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Open Access Journal of Waste Management & Xenobiotics
ISSN: 2640-2718

Assessing the Chemical Composition of Wastewater Released from Hawassa Castel Brewery Plant and its Impact on Groundwater

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Research Article
Volume 4 Issue 2
Received Date: April 23, 2021
Published Date: June 25, 2021
DOI: 10.23880/oajwx-16000164

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Abstract

Brewery plants have been known to cause pollution if they have no proper environmental safety systems by discharging effluent into the receiving stream, ground water and soil. The study aims to assess the physicochemical composition of wastewater generated from Hawassa Castel brewery plant and its impact on the surrounding environment particularly on the quality of ground-water. Thus, the study was conducted on samples taken from effluents of Hawassa Castel brewery plant and ground water from the nearby areas. Physicochemical parameters such as pH, temperature, DO, BOD, COD, TDS, TSS, EC, turbidity, nitrate, phosphate, sulphate, NH3-N, chloride, TN and TP were analyzed both for effluent samples and groundwater samples. Brewery effluent samples were collected from three sampling stations S1 (brewery effluent discharge point), S2 (50 m from brewery effluent discharge point downstream), and S3 (100 m from brewery effluent discharge point downstream) and four groundwater samples namely G1, G2, G3, G4 were also collected from near Hawassa Castel brewery plant. Groundwater samples G1 and G2 were collected approximately 30 m away from effluent discharge point and groundwater samples G3 and G4 were collected 100 m away from the stream. The parameters monitored for the quantitative analysis of brewery wastewater and ground water. The values of BOD (70.9 ± 7.69 mg/L), COD (178.5 ± 42.8 mg/L), TDS (135.5 ± 34.3 mg/L), turbidity (7.44 ± 0.77 NTU), and phosphate (9.08 ± 4.6 mg/L) were found to be above the permissible industrial effluents discharge limits. Moreover, the presence of high levels of TDS (462.8 ± 216.8 mg/L), TSS (143.7 ± 62.7 mg/L), EC (2370.9 ± 595 µS/cm), nitrate (43.5 ± 21.3 mg/L), phosphate (0.61 ± 0.13 mg/L), and chloride (931.9 ± 42.7 mg/L) in the ground-water samples were immensely polluted by anthropogenic activities and making it unsuitable for drinking purpose. Thus, the concerned bodies should act to prevent further deterioration of the quality of groundwater.

Keywords: Castel Brewery Plant; Brewery Process; Brewery Effluent; Physicochemical Parameters

Introduction

The beverage industries are becoming an economic source in the world [1,2]. These industries use large quantities of water and generate enormous amounts of wastewater [3,4]. In Ethiopia, 90% of the industries are releasing their effluents into water bodies, streams, and land without any treatment mechanisms [5]. Moreover, most of the effluent discharged by industries including breweries in Ethiopia does not meet the national discharge standards as many of them release their effluent with little or no prior treatment [6]. The wastewater generated from breweries typically have a high biochemical oxygen demand (BOD) from all the organic components (sugars, soluble starch, ethanol, volatile fatty acids, etc.,) with a temperature ranging from 25°C to 38 ˚C and a pH value ranging from 2 to 12, which is mainly influenced by the amount and type of chemicals used in cleaning and sanitation [7]. Brewery plants have been known to cause pollution by discharging effluent into receiving streams, groundwater, and soil. In general, water consumption for breweries ranges from 4 to 8 cubic meters per cubic meter of beer produced and generates 3to10 liter of wastewater per liter of beer produced. So the discharging of brewery effluents into the environment causes pollution to the nearby receiving streams, groundwater, and soil. Thus the wastewater released from the beverages industries becomes a serious threat to the surrounding environment if it is not properly treated before discharge [1,8]. Therefore, the treatment and safe disposal of brewery wastewater have become important aspects of brewery operations to meet strict discharge regulations set by government entities [9]. However, the continuous discharge of effluents into swamps, streams, and rivers without any adequate treatment raise the level of trace and toxic metals, nitrogen and phosphorous which have considerable adverse effects on freshwater bodies, aquatic biota and human health [10,11]. Due to recent environmental pollution problems that have emerged, monitoring and controlling of quality of liquid effluents being discharged into natural water bodies or municipal treatment plants, especially by the industry has become an important aspect of the environmental research area [12,13]. Thus, this study involves the characterization of Hawassa Castel brewery wastewater and its impact on the surrounding environment particularly on the quality of groundwater.

Brasseries et Glaciers Internationals (BGI) brewery processing plant is one of the leading beer producing company in Ethiopia. In particular, Castel Hawassa Brewery has started its operation in 2012. Castel Hawassa Brewery has contributed a lot to the socio-economic development of Hawassa city despite it generates approximately 936 million liters of wastewater annually. It is situated near the swampy area occupying an area of 70,000 square meters in the industrial zone of Hawassa city according to BGI Ethiopia website. It consumes approximately 8.64 million cubic meters of water per 144 million liters of beer produced annually. The wastewater generated from the brewery processing plant is treated at the onsite effluent treatment facilities and the treated brewery wastewater is discharged through a pipe into a swampy area that is designated as a buffering zone. Thus, the wastewater must be treated to meet national and international effluent discharge limits. A preliminary survey or field observation shows that this brewery plant releases the effluent through a pipe into the nearby river or streams that are used for irrigation purposes. This river also eventually enters into Hawassa Lake. Thus, the study aims to assess the physicochemical composition of wastewater generated from Castel Hawassa brewery plant, one of the many industries located near the swampy area, and its potential impact on the nearby environment.

Materials and Methods

Description of the Study Area

The study was conducted in Hawassa city located 275 km south of Addis Ababa. The city is serving as the capital city of the Southern Nations Nationality and People Region (SNNPR). It is located at 7.0504° N latitude and 38.4955°E longitudes with an elevation of 1697 meter above sea level and its annual rainfall average is 969 mm [14].

One of the dominant surface water bodies in the city is Hawassa Lake and Tikur Wuha River that relates to Cheleleka Wetland where different rivers are drain into it and some of them are perennial streams. Recently, the number of industries is increasing rapidly in Hawassa city due to the completion of Hawassa Industrial Park (HIP) in addition to Hawassa Castel brewery plant that was inaugurated on June 7, 2011. This plant is in Chief-kotijebesa kebele, in Tula sub-city, the southeast part of the Hawassa city industry zone. A preliminary survey of the area has shown that effluents from to Hawassa Castel brewery plant has been discharged into open area at the edge of the shallow swamp and move through the surrounding farmland and reaches into streams and eventually enter a Cheleleka Wetland, which is the source of TikurWuha River that ends up in Lake Hawassa as shown in Figure 1. Thus, the study aims to analyze the effluent quality of Castel Hawassa brewery plant and its impact on the surrounding groundwater.

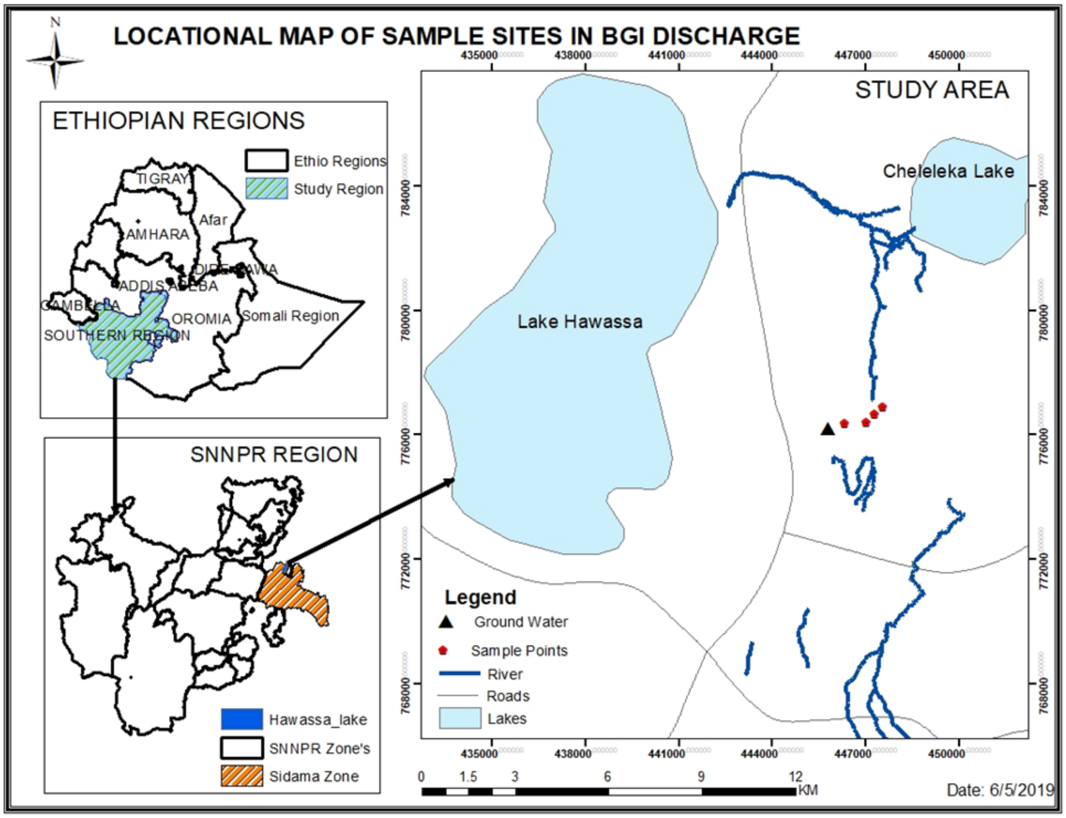

Figure 1: Location map of sample sites.

Sample Collection, Preparation, and Analysis

- **Effluent sample collection**

The field survey was conducted for identification of sampling stations (purposive sampling).Wastewater samples were collected in stopper fitted polyethylene bottles which were prewashed with dilute hydrochloric acid and then rinsed several times with the effluent samples before filling to the required capacity. Three sampling stations S_1 (brewery effluent discharge point), S_2 (50 m from brewery effluent discharge point downstream), and S_3 (100 m from brewery effluent discharge point downstream) were collected in duplicate using universal sample bottle (sterile) of 500 mL capacities. The collected wastewater samples were stored at a temperature below 4 in an ice box containing ice freezer packs before laboratory analysis. The collected wastewater samples were filtered using glass fiber filter paper before analysis for, NH_3-N and NO_3^- whereas analysis of TSS, COD, TP, and TN was done from unfiltered samples. The physicochemical parameters analyzed were pH, temperature, DO, BOD, COD, TDS, TSS, EC, turbidity, NO_3^-, PO_4^{-3}, SO_4^{-2}, NH_3-N, TN, TP, and Cl^-.

- **Groundwater Sample Collection**

Four groundwater samples were collected from near Castel Hawassa brewery plant. Groundwater samples G_1 and G_2 were collected approximately 30 m away from effluent discharge point and groundwater samples G_3 and G_4 were collected 100 m away from the stream. All samples were collected in duplicate using a universal sample bottle (sterile) of 500 mL capacities. The collected water samples were filtered using glass fiber filter paper before analysis for NO_3^- whereas analysis of TSS, and COD was done from unfiltered samples. The physicochemical parameters analyzed were pH, temperature, DO, BOD, COD, TDS, TSS, EC, turbidity, NO_3^-, PO_4^{-3}, SO_4^{-2}, NH_3-N, TH, TA, Cl^-, and F^-. All wastewater samples and groundwater samples were analyzed within one week of collection and the physicochemical parameters were determined using standard methods for the examination of wastewater [15]. The method or instruments used to measure the physicochemical parameters were summarized in Table 1.

Parameter	Instrument/Methods
pH	Digital pH-meter (Beckman pH 211, Microprocessor, USA)
Temperature	Portable calibrated mercury thermometer (Model 3012, UK)
DO	Winker's Titration
BOD	BOD HACH Track instrument (DR/2010 HACH, Loveland, USA)
COD	Titration with 0.25 M Ferrous sulphate
TDS	Conductivity/salinity meter (Hl-8733, Germany)
TSS	Gravimetric method dried at 105 ^{0}C for 24 hrs.
EC	Digital conductivity meter (Hl-8733, Germany
Turbidity	Digital Turbidimetric 2100A
Nitrate, phosphate, sulphate	Spectrophotometer (HACH DR/2010, USA)
NH_3-N	Thermo Gallery photometric analyzer (Thermo Scientific, UK)
TN	Persulphate digestion method using DR3900 model Spectrophotometer (HACH Company, Loveland, CO, USA)
TP	Vanadomolybdphosphoric acid Colorimetric method using DR3900 model Spectrophotometer (HACH Company, Loveland, CO, USA)
Chloride	The titrimetric method with $AgNO_3$
Fluoride	Ion-selective electrode (Jenway 924–305)
TH	The titrimetric method with EDTA, using Eriochrome Black-T (EBT)
TA	The titrimetric method with HCl, using phenolphthalein and methyl orange as Indicators

Table 1: Instruments or methods used for the determination of physicochemical parameters.

Data Analysis

Descriptive statistics and graphical analyses were used to summarize and display the values of the physicochemical parameters both in the affluent and groundwater samples. One-way analyses of variance (ANOVA) tests were used to distinguish whether the differences among effluent sampling stations or groundwater samples were significant. The analysis was performed using IBM SPSS 20 statistical software. Statistical significance was defined by a threshold of $p \leq 0.05$. A multiple comparisons test (Post-Hoc Test) was also carried out to check the mean differences among sampling stations.

Results and Discussion

Assessment of Effluent Discharge Quality

A statistical summary of the physicochemical parameters of Castel Hawassa effluent discharge at three sampling stations (S_1, S_2, and S_3) are shown in Table 2 & Figure 2.

Parameters	Sample Station 1	Sample Station 2	Sample Station 3	Total Average	EEPA (2003)
pH	9.34 ± 0.69	8.45 ± 0.47	8.17 ± 0.52	8.65 ± 0.74	06-Sep
Temp	30.20 ± 1.88	28.40 ± 1.31	27.40 ± 1.8	28.6 ± 2.0	40
DO	4.47 ± 1.35	12.30 ± 1.50	17.6 ± 1.74	11.4 ± 5.74	
BOD	74.40 ± 10.60	72.1 ± 4.34	66.20 ± 5.19	70.9 ± 7.69	60
COD	214.60 ± 10.10	165.20 ± 53.40	155.80 ±29.40	178.50 ± 42.8	125
TDS	173.20 ± 16.30	130.50 ± 11.70	96.80 ± 9.50	133.50 ± 34.30	80
TSS	51.00 ± 10.20	33.6 ± 3.32	24.10 ± 2.10	36.20 ± 12.90	50
EC	721.00 ± 332.90	527.10 ± 53.90	276.30 ± 39.10	508.10 ± 262.70	1000

Turbidity	8.22 ± 0.21	7.57 ± 0.21	6.53 ± 0.43	7.44 ± 0.77	
Nitrate	16.60 ± 2.20	10.20 ± 2.00	4.69 ± 2.60	10.50 ± 5.50	< 10
Phosphate	14.50 ± 3.50	7.44 ± 2.30	5.33 ± 0.70	9.08 ± 4.60	
Sulphat	330.80 ± 23.10	258.70 ± 17.00	195.70 ± 21.60	261.80 ± 60.00	200
NH_3-N	18.60 ± 3.60	9.47 ± 1.20	6.53 ± 0.61	11.50 ± 5.60	20
Chloride	638.10 ± 8.50	591.70 ± 14.50	557.80 ± 7.20	595.90 ± 35.30	
TN	19.00 ± 1.10	9.14 ± 0.90	3.17 ± 0.12	10.40 ± 6.80	10
TP	18.10 ± 1.10	12.90 ± 0.43	9.55 ± 1.30	13.50 ± 3.70	5

Table 2: Results of wastewater quality parameters (Mean ± SD, n=6) for the sampling stations. All units except pH (pH scale), temperature (°C), turbidity (NTU), and EC (**µS**/cm) are.

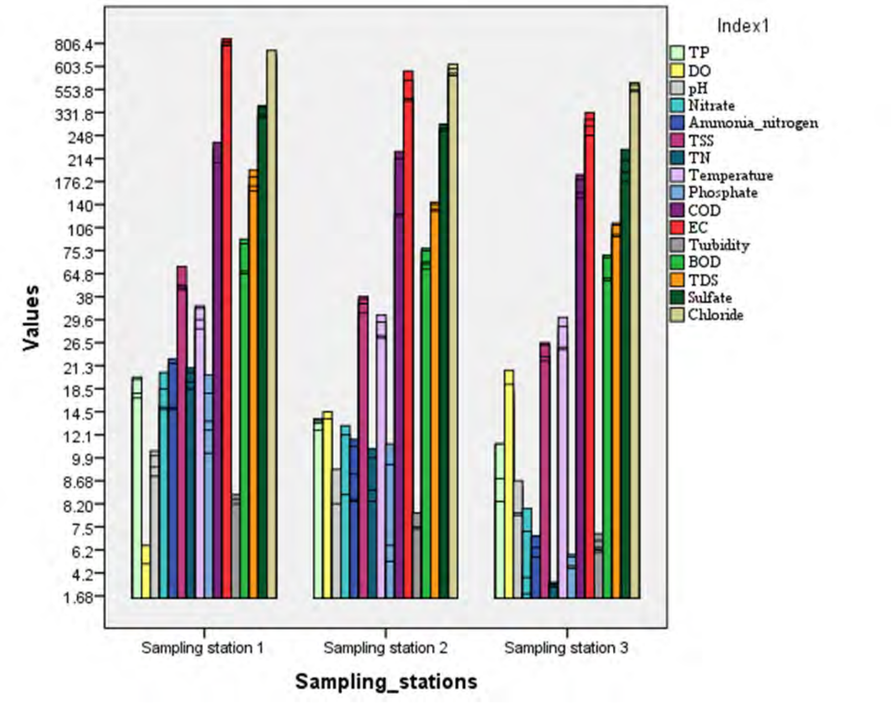

Figure 2: Values of wastewater quality parameters in the sampling stations and all units except pH (pH scale), temperature (°C), turbidity (NTU), and EC (**µS**/cm) are.

Physicochemical Parameters

- **pH**

The mean value of pH ranged from 8.17 to 9.34. It was observed from the result obtained that there was a statistically significant difference (F [2,15] = 6.91, p = 0.07, ANOVA) in the values of pH among sampling stations. The mean value of pH at the discharge point (S_1) was above the Ethiopian effluent allowable discharge limits into water-courses [6] and higher than the reported value from previous studies [16].

- **Temperature**

The mean value of temperature ranged from 27.4–30.3°C with the highest value measured at sampling station one and this was within the natural brewery wastewater temperature range (25°C to 38°C) and possibly rising even higher [17]. Statistical analysis using ANOVA indicated that the mean difference was significant ((F (2,15) = 4.516, p = 0.029, ANOVA) among sampling stations.

- **Dissolved oxygen (DO)**

The results of this study showed that the mean value of DO was in the range of 4.47 to 17.6 mg/L with the lowest value measured at the discharge point (sampling station one) and was below the ranges of maximum allowable concentration ranges (5.00 to 9.00 and 5.00 to 9.50) for fisheries and aquatic life [18,19]. The low level of DO at the discharge point could be due to high levels of organic pollutants in brewery wastewater and their decomposition contributed to the low levels of dissolved oxygen in the effluent [20].

- **Biochemical Oxygen Demand (BOD5)**

The mean value of BOD5 ranged from 66.2–74.4 mg/L with the highest value measured at sampling station one. BOD5 values at all sampling stations were higher than the limit of [6] standards. The values of BOD5 also showed a progressive decrease downstream even though there was no statistically significantly (F [2,15] = 2.078, p = 0.16, ANOVA) difference among the sampling stations. The value of BOD5 in this study was higher than the reported value by previous studies [16,21]. But it was lower than the value of BOD5 reported [22]. This is due to the presence of high levels of biodegradable and complex organic matter in brewery wastewater that contributes to high biochemical oxygen demand (BOD). Also, the presence of high levels of nitrates and phosphates in the wastewater could contribute to high BOD levels. Nitrates and phosphates are plant nutrients and can cause plant life and algae to grow quickly. When plants grow quickly, they also die quickly. This contributes to the organic waste in the water, which is then decomposed by bacteria results in a high BOD level.

- **Chemical oxygen demand (COD)**

The mean value of COD ranged from 155.8–214.6 mg\L with the highest value measured at sampling station one. COD values at all sampling stations were higher than the limit of [6] standards. There was a significant difference (F [2,15] = 4.703, p = 0.026, Games-Howell Post-Hoc Test) in COD values recorded between sampling station one (S_1) and the other sampling stations (S_2 and S_3). The value of COD in this study was found to be higher than the reported value [16,23]. But it was lower than the value of COD reported [22]. The high level of COD is a result of the presence of high levels of biodegradable and complex organics, for example, sugars, soluble starch, ethanol, volatile fatty acids, etc. in brewery wastewater [24].

- **Total dissolved solids (TDS)**

TDS comprises inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulphates) and small amounts of organic matter that are dissolved in water. The mean value of TDS ranged from 96.8 to 173.2 mg\L with the highest value recorded at sampling station one. The values of TDS obtained at all sampling stations were above the effluent allowable discharge limits into watercourses [6]. TDS was significantly different (F (2, 15) = 53.54, p < 0.05, ANOVA) among the sampling stations. The value of TDS in this study was higher than the reported value [16]. The high levels of dissolved solids present in the brewery wastewater (or effluent).

- **Total suspended solids (TSS)**

The mean value of TSS ranged from 24.1–51.0 with the highest value measured at sampling station one and it was above the [6] effluent discharge limits. It was observed from the result obtained that there was a statistically significant difference (F (2, 15) = 28.21, p < 0.05) in the value of TSS among the sampling stations. The value of TSS in this study was found to be higher than the reported value of TSS [16,22,23]. The high levels of TSS could be due to different types of soluble organic substance.

- **Electrical conductivity (EC)**

The mean value of EC ranged from 276.3-721.0 μS/cm with the highest value was recorded at sampling station one and it was below the effluent allowable discharge limits into watercourses [6] for all the sampling stations. However, the value of EC in this study was found to be higher than the reported value of EC [16]. It was observed that electrical conductivity decreased downstream and could be due to dilution from adjacent streams.

- **Turbidity**

Turbidity is commonly caused by the presence of clay, silt, organic matter, algae, and other microorganisms [25]. The mean value of turbidity ranged between 6.53and 8.22 NTU with the highest value was recorded at sampling station one. It was observed from the result obtained that there was a significant difference (F [2,15] = 47.17, p < 0.05) in the value of turbidity among the sampling stations. The value of turbidity in this study was found to be very much lower than the reported value of turbidity [16].

- **Nitrate (NO_3^-)**

The mean value of nitrate ranged from 4.69 to 16.6 with the highest value was recorded at sampling station one. The mean concentration of nitrate recorded at sampling stations one and two was above the effluent allowable discharge limits into watercourses [6]. It was observed from the result obtained that there was a significant difference (F (2, 15) = 41.53, p < 0.05) in the value of nitrate among the sampling stations. The value of nitrate was found to be lower than the reported value of nitrate [16]. However, the levels of nitrate in this study and a previous study were above the effluent allowable discharge limits into watercourses [6].

- **Sulphate**

The mean concentration of sulphate ranged from 195.7 to 330.8 with the highest value was recorded at sampling station one. The mean concentration of nitrate recorded at sampling stations one and sampling stations two was above the effluent allowable discharge limits into watercourses [6]. Statistical analysis using ANOVA indicated that there was a significant difference (F (2, 15) = 63.89, p < 0.05) in the value of sulphate among the sampling stations. The value of sulfate was found to be very much higher than the reported value of sulphate [16].

- **Orthophosphate**

The mean concentration of orthophosphate ranged from 5.33 to 14.5 mg/L with the highest value was recorded at sampling station one. It was observed from the result obtained that there was a significant difference (F (2, 15) = 22.85, p < 0.05, Games-Howell Post-Hoc Test) in orthophosphate values recorded between sampling station one (S_1) and the other sampling stations (S_2 and S_3). The value of orthophosphate was found to be very much lower than the reported value of orthophosphate [22].

- **Ammonia nitrogen (NH_3-N)**

The mean concentration of ammonia-nitrogen ranged from 6.53 to 18.6 mg/L with the highest value was recorded at sampling station one and the values of ammonia-nitrogen at all sampling stations were below the effluent allowable discharge limits into watercourses [6]. It was observed from the result obtained that there was a significant difference (F [2,15] = 48.87, $p < 0.05$, Games-Howell Post-Hoc Test) in ammonia-nitrogen values recorded between sampling station one (S_1) and the other sampling stations (S_2 and S_3). The value of ammonium-nitrogen was found to be slightly higher than the reported value of ammonium-nitrogen [16].

- **Chloride**

The mean concentration of chloride ranged from 557.8 to 638.1 with the highest value was recorded at sampling station one. It was observed from the result obtained that there was a significant difference (F [2,15] = 87.13., $p < 0.05$) in the value of chloride among the sampling stations.

- **Total nitrogen (TN)**

The mean concentration of total nitrogen ranged from 3.17 to 19.0 with the highest value was recorded at sampling station one and it was above the effluent allowable discharge limits into watercourses [6] whereas the value of TN recorded at sampling stations two and three were within the allowable effluent discharge limits into water courses [6]. It was observed from the result obtained that there was a significant difference (F (2, 15) = 63.89, $p < 0.05$) in the value of total nitrogen among the sampling stations. The value of total nitrogen was found to be much lower than the reported value of total nitrogen [16, 22] that were above the effluent allowable discharge limits into watercourses [6] and much greater than the value reported [23].

- **Total phosphorus (TP)**

The mean concentration of total phosphorous ranged from 9.55 to 18.1. Phosphorous concentration at all sampling stations was above the effluent allowable discharge limits into watercourses [6]. Statistical analysis using ANOVA indicated that there was a significant difference (F (2, 15) = 111.60, $p < 0.05$) in the value of total phosphorous among the sampling stations. The value of total phosphorus was found to be lower than the reported value of total phosphorous [16]. These could be due to the use of phosphate containing substances during brewing processes. Tables 3 summarizes some of the most important environmental parameters for selected breweries along with the legal requirements for effluent discharge limits [6].

Parameters	Reference [21]	Reference [22]	Reference [16]	Reference [23]	Current Study	Reference [6]
pH	7.8	7.34	8.58 ± 0.08	7.96 ± 0.14	8.65 ± 0.74	6–9
Temperature, °C	29.6 ± 0.3		24.9 ± 0.6		28.6 ± 2.0	40
EC, µS/cm			220.6 ± 1.1		508.1 ± 262.7	1000
TDS, mg/L			110.6 ± 0.6		133.5 ± 34.3	80
Turbidity, NTUs			529.60 ± 9.00		7.44 ± 0.77	----
BOD_5, mg/L	21.8 ± 1.2	122	49.8 ± 17.0		70.90 ± 7.69	60
COD, mg/L		1012	203.0 ± 15.7	89.7 ± 67.4	178.5 ± 42.8	250
TSS, mg/L	39.6 ± 1.2	42.5	46.7 ± 5.7		36.2 ± 12.9	50
NH_4^+-N, mg/L			17.7 ± 6.9			20
NH_3-N, mg/L		71			11.5 ± 5.6	
TN as N, mg/L^1		30.5	41 ± 7.23	8.72 ± 5.3	10.4 ± 6.8	40
NO_3^--N			19.8 ± 0.7		10.5 ± 5.5	<10
TP as P, mg/L			24.3 ± 1.4		13.5 ± 3.7	5
PO_4^{3-} , mg/L		69.7			9.08 ± 4.6	
SO_4^{2-}, mg/L			3.62 ± 2.1		261.8 ± 60.0	200

Table 3: Characteristics of some breweries wastewater discharge and my study results compared with [6] standards

Assessment of groundwater quality

Water quality parameters whose concentrations are potentially impacted by anthropogenic activities have been investigated in the selected groundwater samples. Table 4 & Figure 3 present the summary statistics for each parameter for all groundwater samples.

Parameters	G_1	G_2	G_3	G_4	Reference [26]
pH	8.5 ± 0.1	8.1 ± 0.06	7.9 ± 0.01	7.4 ± 0.02	6.5 to 8.5
Temp	22.20 ± 0.21	22.2 ± 0.11	22.3 ± 0.11	22.1 ± 0.06	NL
DO	12.3 ± 0.25	10.3 ± 0.12	9.53 ± 0.06	7.73 ± 0.06	NL
BOD	20.2 ± 0.21	17.4 ± 0.1	15.2 ± 0.2	12.4 ± 0.11	NL
COD	177.3 ± 0.6	160.7 ± 0.6	77.3 ± 0.21	28.1 ± 0.06	NL
TDS	750.7 ± 0.6	550.3 ± 0.6	350.3 ± 0.6	199.8 ± 0.2	500
TSS	221.0 ± 1.0	173.4 ± 0.08	120.7 ± 1.2	59.8 ± 0.38	25
EC	3142.7 ± 1.2	2614.7 ± 1.2	2115.7 ± 1.5	1610.7 ± 0.6	750
Turbidity	3.13 ± 0.01	2.43 ± 0.06	2.27 ± 0.06	1.37 ± 0.06	5
Nitrate	65.2 ± 0.1	62.6 ± 0.15	23.2 ± 0.1	23.0 ± 0.1	<10
Phosphate	0.77 ± 0.01	0.67 ± 0.01	0.55 ± 0.01	0.44 ± 0.01	NL
Sulphate	238.7 ± 0.6	204.3 ± 0.6	195.0 ± 1.0	63.7 ± 0.6	250
Chloride	994.3 ± 0.6	940.70 ± 0.11	905.3 ± 0.2	887.3 ± 0.2	< 250
Fluoride	1.45 ± 0.01	0.84 ± 0.01	0.82 ± 0.003	0.78 ± 0.01	1.5
TH	673.3 ± 1.5	610.3 ± 0.6	550.7 ± 0.6	401.3 ± 1.2	NL
TA	390.3 ± 0.6	372.3 ± 2.1	350.3 ± 0.6	343.3 ± 1.5	NL

Table 4: Results of water quality parameters (Mean ± SD, n=3) for groundwater samples. All units except pH (pH scale), temperature (°C), turbidity (NTUs), EC (**µ**S/cm), and TH and TA (mg/L $CaCO_3$) are mg/L.

Note: NL indicates that no standard or guideline or limit has been established or recommended for a given parameter.

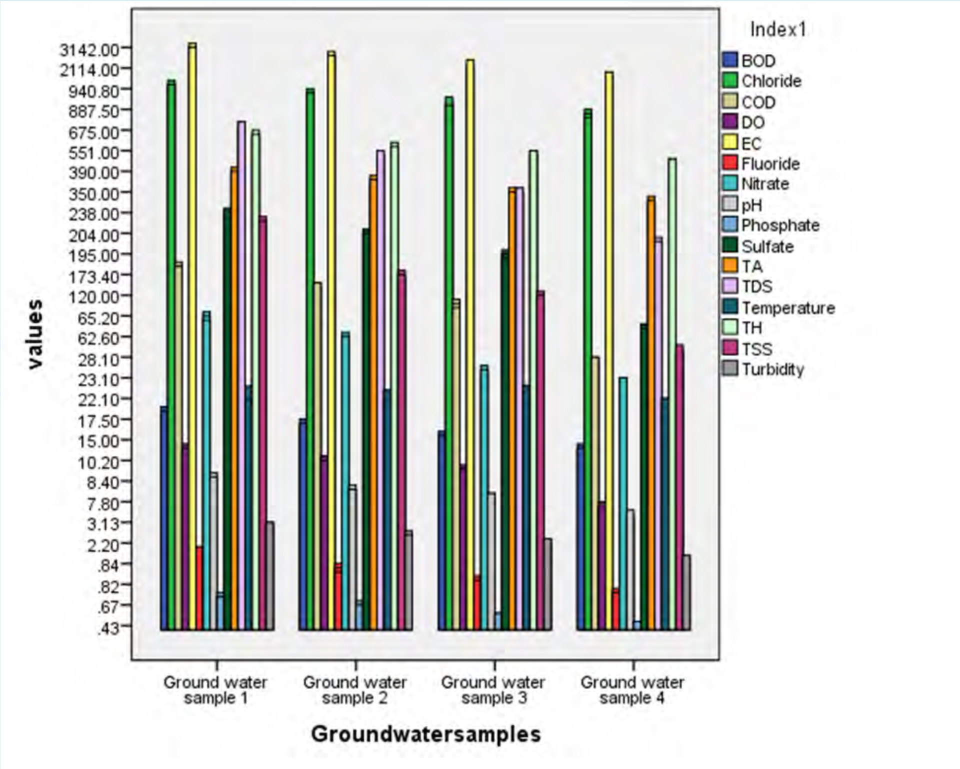

Figure 3: Results of water quality parameters for groundwater samples and all units except pH (pH scale), temperature (°C), turbidity (NTU), EC (**µ**S/cm), and TH and TA (mg/L $CaCO_3$) are mg/L.

Physicochemical Parameters

- **pH**

The mean pH values of groundwater samples varied from 7.4 to 8.5 and it was within the allowable range [26] in waters used for public supply. The guideline suggested that pH less than 6.5 or greater than 8.5 would markedly impair the portability of the water. In general, the pH of most groundwater ranges between 5.0 and 8.0 [27]. The types of dissolved constituents in groundwater can influence pH levels. Dissolved carbon dioxide (CO_2), which forms carbonic acid in the water, is an important control on the pH of natural waters [28]. The pH of groundwater can also be lowered by organic acids from decaying vegetation, or by the dissolution of sulphide minerals [27]. It was observed from the result obtained that there was a significant difference (F [3,8] = 174.487, $p < 0.05$) in the value of pH among the sampling sites.

- **Temperature**

The mean value of temperature ranged from 22.1-22.3**°C. Statistical analysis using ANOVA indicated that the mean value of temperature was not significantly different** ((F [3,8] = 2.061, p = 0.184) among the four groundwater sampling sits. This suggested that groundwater temperatures are relatively the same among the sampling sites.

- **Dissolved oxygen (DO)**

Oxygen is supplied to groundwater through recharge and by the movement of air through unsaturated material above the water table. The concentration of dissolved oxygen in water is affected by many factors, including ambient temperature, atmospheric pressure and the ion activity of the water body [29]. The mean DO concentration of groundwater samples varied from 7.73 to 12.3 mg/L. Statistical analysis using ANOVA indicated that the mean value of DO was significantly different ((F [3,8] = 508.8, $p < 0.05$) among the sampling sites.

- **Biochemical oxygen demand (BOD)**

The mean value of BOD5 ranged from 12.4–20.2 mg/L with the highest value measured at G_1. This suggested the presence of organic matter and bacteria. If there is no organic waste present in the water, there will not be as many bacteria present to decompose it and thus the BOD will tend to be lower and the DO level will tend to be higher. The values of BOD5 also showed a progressive decrease downstream. It was observed from the result obtained that there was a significant difference (F [3,8] = 1231.5, $p < 0.05$) in the value of BOD5 among the sampling sites.

- **Chemical oxygen demand (COD)**

The mean value of COD ranged from 28.1-177.3 mg/L with the highest value measured at G_1. This value usually indicates the presence of organic matter in the groundwater samples. It was observed from the result obtained that there was a significant difference (F [3,8] = 83454.1, $p < 0.05$) in the value of COD among the sampling sites.

- **Total dissolved solids (TDS)**

TDS are a measure of the total amount of dissolved minerals in the water. Essentially, TDS represents the sum of concentrations of all dissolved constituents in a water sample. In general, if a ground-water sample has a high TDS level, high concentrations of major constituents will also be present in that sample. The highest concentration of TDS was recorded at G_1 (750.7 mg/L) and G_2 (550.3 mg/L) exceeding the secondary maximum contaminant level (SMCL) for TDS. However, [30] defines freshwater (water sufficiently dilute to be potable) as water containing TDS of less than 1000 mg/L. The principal influences on TDS levels in groundwater may originate from natural sources or anthropogenic activities-waste disposal, mining, landfills, and runoff from urban or agricultural areas and industrial wastewater. In this study, industrial wastewater could play an important role in the high TDS values in those groundwater samples. Statistical analysis using ANOVA indicated that the mean value of TDS was significantly different ((F [3,8] = 662873.2, $p < 0.05$) among the sampling sites.

- **Total suspended solids (TSS)**

The mean value of TSS ranged from 59.8–221.0 mg/L with the highest value measured at $G_1$and it was above the [26] drinking water standards. It was observed that there was a statistically significant difference (F [3,8] = 23224.3, $p < 0.05$) in the value of TSS among the sampling sites.

- **Electrical conductivity (EC)**

EC is the ability of an aqueous solution to conduct an electrical current. The presence of charged ionic species in a solution makes the solution conductive and as such electrical conductivity is a proxy measure of the total dissolved ions [28]. The mean electrical conductivity values of G_1 and G_2 recorded were higher than the drinking water standards [31]. The lowest electrical conductivity was recorded in G_4 (1610.7 **µ**S/cm). Statistical analysis using ANOVA indicated that the mean value of EC was significantly different ((F [3,8] = 973608.5, $p < 0.05$) among the sampling sites.

- **Turbidity**

Turbidity is an expression of the optical property that causes light to be scattered and absorbed by particles and molecules rather than transmitted in straight lines through a water sample. It is caused by suspended matter or impurities that interfere with the clarity of the water. These impurities may include clay, silt, finely divided inorganic and organic matter, soluble colored organic compounds, and plankton and other microscopic organisms [29]. The mean turbidity values of all groundwater samples were very low, and it was lower than [26] standard for drinking purposes. One-way ANOVA tests indicated that the mean value of turbidity was significantly different ((F [3,8] = 627.2, $p < 0.05$) among the r sampling sites.

- **Nitrate**

Nitrogen may be present in water as several dissolved species: nitrate (NO_3^-), ammonium (NH_4^+), nitrite (NO_2), which is meta-stable, nitrogen gas (N_2) and organic nitrogen. The occurrence and mobility of the inorganic nitrogen species are largely dependent on the redox conditions of the water, with NO_3 being stable under oxidizing conditions and NH_4^+ under reducing conditions. Nitrate (NO_3^-) is the most common form of nitrogen in groundwater [32]. The mean nitrate concentrations in the groundwater samples range from 23.0 to 65.2 mg/L NO_3^-. The concentration of nitrate recorded at all groundwater samples exceeded [26] standards for drinking water. These elevated nitrate concentrations in the groundwater have public health and environmental implications. According to [33], nitrate concentrations between 3.1 and 10 mg/L may represent elevated concentrations of nitrate due to human activities. Thus, the elevated concentrations of nitrate in the groundwater samples could be caused by anthropogenic sources [34] such as agricultural activity (including the excess application of inorganic nitrogenous fertilizers and manures), from wastewater disposal and the oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. It was observed that there was a statistically significant difference ($F [3,8] = 122625.0$, $p < 0.05$) in the value of nitrate among the sampling sites.

- **Phosphate**

Phosphorus is an essential element for life and major nutrient for plants. The dominant natural source of phosphorus in groundwater is apatite, which is a common accessory mineral in many rock types, especially igneous rocks [35], and exchangeable phosphorus on iron oxides. Phosphorus occurs in concentrations of several hundred mg/kg in all common rock types but its concentration in natural waters is usually low due to the low solubility of most of its inorganic compounds [28]. Under alkaline conditions phosphorus is easily sorbed to carbonates and iron oxide minerals; as a result, its mobility is likely to be low [36]. However, in some situations, phosphorus can transfer to groundwater [37]. The mean phosphate concentrations in the groundwater samples range from 0.44 to 0.77 mg/L. It was observed that there was a statistically significant difference ($F [3,8] = 1285.7$, $p < 0.05$) in the value of phosphate among the sampling sites.

- **Sulphate**

Sulphate (SO_4^{2-}), an anion formed by oxidation of the element sulphur, is commonly observed in groundwater. Various geochemical processes, sources, and time and anthropogenic activities may influence the concentration of sulphate in groundwater. Sulphate may be released by the weathering of evaporate minerals such as gypsum and anhydrite or by the oxidation of sulphide minerals such as pyrite (FeS_2), sphalerite (ZnS) or galena (PbS) [35,38]. It is the only major ion that is affected by redox reactions and, as such, its behavior is complex [39]. The highest sulphate concentration was found in G_1, G_2, and G_3. The highest values could be due to natural sources or anthropogenic activities [34]. The presence of sulfate in drinking-water may also cause noticeable taste at concentrations above 250 mg/L and may contribute to the corrosion of distribution systems. One-way ANOVA tests indicated that the mean value of sulfate was significantly different (($F [3,8] = 35416.6$, $p < 0.05$) among the sampling sites.

- **Chloride**

Chloride occurs in evaporite minerals such as halite and sylvite [35]. Chloride in groundwater may originate from various sources including the dissolution of halite and related minerals, rainfall or due to mixing with formation waters [39], marine water entrapped in sediments, and anthropogenic sources [34]. In this study, the mean concentration of chloride was above 250 mg/L, the SMCL for this ion, for all groundwater samples with the highest concentration recorded at groundwater G_1 (994.3 mg/L). This suggested that the concentrations of chloride in groundwater samples were heavily influenced by factors other than its natural sources-dissolution of naturally occurring sulphate-containing substances found in the soils and rocks and it could be due to contamination from sewage, and contamination from various types of industrial wastes [28]. One-way ANOVA tests indicated that the mean value of chloride was significantly different (($F [3,8] = 62545.2$, $p < 0.05$) among the sampling sites.

- **Fluoride**

The principal mineral source of fluoride is the fluorite (CaF_2) and fluorapatite [$Ca_5(PO_4)F$], which are common accessory minerals, particularly in granite [35]. Fluoride is also released from weathering of primary silicates such as biotite and hornblende, where it replaces OH in the mineral lattices [36]. Igneous and volcanic rocks have a fluoride concentration from 100 mg/L (ultramafic) up to > 1000 mg/L (alkalic). Fluoride occurrence in groundwater is almost entirely due to water-rock interactions [36] and, therefore, largely depends on reaction times with aquifer minerals [40]. Concentrations in most groundwater are limited by saturation concerning fluorite, which is relatively insoluble. In this study, the mean concentration of fluoride for all groundwater samples examined were below the [26] standards for Drinking-water. Fluoride is an essential element for humans at low concentrations but can be harmful, causing mottling of teeth [41] and skeletal fluorosis, at higher concentrations. One-way ANOVA tests indicated that the mean value of fluoride was significantly different (($F (3, 8) = 8625.8$, $p < 0.05$) among the sampling sites.

- **Total hardness (TH)**

Total hardness is the concentration of dissolved calcium and magnesium. It is expressed as an equivalent concentration of calcium carbonate. Carbonate hardness includes that part of the total hardness equivalent to the bicarbonate and carbonate (or alkalinity). In hard water, the metallic ions of concern may react with soap to produce an insoluble residue. These metallic ions may also react with negatively charged ions to produce a solid precipitate when hard water is heated [32]. Hard waters can thus consume excessive quantities of soap, and cause damaging scale in water heaters, boilers, pipes, and turbines. Many of the problems associated with hard water, however, can be mitigated by using water-softening equipment. In this study, the measured hardness level was above 200 mg/L (as $CaCO_3$) in all ground-water samples. Thus, the groundwater under considerations can be generally characterized as very hard water in the [42] hardness classification system. Depending on pH and alkalinity, hardness above about 200 mg/L can result in scale deposition, particularly on heating. Soft waters with a hardness of less than about 100 mg/L have a low buffering capacity and may be more corrosive to water pipes. It was observed that there was a statistically significant difference (F [3,8] = 37509.6, $p < 0.05$) in the value of TH among the sampling sites.

- **Total alkalinity (TA)**

The alkalinity of a solution may be defined as the capacity of its solutes to react with and neutralize the acid. The alkalinity in most natural waters is primarily due to the presence of dissolved carbon species, particularly bicarbonate and carbonate. Other constituents that may contribute minor amounts of alkalinity to water include silicate, hydroxide, borates, and certain organic compounds [28]. The mean value of total alkalinity ranged from 343.3–390.3 mg/L $CaCO_3$ with the highest value measured at G_1. At present, no suggested limits have been established for alkalinity levels in drinking water. However, some alkalinity may be desirable in groundwater because the carbonate ions moderate or prevent changes in pH.

Comparisons of Physicochemical Characteristics of Effluent Samples and Groundwater Samples

Comparisons of the results of the analysis of physicochemical parameters of the effluent samples and the groundwater samples are summarized in Table 5 & Figure 4.

Parameters	Effluent samples	Groundwater samples	Reference [6]	Reference [26]
pH	8.65 ± 0.74	8.00 ± 0.41	06-Sep	6.5 to 8.5
Temp	28.6 ± 2.0	22.20 ± 0.15	40	40
DO	11.4 ± 5.74	9.97 ± 1.7		5 to 7
BOD	70.9 ± 7.69	16.3 ± 3.0	60	2 to 5
COD	178.5 ± 42.8	110.8 ± 63.7	125	
TDS	133.5 ± 34.3	462.8 ± 216.8	80	500
TSS	36.2 ± 12.9	143.7 ± 62.7	50	25
EC	508.1 ± 262.7	2370.9 ± 595.0	1000	750
Turbidity	7.44 ± 0.77	2.30 ± 0.66		5
Nitrate	10.5 ± 5.5	43.5 ± 21.3	< 10	45
Phosphate	9.08 ± 4.60	0.61 ± 0.13	5	0.1
Sulphate	261.8 ± 60.0	175.4 ± 69.5	1000	250
NH_3-N	11.5 ± 5.6	----------	20	------
Chloride	595.9 ± 35.3	931.9 ± 42.7		600
TN	10.4 ± 6.8	------------	10	-------
TP	13.5 ± 3.7	------------	5	--------
Fluoride	---------	0.97 ± 0.29	-------	1.5
TH	---------	558.9 ± 105.3	-------	300
TA	----------	364.1 ± 19.4	-------	120

Table 5: Results of water quality parameters for effluent samples (Mean ± SD, n=18) and groundwater samples. (Mean ± SD, n=12). All units except pH (pH scale), temperature (°C), turbidity (NTU), EC (**µS**/cm), and TH and TA (mg/L $CaCO_3$) are mg/L.

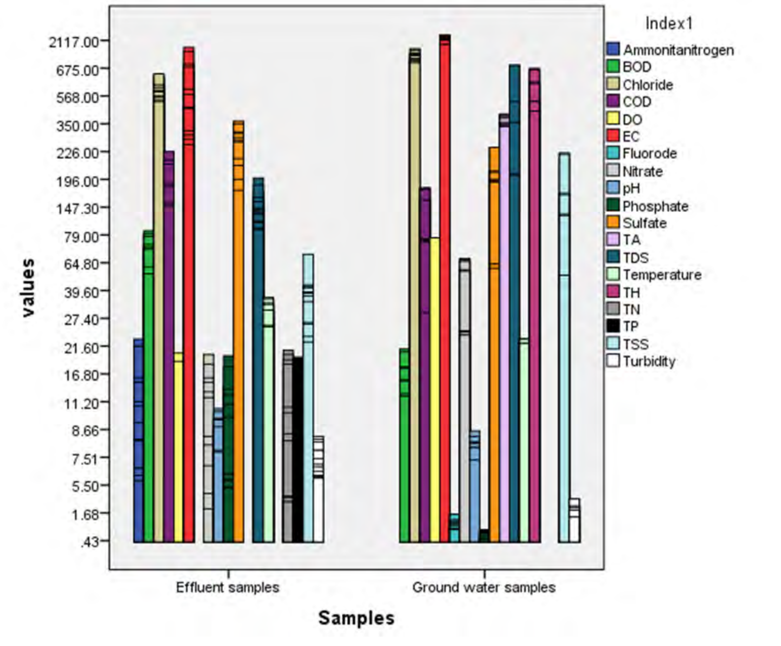

Figure 4: Results of water quality parameters for effluent samples and groundwater samples. All units except pH (pH scale), temperature (°C), turbidity (NTU), EC (**µ**S/cm), and TH and TA (mg/L $CaCO_3$) are mg/L.

Independent Samples Test showed that the mean value of all physicochemical parameters except DO was not the same for effluent samples and groundwater samples. So there was a variation in all physicochemical parameters except DO for the two types of samples examined. The mean pH value was significantly higher for effluent samples than the groundwater samples ($t(28) = 2.846$, $p = 0.008$). Similarly, the mean water temperature was significantly higher for effluent samples than the groundwater samples ($t(28) = 13.6$, $p < 0.05$). It was observed that there was no significant difference ($t(28) = 1.026$, $p = 0.316$) in the mean concentration of DO for effluent samples and groundwater samples. However, the value of DO slightly higher in the effluent samples than groundwater samples.

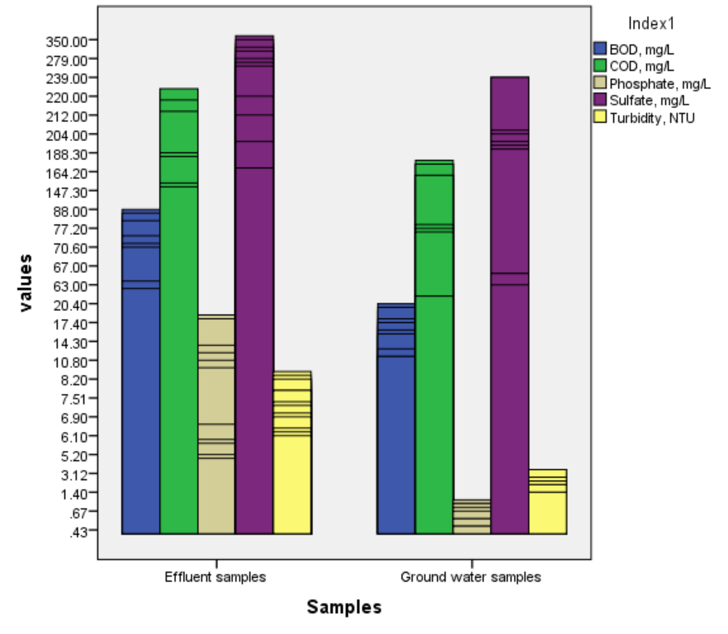

Figure 5: Mean values of selected physicochemical parameters for affluent and groundwater samples.

The mean BOD (t(28) = 27.2, $p < 0.05$), COD (t(28) = 3.22, p = 0.005), turbidity (t(28) = 18.9, $p < 0.05$), sulphate (t(28) = 3.62, < 0.05) and phosphate (t(28) = 7.75, < 0.05) values were significantly higher for effluent samples than the groundwater samples (Figure 5).

The values of BOD, COD, TDS, turbidity, and phosphate were found to be above the permissible limit of [6,43] standards for industrial effluents. Thus, the study concluded that the discharge of the effluent from Hawassa Castel brewery plant was highly polluted with organic matter, phosphate, and sulphate. The mean TSS (t(28) = -5.85, $p < 0.05$), TDS (t(28) = -5.21, $p < 0.05$) EC (t(28) = -10.2, $p < 0.05$), nitrate (t(28) = -5.25, < 0.05) and chloride (t(28) = -23.5, $p < 0.05$) values were significantly lower for effluent samples than the groundwater samples as shown in Figure 6.

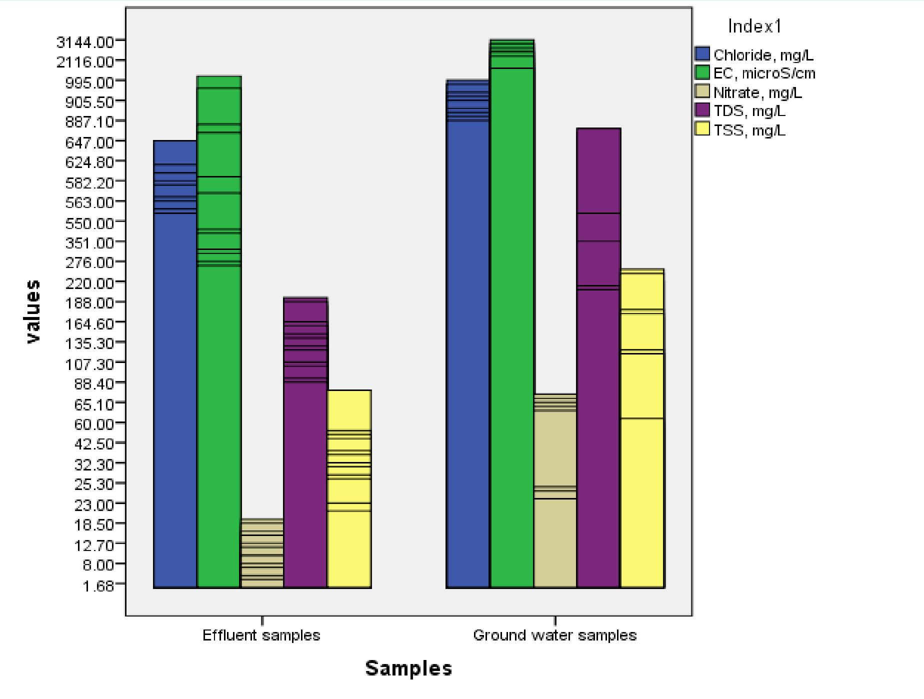

Figure 6: Mean values of selected physicochemical parameters for effluent and groundwater samples.

The presence of high levels of TDS, TSS, EC, nitrate, phosphate, and chloride in the groundwater samples, exceeding [6, 43] standards for industrial effluents discharge and [26] standards for drinking water, suggested that the groundwater was immensely polluted by anthropogenic activities that might include municipal sewage, industrial wastewater, and agricultural operations, septic and underground storage tank. Hence groundwater pollution degrading groundwater quality in the vicinity of Hawassa Castel brewery plant and making it unsuitable for drinking purposes.

Conclusion

Effluent discharge from brewery operation did not meet the standards for industrial effluent discharge limits and this could be the major source of groundwater pollution. The analysis of groundwater of the surrounding area of Hawassa Castel brewery plant concluded that the effluents were highly polluted with organic matter, phosphate, nitrate, and sulphate, degrading the groundwater quality and making it unsuitable for drinking purpose. Thus, the concerned bodies should act to prevent further deteriorate of the quality of groundwater.

Data Availability

All the data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Funding Statement

This research was funded by Ethiopian Ministry of

Education.

Acknowledgement

We would like to acknowledge the thesis "Proposed Brewery Development St. James's Gate Environmental Impact Statement Volume 2 Main Report" for the background work of this research, Ethiopian Ministry of Education for funding the research, Hawassa Castel Brewery and Hawassa University for supporting the research.

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