663	.234	.939	.009													
NO ₃ ⁻	Pearson Corr.	-.412*	-.022	.117	.143	-.123	-.009	.195	.428*	.273	1											
	Sig. (2-tailed)	.019	.906	.525	.434	.503	.962	.285	.015	.131												
NO ₂ ⁻	Pearson Corr.	-.281	.013	.090	.182	-.082	.046	.154	.319	.180	.911**	1										
	Sig. (2-tailed)	.113	.941	.620	.310	.652	.800	.391	.070	.317	.000											
Cl ⁻	Pearson Corr.	.330	.882**	.543**	.880**	-.261	.816**	.822**	-.051	.141	.225	.298	1									
	Sig. (2-tailed)	.061	.000	.001	.000	.142	.000	.000	.779	.435	.216	.092										
SO ₄ ²⁻	Pearson Corr.	.358*	.914**	.658**	.934**	-.179	.917**	.789**	-.395*	-.136	.043	.151	.845**	1								
	Sig. (2-tailed)	.041	.000	.000	.000	.318	.000	.000	.023	.450	.813	.402	.000									
PO ₄ ³⁻	Pearson Corr.	-.105	.111	.010	.031	-.066	-.031	.221	.618**	.411*	.170	-.095	.277	-.131	1							
	Sig. (2-tailed)	.573	.551	.956	.868	.725	.870	.231	.000	.022	.360	.610	.132	.484								
HCO ₃ ⁻	Pearson Corr.	.209	.919**	.540**	.891**	-.276	.850**	.851**	-.236	.051	-.002	.002	.707**	.787**	.058	1						
	Sig. (2-tailed)	.244	.000	.001	.000	.120	.000	.000	.186	.777	.990	.992	.000	.000	.758							
CO ₃ ²⁻	Pearson Corr.	.687**	.587**	.402*	.594**	-.134	.662**	.477**	-.490**	-.403*	-.204	-.167	.534**	.651**	-.107	.305	1					
	Sig. (2-tailed)	.000	.000	.020	.000	.457	.000	.005	.004	.020	.263	.354	.001	.000	.567	.084						
F ⁻	Pearson Corr.	.316	.662**	.631**	.643**	-.212	.652**	.526**	-.418*	-.197	-.136	-.108	.409*	.630**	-.149	.642**	.526**	1				
	Sig. (2-tailed)	.078	.000	.000	.000	.244	.000	.002	.017	.280	.457	.555	.020	.000	.425	.000	.002					
NH ₃	Pearson Corr.	-.064	.203	.071	.123	-.043	.065	.242	.401*	.655**	.208	-.035	.315	-.011	.815**	.158	-.110	-.058	1			
	Sig. (2-tailed)	.723	.258	.695	.496	.813	.721	.175	.021	.000	.253	.846	.074	.950	.000	.380	.541	.754				
Alk.	Pearson Corr.	.404*	.977**	.581**	.956**	-.294	.945**	.879**	-.371*	-.083	-.073	-.050	.781**	.887**	.000	.942**	.594**	.724**	.100	1		
	Sig. (2-tailed)	.020	.000	.000	.000	.097	.000	.000	.034	.645	.690	.782	.000	.000	.999	.000	.000	.000	.000	.579		
TH	Pearson Corr.	-.319	-.222	-.365*	-.244	-.185	-.396*	-.049	.953**	.696**	.436*	.317	.007	-.363*	.639**	-.172	-.530**	-.402*	.543**	-.326	1	
	Sig. (2-tailed)	.070	.215	.037	.172	.303	.022	.785	.000	.000	.013	.072	.970	.038	.000	.339	.002	.023	.001	.064		
N		33	33	33	33	33	33	33	33	33	32	33	33	33	31	33	33	32	33	33	33	

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

BOD value varies from 3 mg/L (S02) to 63 mg/L (S04). The concentration of BOD obtained in station S04 was high due to the industrial discharge of untreated wastes from textile and garment, tanneries, and slaughter and abattoir houses that contained extra organic load. BOD level; 1 to 2 mg/L can be grouped as a very good water quality, 3 to 5 mg/L grouped fair or moderately clean water type like station S02, 6 to 9 mg/L grouped as poor water or somewhat polluted and usually indicates the presence of organic matter and bacteria are decomposing, and 100 and greater than 100 mg/L the water quality of the river become very poor and contains organic wastes [29].

Table 4. Water Quality Criteria for Domestic Water Supply as per WHO standards

Category	Parameters	Unit	WHO Guidelines 4 th edition 2011
Physical	Partial Physical		
	EC at 25 °C	mg/L	1500
	TDS	mg/L	1000
	TS	mg/L	1000
Chemical	Turbidity	NTU	5
	Partial Chemical		
	pH	----	6.5 - 8.5
	Sodium, Na ⁺	mg/L	200
	Potassium, k ⁺	mg/L	12
	Total Hardness, TH	mg/L	300
	Magnesium, Mg ⁺²	mg/L	150
	Calcium, Ca ⁺²	mg/L	75
	Chloride, Cl ⁻	mg/L	250
	Fluoride, F ⁻	mg/L	1.5
	Sulfate, SO ₄ ²⁻	mg/L	250
	Phosphate, PO ₄ ³⁻	mg/L	5
	Nitrate, NO ₃ ⁻	mg/L	50
	Nitrite, NO ₂ ⁻	mg/L	3
	Alkalinity	mg/L	100
	Bicarbonate, HCO ₃ ⁻	mg/L	-----
	Carbonate, CO ₃ ²⁻	mg/L	-----
	Iron, Fe ^{tot}	mg/L	0.3
	Chromium, Cr ^{+3/+6}	mg/L	0.05
	Zinc, Zn ⁺²	mg/L	0.01
Manganese, Mn ^{dis}	mg/L	0.1	
Copper, Cu ⁺²	mg/L	2.0	
Boron, B	mg/L	1.0	
Ammonia, NH ₃	mg/L	0.2	
Organic & Oxygen Demand	Organic & Oxygen Demand		
	Dissolved Oxygen, DO	mg/L	WHO, 2008 > 5
	Biological Oxygen Demand, BOD	mg/L	2 - 5
	Chemical Oxygen Demand, COD	mg/L	10

As seen in Figure 4, COD values in the study ranged minimum in S03 (60 mg/L) and maximum in S04 (200 mg/L). All sample sites showed high COD level than the WHO limit. Water with high COD value in station S04 indicates that there is inadequate oxygen available in the water samples. High COD level also impacting toxic state and the presence of biologically resistant organic substances [32]. As seen in Table 2, a high concentration of NO₃⁻ (251.1 mg/L) and PO₄³⁻ (3.72 mg/L) were seen in station S04, correspondingly in the same station with a

high concentration of BOD 63 mg/L and 200 mg/L COD were recorded (Figure 4).

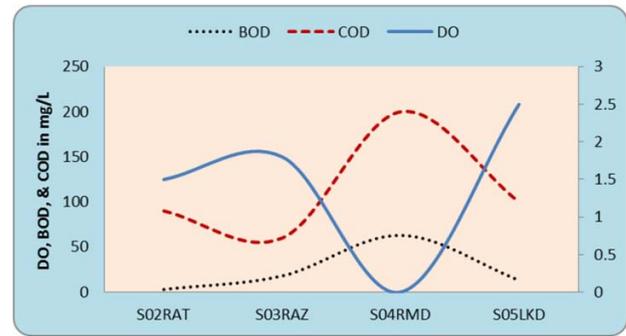


Figure 4. Level of DO, BOD, & COD in Selected Sample sites of Upstream Koka

Increased levels of nitrogen in the water, combined with phosphorus, can cause excessive algal growth that depletes oxygen levels, possibly to lethal levels. Some algal blooms produce toxins that can affect aquatic life or the humans that consume them [33]. These parameters might be contributed for escalating of BOD and also lowers DO concentration because NO₃⁻ and PO₄³⁻ behave as fertilizers and helps for the growth of algae in water bodies [30].

XII. Heavy Metals Concentration

In this study, the value of iron ranged maximum 0.78±0.07 mg/L in S01 to minimum 0.10±0.07 mg/L in S09. According to the guidelines of WHO 1984, for drinking water quality, guidelines published in 1984, a guideline value of iron 0.3 mg/L was established [34]. As per WHO guidelines for domestic water, iron should not exceed the limits of 0.3 mg/L. As shown in Figure 6 four sample sites showed high concentrations of iron 0.35 mg/L.

In Figure 5, Hexavalent chromium (Cr⁺⁶) ranges from 0.14 ± 0.07 mg/L to 0 mg/L. It exceeded the standards of WHO in station S04 & S11 with 0.6 mg/L and 0.14 mg/L, respectively. However, Cr⁺⁶ is hazardous and the most toxic form of Cr and having equivalent toxicity with that of cyanide can cause skin ulcer, convulsions, kidney, and liver damage. Intensive exposure may lead to lung cancer [34]. Recent studies even showed that death of livestock resulting from watering in chromium-contaminated water has been reported from time to time [25].

The highest manganese concentrations were reported at S03 (0.16 ± 0.04 mg/L) and the lowest at station S09 (0.01 ± 0.0 mg/L). Six sampling sites showed below the standards of WHO guidelines. Whereas the rest 6 sampled sites were above the limits of WHO (0.1mg/L). When the concentration of Mn is higher than 0.05 mg/L and high exposure to it has been associated with toxicity to the nervous systems [27].

The highest value of Zinc was seen in station S12 that is 0.38 ± 0.04 mg/L while the lowest value was recorded almost nil. When the concentrations of Zn is above the limits of WHO or/and elevated intake which can cause muscular pain and intestinal hemorrhage [35,36]. The highest concentration of copper was seen in station S02RAT (0.11 mg/L) and lowest concentration was seen trifling/zero, yet, all sampling points showed below the prescribed limit of WHO.

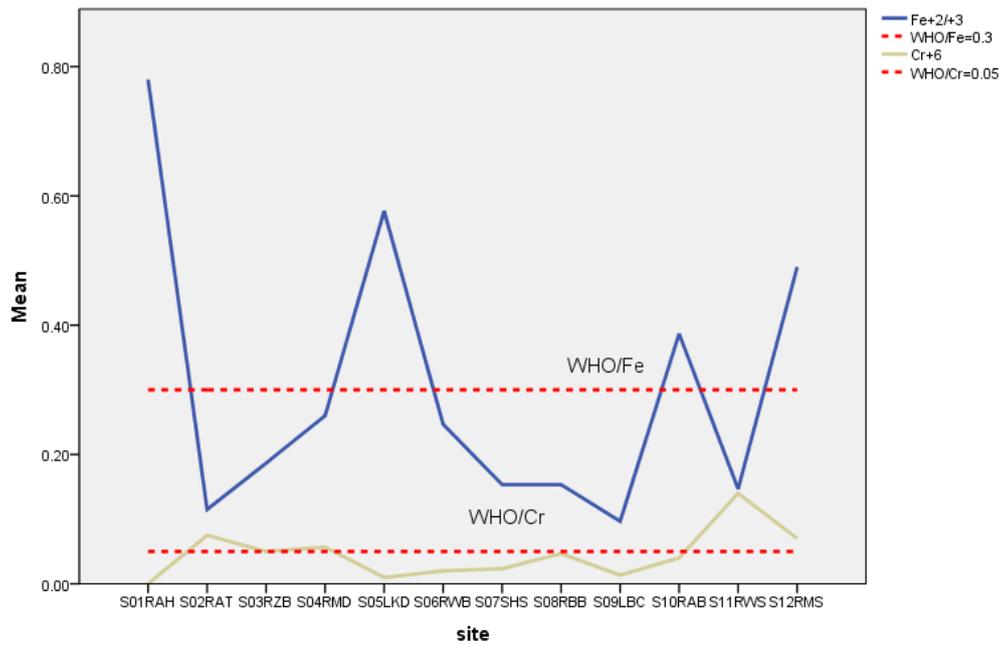


Figure 5. Comparison concentrations of Cr and Fe (in mg/L) with WHO Standards

3.2. The Surface Water Quality Analysis for Irrigation Use

The most common parameters used to determine the irrigation water quality of River Awash are TDS, EC, SAR, RSC, B, Na %, HCO₃⁻, Cl⁻, and NO₃⁻ based on the standard guidelines of FAO and other considerations.

I. EC & TDS (Salinity)

EC is recorded maximum 3,700 μS/cm and a minimum 77 μS/cm. six sampling stations showed lower than 750 μS/cm EC values and categorized as good water with low salinity effects, 3 sampling stations revealed EC value between 750 μS/cm into 1, 500 μS/cm grouped under fair water with medium salinity effect. 2 sample stations were a band together under slightly poor water type with high salinity effect, and one sampled station: S09 showed very poor water type with high salinity effect (3,373±227.5 μS/cm) and which is strictly non-recommendable to use for irrigation water due to its high salinity [37,38]. The soil salinity increase in direct proportion to the salinity of the irrigation water [39]. TDS less than 500 mg/L in irrigation water considered as low salinity hazard was observed in S01, S02, S03, S05, S06, and S08; 500 to 1,000 mg/L medium salinity hazard was seen in S10, S11, and S12; 1,000 to 2,000 mg/L, high salinity hazard was recorded in S04, and S07 and greater than 2,000 mg/L very high salinity hazard was seen in station S09 (2,295±179 mg/L).

II. SAR and % Na (Sodicity)

The estimated sodium hazard of SAR was calculated using equation 1, its high value was recorded in S09 (479.36 mg/L), while a low value of sodium hazard was seen in station S02 (15.24 mg/L). However, due to its unusual amount of sodium in saline LB, the downstream water quality becomes degraded (S10, S11, and S12). Irrigation water has high SAR levels can lead to building up of high soil Na levels over time which intern can adversely affect soil infiltration and percolation rates. In addition excessive SAR level can lead to soil crusting, poor seedling emergence, and poor aeration [40].

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+}) / 2}} \quad (1)$$

LB was saline and too poor water (SAR > 26) to use for irrigation purpose. Six sample stations showed high sodium percentage greater than 70 % and generally unsuitable for irrigation, and five sample sites revealed SAR value greater than 9 grouped under high salinity [38]. Sever problems are likely, if the irrigation water has low salinity and high sodicity (high SAR) [5,41]. The amount of sodium in irrigation water at station S09 was extremely high (197 mg/L or 39.39 meq/L) which is greater than FAOs consideration, followed station S07 (590 mg/L or 25.65 meq/L) both affect and degrade soil structure and also constraining water movement, lastly it affects the proper growth and development of plant. A high percentage of sodium on irrigation water may stunt the plant growth, deflocculating, and reduce the soil permeability [24,42].

$$\% Na = \frac{Na^+}{Na^+ + k^+ + Ca^{2+} + Mg^{2+}} * 100 \quad (2)$$

III. RSC and Bicarbonates

In this study, the RSC values varied the lowest in station S01 while the highest value observed in station S09. In most stations, such as S04, S07, S09, S10, S11, and S12; 4.99, 20.1, 25.2, 6.01, 5.89, and 6.0 meq/L values were recorded respectively. RSC value greater than 2.5 meq/L the water is grouped as unsuitable for irrigation water, between 1.5 and 2.5 meq/L the water is grouped as under marginal suitable for irrigation such as station S02, S03, S05 and S08 exhibit 2.28, 1.41, 1.65, and 1.32 meq/L respectively, and station S01 and S06 exhibited -0.37 (is not negative concentration, rather a high concentration of Ca & Mg) and 0.54 meq/L respectively showed less than 1.5 meq/L is grouped as safe for irrigation purposes [43,44].

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (3)$$

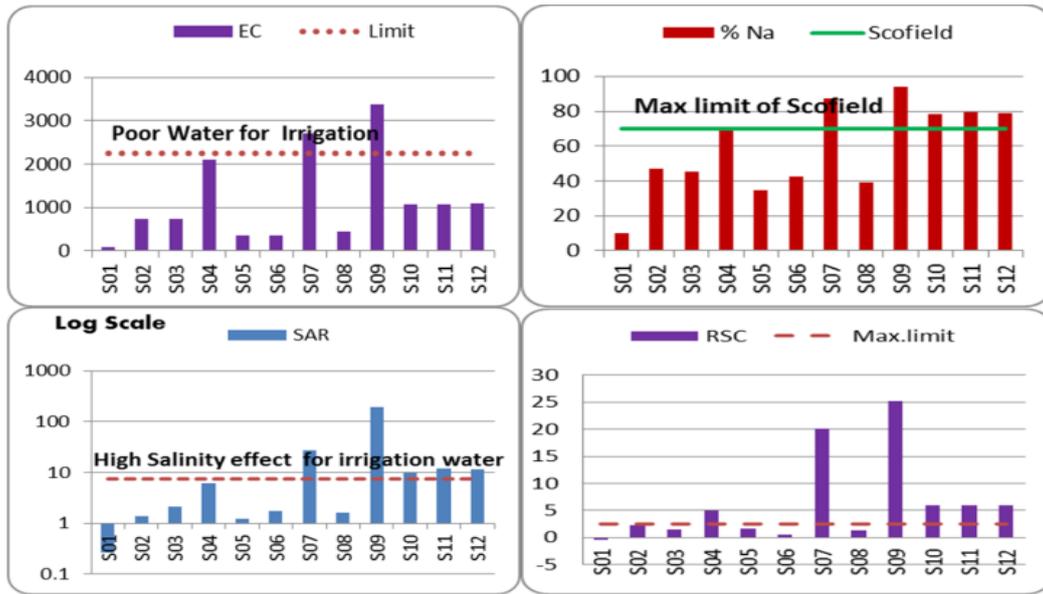


Figure 6. Some Important Irrigation Water Parameter (N.B: The unit of EC, RSC, SAR and % Na are in $\mu\text{S}/\text{cm}$, meq/L and unitless respectively.)

Table 5. Mean value of some elements (ions) to determine degree of specific toxicity

Parameter	S02RAT	S03RZR	S04RMD	S05LD	S06RWB	S07SHS	S08RBB	S09LBC	S10RAB	S11RWS	S12RMS
Na^+ SAR	1.40	2.09	6.13	1.22	1.73	27.1	1.63	197	9.81	11.8	11.7
Cl^- meq/L	1.22	1.88	6.71	0.58	0.49	4.34	0.58	7.61	2.04	2.08	2.31
B mg/L	0.15	0.20	1.70	0.01	0.05	2.30	0.05	2.92	0.95	0.85	0.40

N.B:- SAR has unit less

If the concentration of HCO_3^- lied between 180-600 mg/L, the water is grouped as unsuitable because of its sever effect, 100-180 mg/L is grouped as under moderate based on its effect on irrigation and 0-100 mg/L water is grouped as safe water type and has low effect when used for irrigation [45]. Except for two sample sites S01 (41.48 mg/L) and S06 (99.32 mg/L), the remaining ten stations were categorized under unsuitable water group if used for irrigation.

IV. Specific Toxicity of Sodium as SAR, Chloride and Boron

Most studies indicate that the most common known ions which might cause toxicity problems are chloride, sodium and boron ions [46]. Based on toxicity level they are classified into three, namely Sever effect ($> 9 \text{ mg}/\text{L}$), slight to moderate effect (3 to 9 mg/L) and none effect ($< 3 \text{ mg}/\text{L}$). In the study, it is observed that Na^+ as SAR was recorded 197 (high), 9.81, 11.8, and 11.7 and has seen (Table 5) its effect in station S09, S10, S11, and S12 respectively.

Chloride in irrigation water in all sampled stations obtained has no severe effect in soil salinity. However in some stations like S09, the highest value of chloride was recorded (7.61 meq/L), followed station S04 (6.71 meq/L), and station S07 (4.34 meq/L) were seen from slight to moderate effect in toxicity content of chloride [46]. Excessive chloride leads to salinity, which deteriorates the soil salinity [47]. Boron has been identified as a danger to crops when present in irrigation water at 1-2 mg/L concentration range [48]. The highest concentrations of B was obtained from S09 (2.92 mg/L) which is indicative of the potential toxicity while the lowest concentrations were seen in S05 is 0.01 mg/L. In 5 sampled stations; S04, S07, S09, S10, and S11 were recorded at 0.7 to 3.0 mg/L.

V. Nitrates (NO_3^- -N)

In this study, the value of nitrate varied between 0.01 to 3.47 meq/L in station S07 and S04 respectively. When the concentration of NO_3^- -N below 5 meq/L in the irrigation water it has no effect, 5 to 30 meq/L of NO_3^- -N has slight to moderate effect and above 30 meq/L in irrigation water has severed effect [48,49]. Nonetheless, all sampled stations showed below the prescribed limit of WHO. Excess application of fertilizers in soil cause a negative impact in crop production similarly the presence of excess NO_3^- -N in the irrigation water behaves as fertilizers.

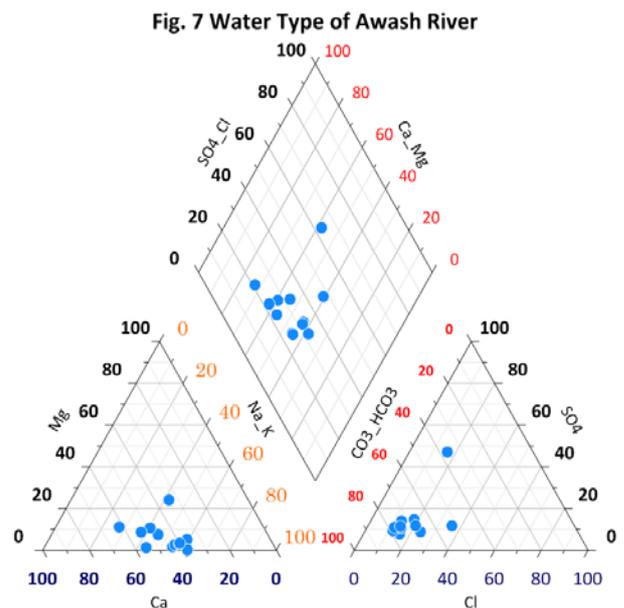


Figure 7. Chemical Composition of Major Anions and major Cations (All units are in mg/L).

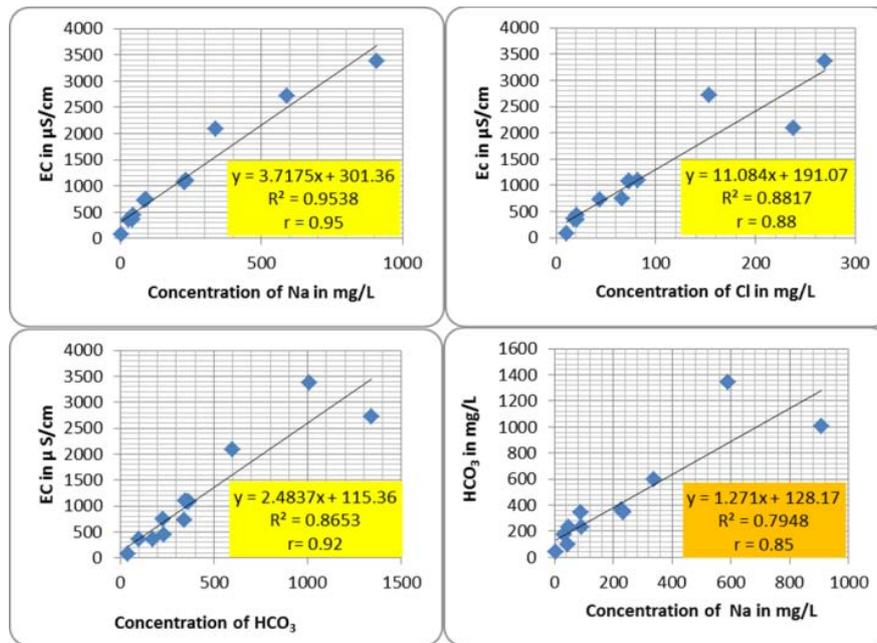


Figure 8. The Regression and Pearson Correlation Coefficient of different sets of data

The findings show that the water type of AR in the study area is dominated by Na^+ and HCO_3^- except station S01 and S05. The potential source of this major cation (Na^+) and anion (HCO_3^-) variation in each station was due to different origins. This piper diagram is plotted using Grapher-14 software. It is very useful software to identify the characteristics and water type of the river. Piper diagram divided water into four basic types according to their placement near to the four corners.

The ternary plot of anions lay near to the left corner and rich in HCO_3^- & CO_3^{2-} while cations lay at base side between 40 to 60% of Ca^{2+} and $\text{Na}^+ + \text{K}^+$. However, few samples from hot spring, LB and Modjo River lay somewhat far towards to the no dominant type area. Thus, it indicates AR is also rich in Na^+ , Ca^{2+} , & HCO_3^- ions. As seen in the Figure 7 the relative percentage of most samples (cations and anion) are situated at the left corner of a diamond.

In this finding of HCO_3^- and EC, the study obtained $r = 0.919$ and $p < 0.001$. There is a great of linear correlation which is significant as the p value is smaller than 0.01. In the same way the correlation coefficients (r) are determined for selected pairs of major ions (Na^+ , Cl^- , & HCO_3^-) and EC between two sets of data. For instance, Figure 8 shows a correlation value of Na^+ Vs EC, Cl^- Vs EC, and Na^+ Vs HCO_3^- having 0.946, 0.882 and 0.850 respectively. Increasing the concentrations of sodium, chloride and bicarbonate ion corresponds with an increase in EC and has a high positive correlation between each of parameters and associated with a significant test value as $p < 0.01$ or 99% of confidence limit.

4. General Discussions

For the degradation of surface water quality of AR, the upstream Koka sub-basin is the first and major contributor for the deterioration of the river water because of the existence of a great number of industries, the rapid expansion of urbanizations, and agricultural farming. Thus,

out of five sampled stations in upstream Koka sub basin; station S04 is the one that carries an excess amount of pollutants load than other stations. For instance, high concentrations of EC (2093 $\mu\text{S}/\text{cm}$), TDS (1319 mg/L), Na^+ (338 mg/L), K^+ (60 mg/L), Ca^{2+} (68.8 mg/L), Mg^{2+} (16.8 mg/L), NO_3^- (215 mg/L), NO_2^- (4.89 mg/L), Cl^- (238 mg/L), HCO_3^- (598 mg/L), SO_4^{2-} (107 mg/L), PO_4^{3-} (372 mg/L), NH_3 (14.5 mg/L), DO (nil), BOD (63 mg/L), COD (200 mg/L), and other parameters. In all upstream study sites (S03 & S04), the levels of DO, NO_3^- , NH_3 , NO_2^- , are above the prescribed limits of WHO due to aforementioned and other unspecified reasons.

The second contaminant is saline LB. Its effect was seen at station nearer to LB (S10), EC is 2.5 times higher than non-Beseka mixed sampled station (S08). The mixed Beseka's water changes the concentration of AR in station S10; the hydro-chemical composition of sampled station shockingly changed. For instance; TDS (2 times), Na^+ (4.5 times), Cl^- (2.5 times), alkalinity (2 times), sulfate (2 times), bicarbonate (1.5 times), K^+ , and others showed much to increase their concentration. Station S10, S11, and S12 showed increasing trend and the elevated concentrations of SAR, EC, %Na, Cl^- , NO_3^- , NH_3 , HCO_3^- , and etc are indicative parameters of the river and which alarms to get rapid and urgent solutions to improve the existing surface water quality deterioration of AR. Based on these, it is possible to predict the effect of the quality of water in human health, livestock watering, soil salinity, and the whole aquatic life.

5. Conclusion

The study revealed that the pollution status of AR is highly related to the deterioration of its physicochemical, toxic metals and organic nutrients. Even though the source of deterioration can be both natural and anthropogenic activities, the measured mean water quality parameters were seen high in station S02, S04, S07, and S09. The degradation effect of station S02 and S07 after joined the

main river were not seen as a significant difference when compared with the upstream and downstream stations. But, station S04 and S09 of the most physicochemical analyzed parameters were at the level of pollution and significantly degraded the downstream water stations. Thus, water that joined from these stations into main river alarms to take the possible implementable solution to keep safe the surface water quality of AR.

Some parameters were at the level of pollution (exceeding natural values). For instance, EC in station S04, S07, and S09; pH in S03, S09 and S10; Na⁺ in S04, S07, S09, S10, S11, and S12; TH in site S02, S03, S04, S06, and S08; nitrate in site S02 and S04; nitrite in station S04; chloride in S04 and S09; alkalinity in S07, S09, S10, S11 and S12; the concentration of HCO₃⁻, SO₄²⁻, and PO₄³⁻ in station S04, S07, and S09 were recorded high and exceed the standard guideline limit of WHO and FAO. Some irrigation water quality parameters EC, %Na, SAR, RSC, HCO₃⁻, pH, and Cl⁻ showed their concentrations progressively increase from station S10 to S12 and which is an indicative result for the presence of excess amount pollutants in main river before brought the adverse effect on plant growth, soil salinity and permeability problems.

The ANOVA test also showed that there are significant difference among the 12 different sampling sites, which might be due to high level of untreated wastewater and sewage discharge, agriculture runoff, inadequate removal of nutrients, chlorides, sulfates, chromes, and the presence of excess organic matter in the wastewater discharge, and unregulated ratio of LB largely affect the balance of the chemical composition of the surface water quality and also degrades the primary receiver of the AR. In order to reduce contaminants from the waste of industries and domestic dump and also to ensure better surface water quality in the Awash basin corrective actions are highly needed to solve the current problem that faced AR for development and sustainable tomorrow. Generally, in order to improve the existing water quality problem and also to ensure acceptable protection for the surface water quality deterioration of AR; immediate corrective actions are required from Government and other concerned bodies to set and develop discharge fee and enforcement law, industries to release properly treated wastewater for better surface water quality and livelihood. Thus the study alarms to take possible and urgent solution in expansion as well as unregulated mixing ratio method of LB.

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