Physicocemical characterization and heavy metals analysis from industrial discharges in Upper Awash River Basin, Ethiopia

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Physicochemical characterization and heavy metals analysis from industrial discharges in Upper Awash River Basin, Ethiopia

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ABSTRACT

The recent expansion of industries in Addis Ababa is causing additional environmental pollution through wastewater discharges; this is becoming a critical concern. Addis Ababa is located in the upper Awash River basin, and is the main source of industrial pollutants to the river. In this study, physicochemical parameters, nutrients and heavy metal content of wastewaters released from 16 factories, 6 tanneries, 6 beverages and 4 diverse factories, and the Akaki-Kality central wastewater treatment plant in Addis Ababa, were sampled to assess the level of pollutants. Heavy metals were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). Analysis of nutrients were conducted using Palintest Photometer. Physicochemical characteristics were measured either in situ using a portable micro meter or in the laboratory. Among the measured physicochemical properties, critical issues were observed with electrical conductivity, total dissolved solids and total hardness. Effluents from all of the tanneries, and a number of other factories, were found at levels higher than the maximum limits of various guideline standards. In addition, samples from two of the tanneries (T1 and T5), two beverage factories (B3 and B6) and the central wastewater treatment plant showed elevated concentrations of PO_4^{3-}, which violated the limit (10 mg/l) set by Environmental Protection Agency of Ethiopia (ETHEPA). The two tanneries (T1 and T5) also contained higher SO_4^{2-} than the guideline limit of 1000 mg/l. On the other hand, only one factory, one brewery (B3), exhibited NO_3^- above the standard limit of 20 mg/l. Whereas NH_3, NH_4^+, Cl^-, S^{2-} and NO_2^- were within the limits in all of the samples. Severe pollution was found in wastewaters from tanneries, where half of them (T1, T5 and T6) contained Cr beyond the maximum limit of 2000 μg/l. Furthermore, a third of the tanneries (T1 and T5) and a beverage factory (B5) contained Fe, Mn, Zn and Cu, higher than the ETHEPA limits of 10000, 5000, 5000 and 2000 μg/l, respectively. Waste disposal from factories without proper treatment can cause great harm to the local people and the environment. Hence, the results of this study call for regulatory bodies to pay close attention to factories, particularly tanneries, in Addis Ababa in implementing adequate treatments of their wastewater discharges

1. Introduction

Ecological and human disasters can arise from discharge of industrial wastes causing degradation to ecosystems and human health [1–3]. With ever-increasing population growth and industrial development, human societies have always had an influence on rivers and their ecosystems. Human activities on rivers and their ecosystem affects one or more of the five attributes of watersheds and streams: water quality, habitat structure, stream flow patterns, sources of energy and nutrients, and biotic interactions [4,5]. Compromised environmental quality as a result of effluent discharge from industrial sectors has become a serious environmental concern for many countries especially in developing nations like Ethiopia [6,7].

It is reported that around 70% of the industrial waste in developing

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nations are discharged untreated to contaminate the surrounding water bodies [8,9]. Most companies in Uganda, for example, use outdated manufacturing technology and lack functional effluent treatment plants [10], while wastewater in Bangladesh and Ethiopia is frequently discharged into freshwater systems without treatment [11,12]. Many of the pollutants in industrial wastes act as teratogenic, carcinogenic and allergic agents in humans and have shown growth inhibition characteristics on different microbes, plants and animals [13]. Besides, the discharge of industrial wastewater is known to contain easily fluctuating pH, high temperature, heavy metals, and substantial amounts of suspended solids. Pollution from industrial wastewater causes serious health issues in surrounding areas, affecting fertility of land, and destroying fisheries, aquatic life and ecosystems. Hence, the first step in a pollution prevention strategy for a waterbody is a thorough assessment and characterization of wastewater discharges from manufacturing industries [14,15].

Tariq et al. [16] showed that 90–96% of industries in Ethiopia discharge their waste to nearby water bodies and open spaces without any form of treatment. It has also been estimated that only 13% of the wastewater discharged from industries is free from chemical contamination [17]. Various studies conducted in Ethiopia have indicated that disposal of untreated wastewater from various industries, urban wastes and agrochemical wastes in lowland, open water bodies have reached a critical situation and are also worsening [12,18].

Approximately 65% of Ethiopia's industry is located in Addis Ababa; the city is experiencing various water quality challenges, including discharge of wastewater from factories, without any treatment of pollutants [19–21]. A recent review by Getachew et al. [22], highlighted that water pollution in Akaki River catchment of Upper Awash River basin resulted from rapid urbanization and industrial expansion without adequate solid waste management and wastewater treatment facilities, and agricultural activities. The issue has therefore, become a matter of increasing public concern given the negative effects that pollutants can have on the environment and human health [23,24].

Effluent is being discharged into rivers and streams that feed into the Big and Little Akaki rivers (BAR and LAR), that flow into and join at lake Aba Samuel, which subsequently flows into the Awash River. Subsequently, Lake Aba Samuel has always been a sink for pollutant loads flowing down the catchment through both LAR and BAR containing untreated or inadequately treated industrial wastewater from the city and surrounding areas [20,25,26].

The two rivers crossing the city are also used for irrigation purposes in and surrounding the catchment mostly in the downstream area [26]. Due to the pollutant carried in the rivers, the use of this water for irrigation can induce health risks for both farmers and consumers. The investigation made by [27] showed that As and Zn in soil irrigated by the Akaki River were higher than the normal limits set by FAO/WHO-Codex alimentarius commission. The concentrations of Pb, Cd, Mn, Ni and Zn in sediments in the Little Akaki river were relatively greater than other trace metals at levels that may have adverse biological effects on the surrounding biota [28]. In addition, in the Akaki rivers, the mean concentrations of heavy metals including Mn, Cr, Ni, Pb, As and Zn were also above the allowable limits of the Canadian Council of Ministers of Environment Water Quality Index [29]. Despite the risk associated, there is a little to no awareness on the poor water quality of the rivers among residents of Addis Ababa nor the downstream communities [30]. To support the enforcement of environmental regulations, raising public awareness to risks and the impact of pollution, identifying and evaluating the sources of pollution is critical. Therefore, this study aimed to determine the physicochemical quality and heavy metal contents in effluents discharged from selected industries in Addis Ababa and evaluated them against regulatory standards set by the Environmental Protection Agency of Ethiopia (ETHEPA), the Environmental Protection Agency of USA (USEPA) and the United Nations Food and Agricultural organization (FAO).

2. Materials and Methods

2.1. Description of the study area

Fig. 1 shows the location of the Upper Awash River Basin in Ethiopia, alongside the locations of the studied factories in this study (red dots) together with streams and rivers of Akaki watersheds, as well as the receiving lake (Aba Samuel Reservoir). The catchment is located between 8°460–9°140 N and 38°340–39°040E and covers around 1500 km^2. Addis Ababa is in the heart of the catchment area and has altitude of 2355 m above sea level. Legedadi, Gefersa, Dire, and Aba Samuel are surface water reservoirs in the research region [31]. The daily average temperature ranges from 9.9° to 24.6°C and the mean annual rainfall is 1254 mm [32].

Initially, thirty-three factories were identified for sampling, however, after preliminary investigation only fifteen were chosen for further investigation. As a result, fifteen different factories, as well as an industrial park (comprising a number of textiles factories) and Kality central wastewater treatment plant were selected for sampling (Table 1). Kality central wastewater treatment plant is a secondary sewage treatment plant located downstream of the Addis Ababa City. Two of the factories, Giohn Berkina (G) and Repi Soap and Detergent Factory (SD), did not have wastewater treatment facilities. In contrast, the other factories had wastewater treatment facilities with different levels of technologies, ranging from primary to tertiary (Table 1).

2.2. Chemicals and reagents

Palintest photometer reagent tablets (nitratest, nitricol, alkalinity, hardicol, ammonia No 1 and ammonia No 2, chlorine, total hardness, phosphate, sulphate, and sulphide) were used for the analysis of nutrients. All working solutions were made using high-purity deionised water. Ar (99.99%), HNO_3 (65%) and multi-element standard solutions (1000 mg/l) (Perkin Elmer, USA) were used in the study. All working solutions were made in a 0.5% HNO_3 using high-purity water (18.2 MΩ/cm).

2.3. Wastewater sampling, preservation and assay

Samples were collected from each factory outlet, while wastewater was discharging into the environment. Samples were collected between 08:00 and 11:00 AM during the dry season of 2021, using a time-composite sampling technique. Time-composite sampling refers to the collection of numerous individual discrete wastewater samples taken at regular intervals over a period of hours [33]. The collection was carried out on a day when the factory was operating at full capacity. Each wastewater sample was collected from a point of fast flow at a depth half that of the total depth, in order to avoid debris and only collecting surface water.

A total of 17 wastewater samples were collected from the study site. Every 500 ml wastewater sample was taken using pre-cleaned, tight-capped and labelled polyethylene bottles. The collected samples were kept in an ice box until transported to the laboratory of Ministry of Water and Energy (MoWE), Ethiopia, for further physicochemical parameter analysis. The nutrients of wastewater samples (NH_3, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, chloride, total alkalinity and total hardness) analysis were then conducted within 12 h of collection using photometry (Palintest Photometer 7500). In addition, temperature, pH, total dissolved solids (TDS) and electric conductivity (EC) were measured in situ by a multimeter (Micro 800), using a grab-sampling technique. The detection range for nitrate, nitrite, alkalinity, hardness, ammonia, chloride, phosphate and sulphate tablet reagents were 0–20, 0–1.6, 0–500, 0–500, 0–1.2, 0–50, 0–4 and 0–200 mg/l, respectively. The working principle of the Palintest photometer for each parameter is summarized in Table 2. For metal analysis, the wastewater samples were acidified with nitric acid to pH lower than 2 and stored at 4 ^{0}C.

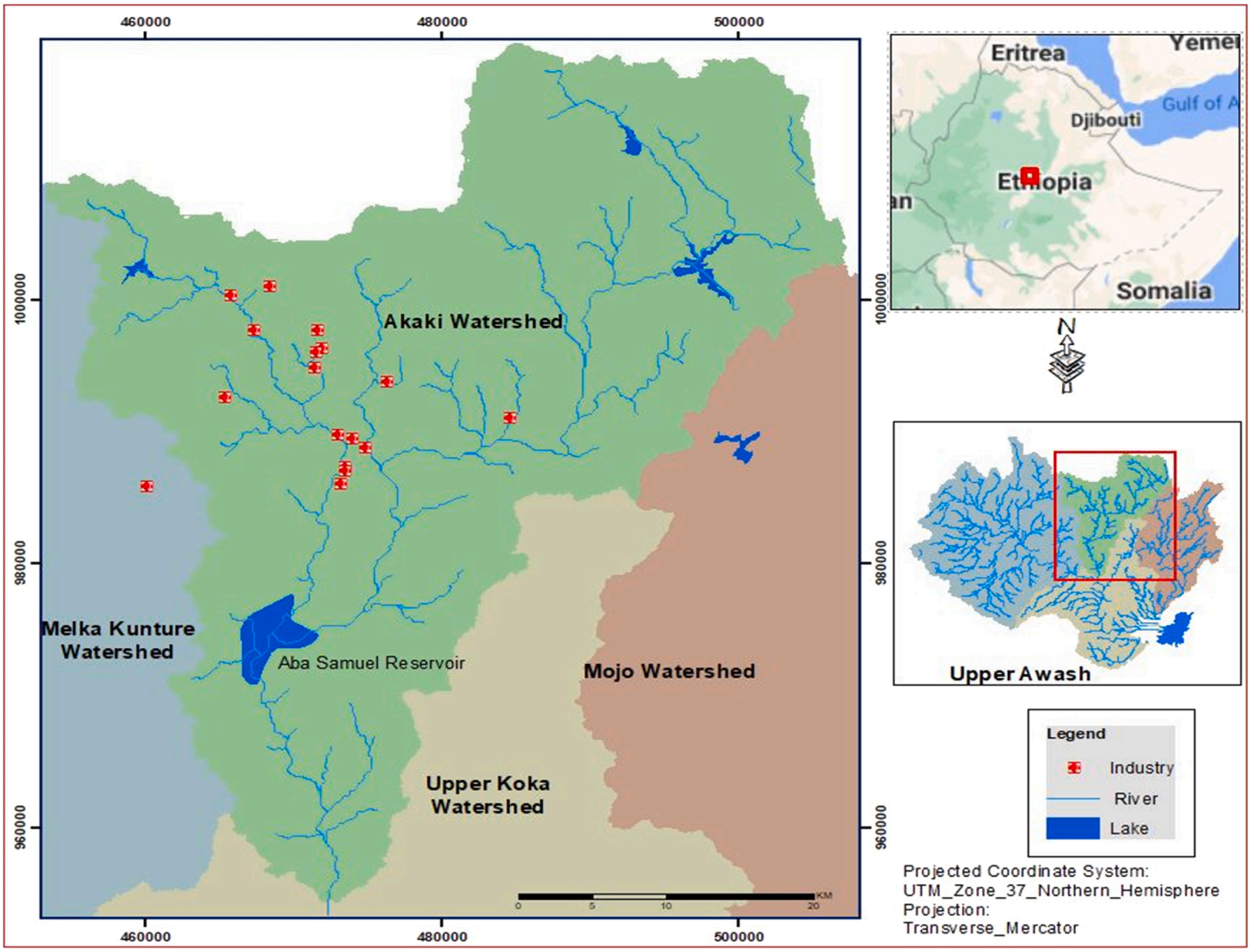

Fig. 1. Location map of industrial wastewater sampling sites (red dots).

2.4. Heavy metal analysis

The levels of heavy metals were determined after digestion of wastewater samples based on the protocol of the American Public Health Association (APHA) [34]. The levels of heavy metals in the digested wastewater samples were determined using ICP-OES (Perkin Elmer 8000, USA) at the Abbay Basin Development office, Ethiopia. Optimization of the instrument carried out by running the performance check solution and operating parameters like torch position, nebulizer flow rate, Radio frequency (RF) power and the interference corrections were adjusted before sample analysis.

Calibration curves were constructed with known concentrations of standards for each element and good linearity was obtained, with correlation coefficients (> 0.998). Spiking experiments were used to assess the accuracy of the method. Accordingly, a known amount of standard of a heavy metal of interest, equivalent to the amount found in the sample, was added to the wastewater sample and subjected to digestion following a similar procedure to that of the unspiked sample. The percentage recoveries ranged from 93.4% to 104.3% (Table 3), indicating that the method was accurate. The limits of detection (LOD) of the method were determined from the measurement of the blank samples that were digested and analyzed along with the samples. The limits of detection of Fe, As, Cr, Mn, Cu, Ni, Pb and Zn were 0.158, 0.198, 0.009, 0.096, 0.009, 0.023, 0.010 and 0.033 μg/l, respectively (Table 3).

2.5. Statistical analysis

All data analyses were carried out using the statistical software package SPSS 24 (IBM Corporation, USA). Cluster analysis (CA) was applied to determine if there were similarities among the factories, both the physicochemical and trace elements contents of their wastewater discharges. Linear discriminant analysis (LDA) was performed in order to evaluate those physicochemical characteristics and trace elements that discriminate among the factories. Data are presented as the mean and standard deviation of replicate measurements made on a sample.

3. Results and Discussion

3.1. Physicochemical characteristics

The physicochemical characteristics of the effluent samples vared considerably between the different factories assessed in Addis Ababa for the effluents discharged discussed shown (Table 4) below.

3.1.1. Electric conductivity

The measured electric conductivity (EC) in the wastewater samples varied from 575 to 30,800 μS/cm (Table 4) across the different factories. The lowest EC was recorded for Repi Soap and Detergent Factory (SD), while the highest was detected in Ghion Berekina (G), which was more than fifty-fold higher than Repi Soap and Detergent Factory (SD). This may be explained by the presence or absence of a wastewater treatment

Table 1
Geographical coordinates and wastewater treatment plants of the studied factories in Addis Ababa.

Name of Factory	Code	Coordinates		Level of the treatment plant	Status of treatment plant
		X	Y		
New wing Addis Tannery	T6	474790.9	988794.9	Secondary	Functional
Batu Tannery	T2	473428	987287.1	Secondary	Functional
Akaki Kality wastewater TP	WW	473124.1	986011.5	Tertiary	Functional
Heineken Brewery	B3	471447.5	994821.7	Tertiary	Functional
Kadisco Paint Factory	PT	473415	986989	Secondary	Functional
Awash ELICO Tannery	T3	473964.8	989395.3	Secondary	Functional
Abissinia Tannery	T4	472934	989701	Secondary	Functional
Moha soft Drinking Factory	B6	471608	997669.5	Secondary	Functional
Bole Lemi Industry Park	PA	484561.1	991036	Secondary	Functional
BGI Brewery	B5	471509	995971	Tertiary	Functional
East Africa Bottling	B7	476324.7	993758.6	Tertiary	Functional
Repi Soap & Detergent Factor	SD	465312.7	992601.4	NTP	—
National Alcohol& Liquor Factory	B1	471920.9	996258.5	Secondary	Functional
Balezaf Alcohol Factory	B2	460058	985902	Primary	Functional
Addis Ababa Tannery	T1	465752.8	1000334	Primary	Not functional
Dire Tannery	T5	467333.4	997704.1	Primary	Not functional
Ghion Berekina	G	468411	1001023	NTP	—

NTP = no treatment plant; primary = the waste is processed through a physical procedure with equipment and filtration; secondary = the waste is purified through biological processes using microorganisms; tertiary = includes removal of nutrients such as phosphorus and nitrogen, and practically all suspended and organic matter from wastewater

Table 2
Working principle of Palintest photometer 7500.

Parameter	Principle	Observed colour
NO_3^-	Diazonium- reduction of nitrate to nitrite and react with sulphanilic acid in the presence of N-(1-naphthyl)-ethylene diamine	Reddish dye
NO_2^-	Nitrite react with sulphanilic acid and couple with N-(1-naphthyl)-ethylene diamine	Reddish dye
Alkalinity	Colorimetric method carbonates/bicarbonates/ hydroxides/borates/phosphates/silicates etc. react with alkaphot indicator.	Blue
Hardness	Colorimetric method- calcium and magnesium ions react with hardicol indicator	Purple
NH_3	Ammonia reacts with salicylate in the presence of chlorine	Green blue
Cl^-	Chlorides react with silver nitrate to produce turbid insoluble silver chloride	Turbid
PO_4^{3-}	Phosphate reacts with ammonium molybdate, under acidic environment, to form phosphor-molybdic acid. Then it is reduced by ascorbic acid	Blue
SO_4^{2-}	Barium reacts with sulphate to form turbid insoluble barium sulphate	Turbid
S^{2-}	Sulphide reacts with diethyl-p-phenylene diamine and potassium dichromate	Blue

Table 3
Limits of detection and percentage recoveries of elements determined in the industrial wastewater samples using ICP-OES.

Element	Wavelength (nm)	LOD (μg/l)	Unspiked (μg/l)	Spiked (μg/l)	Recovery (%)
Fe	238	0.158	801.9	1584.6	97.6
Zn	206	0.033	293.9	592.8	101.7
Cu	327	0.009	49.6	96.9	95.4
Mn	258	0.096	807.8	1608.3	99.1
As	194	0.198	< 0.198	–	–
Pb	220	0.010	16.7	32.3	93.4
Cd		0.004	< 0.004	–	–
Cr	206	0.009	634.0	1295.3	104.3
Ni	232	0.023	18.8	36.8	95.7
Co		0.003	< 0.003	–	–

step before discharge to the environment. However, neither factory had wastewater treatment facilities during the time of sampling. Therefore, the observed differences may be attributed to the nature of the chemicals and technologies used for production by the two factories, as one is a bleach factory (G) and the other produces soap and detergents (SD). Furthermore, soap manufacturing does not involve many ionic chemicals, and the main ionic ingredient NaOH is neutralized in the saponification reaction. After Ghion Berekina (G), higher values of EC were recorded for the six tanneries (5680–16,930 μS/cm). The use of wastewater treatment processes appear to play a critical role in the EC pollution among the tanneries. Significantly higher EC values (one-way ANOVA, $p < 0.05$), compared to the other tanneries, were found in samples from Dire Tannery (T5) and Addis Ababa Tannery (T1), where their treatment facilities were not functional. Generally, the EC found in the effluents of the tanneries was higher than the values reported from different industries in Nigeria [6,35–37], while comparable to that reported for Hafde Tannery in Ethiopia [17] and also fall within the range of Vapi Industrial Area, India, [38] (Table 5).

Electrical conductivity is one of the most important parameters to be measured during wastewater quality monitoring. It indicates the salinity or total salt content of wastewater, and determines its suitability for irrigation and industrial reuse [3]. However, the level of EC of the wastewater discharge of most of the factories, except PA, B7, SD, B1 and B2, were beyond the recommended limits of irrigation water quality set by FAO (3000 μS/cm) (Table 4).

3.1.2. *Total dissolved solids*

The total dissolved solids (TDS) determined in the industrial wastewater samples were in the range of 287–15,410 mg/l. The lowest and the highest TDS values were recorded in wastewater from Repi Soap and Detergent Factory (SD) and Ghion Berekina (G), respectively. As both of these factories were discharging their wastewater without treatment, the high value of TDS might be due to differences in the nature and quantity of chemicals used.

The measured TDS values, in this study, are higher than those reported by Olugbuyiro [35] and James et al. [39] from Nigeria and various textile factories from Ethiopia [40] (Table 5). The TDS levels of all wastewater effluents from the tanneries (T1 - T6) and Ghion Berekina (G) were found to be above the ETHEPA limit (3000 mg/l), except Abyssinia Tannery (T4), the FAO Irrigation Water Quality Guidelines (2000 mg/l) and the USA Environmental Protection Agency (USEPA) (2100 mg/l). In contrast, all of the other types of factories were found to have TDS within the ETHEPA limit for industrial effluents. Total dissolved solid is a measure of all dissolved organic and inorganic substances in water and high TDS is toxic to aquatic life through increased salinity [41,42]. Excess levels of salinity have human and ecotoxicity including skin dehydration in animals and gives a laxative effect and

Table 4
Physicochemical characteristics of the wastewater samples from the studied factories. Values are mean ± standard deviation.

Code	EC (μS/cm)	TDS (mg/l)	pH	T (°C)	TA (mg/l)	TH (mg/l)
T6	**9220** ± 9.33	**4615** ± 3.17	8.24 ± 0.05	30.3 ± 1.05	1395 ± 5.23	**810** ± 3.64
T2	**8890** ± 15.55	**4481** ± 2.78	7.86 ± 0.09	22.8 ± 0.93	1215 ± 4.63	**720** ± 3.19
WW	1021 ± 3.24	511 ± 1.62	7.89 ± 0.05	20.4 ± 0.54	600 ± 2.7	120 ± 0.86
B3	**3840** ± 4.78	1922 ± 2.39	8.49 ± 0.07	28.7 ± 0.80	4080 ± 13.98	510 ± 2.75
PT	591 ± 4.88	296 ± 2.44	8.43 ± 0.07	16.7 ± 0.76	930 ± 3.81	165 ± 0.63
T3	**8750** ± 5.97	**4372** ± 2.985	8.35 ± 0.09	22.9 ± 0.93	1260 ± 4.70	**870** ± 3.22
T4	**5680** ± 5.11	**2831** ± 2.22	8.22 ± 0.06	22.9 ± 0.69	1620 ± 3.47	**900** ± 2.39
B6	**3840** ± 3.98	1912 ± 1.73	8.39 ± 0.04	24.1 ± 0.54	530 ± 2.70	210 ± 0.86
PA	1079 ± 3.35	538 ± 1.45	**9.81** ± 0.04	19.6 ± 0.46	370 ± 1.27	210 ± 0.57
B5	**3330** ± 3.27	1674 ± 1.42	8.43 ± 0.01	33.4 ± 0.44	3510 ± 2.22	**1904** ± 1.53
B7	2250 ± 4.67	1128 ± 2.03	8.05 ± 0.03	28.3 ± 0.64	2940 ± 3.18	**1500** ± 2.19
SD	574.7 ± 3.19	287 ± 1.38	7.88 ± 0.04	29.6 ± 0.43	285 ± 1.17	140 ± 0.50
B1	2120 ± 2.89	1064 ± 1.25	8.35 ± 0.39	26.4 ± 0.39	1080 ± 1.20	180 ± 0.36
B2	828.1 ± 5.46	414 ± 2.37	6.91 ± 0.07	27 ± 0.74	410 ± 0.72	420 ± 2.57
T1	**11,860** ± 6.54	**5940** ± 2.84	8.19 ± 0.08	17.2 ± 0.89	1620 ± 4.46	**2400** ± 6.08
T5	**16,930** ± 27.21	**8435** ± 3.13	8.24 ± 0.09	20.5 ± 0.98	3150 ± 4.91	**1425** ± 3.39
G	**30,800** ± 26.54	**154,10** ± 7.19	**12.6** ± 0.02	18.9 ± 1.44	2970 ± 7.19	480 ± 4.96
ETHEPA	–	*3000*	*6 – 9*	*40*	–	–
USEPA	–	*2100*	*6 – 9*	*40*	–	–
FAO	*3000*	*2000*	–	–	–	*200–600*

ETHEPA, Environmental Protection Agency of Ethiopia industrial wastewater discharging standards applied for all effluents. USEPA, USA Environmental Protection Agency. FAO, Irrigation Water Quality Guidelines. TA, total alkalinity. TH, total hardness. Values in bold are above the guideline limits.

unpleasant mineral taste to water. It also increases the osmotic pressure of soil water that leads to increased respiration rate thus declining the growth and yield of plants [43].

3.1.3. pH and temperature

The measured pH values were in the range of 6.91–12.6 across the different factories studied (Table 4). The highest pH was found in wastewater from Ghion Berekina (G), while the lowest was found in Balezaf Alcohol Factory (B2). The high pH of wastewater from Ghion Berekina (G) might be due to the absence of wastewater treatment by the factory as well as the production of basic salts like sodium hypochlorite and calcium hypochlorite as in bleaches.

Except for Ghion Berekina (G) and Bole Lemi Industry Park (PA), the pH values of the samples were, generally, within the limit values set by the Environmental Protection Agency of Ethiopia (ETHEPA) for industrial effluents discharge (pH = 6 to pH = 9). The pH value of water is an important factor affecting the productivity of aquatic ecosystems [1,44]. Moreover, pH affects the solubility of most metals in water, and also affects corrosion in piping installations of wastewater treatment plants. Hence it must be closely monitored during wastewater treatment operations [23].

The temperatures of the industrial wastewater effluents were in the range of 16.7–30.3 °C. The lowest temperature was recorded for Kadisco Paint Factory (PT), while the highest was in New Wing Addis Tannery (T6). The temperature of all wastewater samples investigated under this study are within the temperature range reported for different factories from various countries in the literature, except a liquor factory in Addis Ababa, Ethiopia, for which a temperature of 55 °C was reported [45]. Additionally, the temperatures of all the wastewater samples are within the standard limit set by the ETHEPA and USEPA (40 °C).

3.1.4. Total hardness and alkalinity

The hardness of water, which is expressed as milligrams of $CaCO_3$ equivalent per liter, signifies the quality of water mainly in terms of Ca^{2+} and Mg^{2+} (Table 4). The value of total hardness in the samples were in the range of 120 mg/l (central wastewater treatment plant (WW)) to 2400 mg/l (Addis Ababa Tannery (T1)). TH investigated in this study is higher than that reported (149 – 261 mg/l) for chemical producing industries in Sango-Ota, Ogun-State, Nigeria [36] (Table 5). The level of total hardness of effluents of all the tanneries (T1 - T6), BGI Brewery

Table 5
Physicochemical characteristics of wastewater effluents from different industries and countries.

Country	Industry	EC (μS/cm)	TDS (mg/l)	pH	T (°C)	TA (mg/l)	TH (mg/l)	References
Ethiopia	Ayka Addis Textile	5700–5710	—	7.8	30	—	—	[17]
	Meta Abo Brewery	5400–5450	—	4.5	18	—	—	
	Balezaf Alcohol and Liquors	2389–2390	—	4.5	25	—	—	
	Hafde Tannery	10450–10470	—	7.5	21	—	—	
	Sabata Agroindustry	5489–5490	—	7.7	30.1	—	—	
India	Textile industries	—	2931–17739	8.1–8.6	—	—	439–1308	[13]
Ethiopia	DH-GEDA Textile Factory	—	511.5 ± 3.5	7.97 ± 0.33	28.5 ± 0.1	—	—	[40]
	NOYA Textile Factory	—	183.5 ± 1.5	8.05 ± 0.25	27.0 ± 0.2	—	—	
	ALMHADI Textile Factory	—	501.5 ± 4.5	8.43 ± 0.01	24.6 ± 0.2	—	—	
	ALSAR Textile Factory	—	291.5 ± 0.5	7.89 ± 0.02	22.1 ± 0.1	—	—	
Nigeria	Paint Industries	149–881	490–2330	6.6–7.5	—	—	—	[6]
Palestine	Leather Industries	—	52,000	7.15	—	—	—	[47]
Ethiopia	Liquor Factory	80,000	34,900 ± 12.1	3.4 ± 0.03	55 ± 1	—	—	[45]
India	Vapi Industrial Area	2900–59,130	1943–39,643	5.04–8.05	27.9–29.0	—	—	[38]
India	Engineering Factory	—	433–922	6.8–7.4	27.1–30.5	—	—	[48]
	Paper Factory	—	1942–4392	7.01–8.98	28.3–33.9	—	—	
	Chemical Factory	—	825–3927	5.98–6.98	29.7–35.8	—	—	
	Dye Factory	—	3510–7910	5.46–7.91	26.3–31.9	—	—	
	Paint Factory	—	2002–6535	7.10–9.83	24.2–34.1	—	—	
	Pharmaceutical Factory	—	1950–4009	4.10–6.77	25.8–30.9	—	—	
	Textile Factory	—	8704–12,933	6.03–7.21	25.2–29.2	—	—	
	Petrochemical Factory	—	542–3920	5.10–8.04	28.3–33.4	—	—	
Nigeria	Various Industrial Effluents	18.6–349	0.02–141	1.71–4.91	27.0–35.4	—	—	[35]
Nigeria	Chemical Producing Industries	43.86–1927	21.24–956.4	5.48–10.35	31.0–33.5	412.5–1233	148.5–261.0	[36]
Nigeria	Pharmaceutical Industries	199–413	134–277	4.7–7.2	—	30—40	—	[39]

(B5) and East Africa Bottling (B7) are above the maximum limits of irrigation water quality guideline set by FAO (600 mg/l). It indicates that the wastewater is hard and should be softened before being discharged into the receiving water bodies. The increase in the magnitude of total hardness is probably owing to the presence of non-carbonate and carbonate compounds [46]. It causes an increased alkalinity and pH in the neighboring environments.

The total alkalinity (TA) levels found in the samples were in the range of 370–4080 mg/l $CaCO_3$. The TA of most of the effluents samples are comparable with the TA value of discharges of chemical producing industries in Nigeria (412–1233 mg/l $CaCO_3$) reported by Osobamiro and Atewolara-Odule (2015) [36]. Whereas, these measured TA values are far greater than that reported (30–40 mg/l $CaCO_3$) for effluents from pharmaceutical industries in Sango Industrial Area of Ogun State, Nigeria [39]. High TA values were found in effluents from the two breweries included in the study, Heineken Brewery (B3) and BGI Brewery (B5). Both of these factories had a tertiary treatment plant that was functional. Hence, the high TA found in the effluents may be due to the use of NaOH in washing bottles for reuse, as this is the practice commonly used in Ethiopia.

3.2. Concentrations of nutrients in the industrial wastewaters

As was the case for physicochemical characteristics, the concentrations of nutrients found in the wastewater discharge varied greatly across the different factory sites (Table 6).

3.2.1. Nitrate and nitrite

The concentration of NO_3^- varied from 0.61 to 32.54 mg/l, except Bole Lemi Industry Park (PA) which was below detection limit (Table 6). The highest concentration of NO_3^- was found in wastewater effluent from the Heineken Brewery (B3), which was 53 times higher than the lowest value detected from the Batu Tannery (T2). The concentration of NO_3^- found in all of the effluent samples, except from the Heineken Brewery, are within the range reported for various textile factories from Ethiopia [40]. Additionally, the concentrations of NO_3^- in this study were lower than the highest value reported for Vapi industrial area, India [38]. However, the values of NO_3^- investigated from WW, B3, PT, T1, T3, T4, T5, B6 and G were higher than reported from Pharmaceutical Industries in Nigeria [39].

Besides from the Heineken Brewery, the concentrations of NO_3^- in all the factories' wastewater effluent were within the maximum limit set by the ETHEPA and USEPA (20 mg/l). Nitrate contamination deteriorates water quality, and causes eutrophication and algal blooms [49]. In addition, high concentration of nitrate in drinking water can cause disease to humans and animals, such as methemoglobinemia, diabetes, spontaneous abortions, thyroid problems and cancer [50,51]. The toxicity of nitrate to humans is mainly due to its reduction to nitrite, which causes the oxidation of ferrous in haemoglobin to the ferric ion, where oxygen delivery will be impaired [52]. Another mechanism of toxic action is through its conversion into nitric oxide, which is potentially mutagenic and carcinogenic [53] in the body by the action of bacteria in the tongue and further reactions with ascorbic acid in gastric juice. Nitrate can become a health hazard to babies if they ingest water that contains relatively low concentrations (10 mg/l N) of nitrate. The ingested nitrate interferes with oxygen in the blood of babies, the result being methemoglobinemia or "blue baby syndrome" [54].

Nitrite levels found in the samples ranged from of 0.03–4.28 mg/l. The highest was found in the Abissinia Tannery (T4), while the lowest in the Kadisco Paint Factory (PT). Nitrite is added to some industrial process water as a corrosion inhibitor. It can also be formed from the reduction of nitrate in the presence of high organic matter pollution at oxygen deficient conditions in water [7].

3.2.2. Ammonia and ammonium

The ammonia content of the samples was in the range of 0.05–4.95 mg/l, except at the Kadisco Paint Factory where it was not detected. The maximum concentration measured was in the wastewater discharge from Dire Tannery (T5), while the minimum was from the Akaki Kality central wastewater treatment plant (WW). The NH_3 content of samples was significantly lower than the levels (19.4–670 mg/l) reported for different factories from Ethiopia [17] and Palestine [47] (Table 6). Furthermore, the levels of ammonia found in all of the samples were below the permissible limit (5 mg/l) set for industrial effluents by the ETHEPA.

Observations of NH_4^+ were similar to that of NH_3; the concentration of NH_4^+ was in the range of 0.05–5.31 mg/l. The maximum (5.31 mg/l) and minimum (0.01 mg/l) concentrations were found in samples from the Dire Tannery (T5) and the Akaki Kality wastewater treatment plant (WW), respectively. Also, NH_4^+ was not quantified in the wastewater sample from the Kadisco Paint Factory. Since the pKa of NH_4^+ is 9.26, most NH_3 in water is expected to be present as NH_4^+ rather than as NH_3. However, as the pH of the wastewater samples were in slightly basic region, and hence NH_4^+ and NH_3 were found in comparable concentrations.

Table 6
Concentration (mg/l) of nutrients determined in the wastewater effluents from the studied factories. Values are mean ± standard deviation.

Code	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	NH_3	NH_4^+	Cl^-	S^{2-}
T6	0.97 ± 0.02	0.7 ± 0.031	1.26 ± 0.011	175 ± 10.33	0.50 ± 0.018	0.50 ± 0.019	38 ± 1.245	0.11 ± 0.002
T2	0.40 ± 0.01	0.61 ± 0.015	0.9 ± 0.001	165 ± 9.168	1.62 ± 0.009	1.71 ± 0.001	40 ± 1.623	0.02 ± 0.001
WW	1.24 ± 0.05	10.07 ± 0.077	**36 ± 2.001**	21 ± 0.84	0.01 ± 0.047	0.01 ± 0.052	24 ± 3.113	0.07 ± 0.006
B3	1.03 ± 0.03	**32.54 ± 2.046**	**112 ±** 13.22	34 ± 4.504	0.40 ± 0.028	0.40 ± 0.029	22 ± 1.868	0.17 ± 0.004
PT	0.03 ± 0.01	11.88 ± 1.015	1.5 ± 0.002	3 ± 0.168	Trace	Trace	19 ± 0.623	0.07 ± 0.001
T3	0.48 ± 0.01	13.34 ± 1.153	1.26 ± 0.010	185 ± 11.163	0.05 ± 0.009	0.05 ± 0.001	44 ± 2.622	0.09 ± 0.001
T4	4.28 ± 0.17	10.21 ± 1.260	1.53 ± 0.012	155 ± 12.86	0.35 ± 0.161	0.40 ± 0.172	36 ± 4.584	0.16 ± 0.021
B6	0.06 ± 0.04	11.94 ± 1.061	**25.6±** 6.176	185 ± 8.673	0.05 ± 0.038	0.05 ± 0.047	34 ± 2.490	0.06 ± 0.005
PA	0.14 ± 0.01	Trace	11.7 ± 0.410	155 ± 10.168	0.54 ± 0.010	0.58 ± 0.013	42 ± 3.623	0.06 ± 0.001
B5	0.74 ± 0.05	2.47 ± 0.076	**26.1 ± 2.130**	138 ± 6.841	0.56 ± 0.047	0.59 ± 0. 056	11 ± 3.113	0.65 ± 0.006
B7	0.33 ± 0.01	1.73 ± 0.015	2.79 ± 0.007	56 ± 2.168	0.50 ± 0.009	0.53 ± 0.010	12 ± 0.522	0.22 ± 0.001
SD	0.27 ± 0.01	2.16 ± 0.015	0.56 ± 0. 153	11 ± 0.169	0.58 ± 0.011	0.62 ± 0.023	9.0 ± 0.643	0.09 ± 0.001
B1	0.23 ± 0.01	1.4 ± 0.015	1.05 ± 0.060	34 ± 1.167	0.58 ± 0.009	0.62 ± 0.023	9.8 ± 0.523	0.17 ± 0.001
B2	0.97 ± 0.10	0.91 ± 0.161	6.21 ± 1.333	58 ± 2.682	0.94 ± 0.094	1.00 ± 0.099	8.8 ± 0.226	0.21 ± 0.012
T1	1.53 ± 0.20	6.12 ± 0.306	**10.9** ± 1.453	**1360 ± 33.364**	2.97 ± 0.189	3.15 ± 0.276	25 ± 1.245	1.44 ± 0.025
T5	3.38 ± 0.08	9.36 ± 0.723	**15.3 ± 3.561**	**1140 ± 21.346**	4.95 ± 0.076	5.31 ± 0.088	14 ± 4.980	1.08 ± 0.010
G	1.40 ± 0.09	7.65 ± 0.138	5.13 ± 0.505	155 ± 19.513	1.44 ± 0.085	1.53 ± 0.089	30 ± 1.603	0.04 ± 0.011
ETHEPA	*–*	*20*	*10*	*1000*	*5*	*–*	*1000*	*2*
USEPA	*–*	***20***	***10***	*1000*	*20*	*–*	*–*	*2*

ETHEPA = Environmental Protection Agency of Ethiopia: industrial wastewater discharging standards applied for all effluents. USEPA, USA Environmental Protection Agency. Trace = Not quantified. Values in bold are above the guideline limits.

3.2.3. Phosphate

The amount of PO_4^{3-} varied from 0.56 to 112 mg/l; the lowest concentration was measured in the Repi Soap & Detergent Factory (SD) and the highest was from the Heineken Brewery (B3). Levels of PO_4^{3-} in the Heineken Brewery (B3), BGI Brewery (B5), Moha Soft Drinking Factory (B6), Addis Ababa Tannery (T1) and Dire Tannery (T5), as well as the Bole Lemi Industry Park (PA) and the Akaki-Kality wastewater treatment plant (WW), were found above the standard limit (10 mg/l) set by the ETHEPA and USEPA. The levels of PO_4^{3-} determined in this study are lower than the upper limit reported for Vapi industrial area of India (7–87 mg/l) (Table 6). High concentrations of PO_4^{3-} is detrimental to water bodies as it causes eutrophication, and hence lead to extermination of aquatic life. The eutrophication of surface water is due to an increased growth of algae and aquatic weeds, with a subsequent oxygen shortage. Although nitrogen and carbon are also essential to the growth of aquatic biota, most attention has been focused on phosphorus inputs. The process of water eutrophication depends not only on nutrient concentrations, but also on their ratio. A C:N:P ratio of 40:7:1 favours eutrophication; hence, phosphorus is often the limiting element and its control is of prime importance in reducing the accelerated eutrophication of fresh waters [55]. Ingestion of high levels of phosphorus interferes with the metabolism of calcium and results in bone loss in both humans and animals. Thus, these factories should work towards reducing their PO_4^{3-} release to the environment.

3.2.4. Sulfate and sulfide

The most abundant nutrient ion found in the wastewater effluent samples was SO_4^{2-}. The measured concentrations were in the range of 3–1360 mg/l. The highest SO_4^{2-} was measured in the wastewater released from Addis Ababa Tannery, a level of risk to human health. Bezuneh & Kebede [45] reported a mean value of SO_4^{2-} (2500 ± 8.9 mg/l) in wastewater of the Liquor Factory in Ethiopia. Besides, Nirgude et al. [38] reported highest SO_4^{2-} concentration of 2789 mg/l in Vapi Industrial Area in India. Both values are substantially greater than those found in this study (Table 6). However, the SO_4^{2-} concentration of most of the samples determined in this study were significantly higher than the level reported for effluents of pharmaceutical industries in Nigeria (Table 7). The concentration of SO_4^{2-} found in all of the samples, except in the Addis Ababa Tannery (T1) (1360 ± 33 mg/l) and the Dire Tannery (T5) (1140 ± 21 mg/l), are below the industrial discharge limit set by the ETHEPA and USEPA (1000 mg/l). At high levels, SO_4^{2-} can give water a bitter or medicinal taste and can have laxative effects. People who are not used to drinking water with high sulfate can get diarrhea and dehydration, with infants often being more sensitive to sulfate than adults. Aquatic or terrestrial animals are also sensitive to high levels of sulfate. In young animals, high levels may be associated with severe, chronic diarrhea and even death [55]. Hence, both the Addis Ababa Tannery (T1) and the Dire Tannery (T5) should employ wastewater treatment systems to remove SO_4^{2-}, before discharging to the environment.

Levels of S^{2-} found in the samples varied similarly in the range of 0.02–1.44 mg/l, with the highest recorded for wastewater samples from the Addis Ababa Tannery (T1). The measured concentrations of S^{2-} are within the range of 0.22 – 2.29 mg/l and 0.01–1.94 mg/l reported for various textile factories from Ethiopia [40] and Chemical Producing Industries from Nigeria [39], respectively. The levels of sulfide determined in this study are within the 2 mg/l limit as prescribed by industrial wastewater discharge standard of the ETHEPA and USEPA.

3.2.5. Chloride

Chloride contained in wastewater is due to the use of substances such as HCl, HOCl and Cl_2 gas during different processes. For most of the samples, chloride was found to be the second most abundant anion after SO_4^{2-}. The amount of Cl^- varied from 8.8 to 44 mg/l. The lowest and the highest concentrations were measured in wastewater from the Balezaf Alcohol Factory (B2) and the Awash ELICO Tannery (T3), respectively. The amount of Cl^- found in the samples is lower than the amounts reported for different factories from different countries (Table 7). In addition, the measured values are within the standard limits set by the ETHEPA for industrial wastewater discharge (1000 mg/l). Chloride toxicity has not been observed in humans except in the special case of impaired sodium chloride metabolism, e.g., in congestive heart failure [16]. This anion is a crucial parameter in industrial effluents that affects agricultural crop productivity [57]. It kills the microorganisms in water and disturbs the aquatic food chain, increases corrosiveness and may cause adverse health effects to humans [56]. Fig. 2.

3.2.6. Cluster analysis

Hierarchical cluster analysis based on the squared Euclidean distance was performed to identify groups of factories with similar polluting

Table 7
Concentration (mg/l) of nutrients in wastewater effluents from different factories and countries. Values are mean ± standard deviation.

Country	Industry	NO_3^-	PO_4^{3-}	SO_4^{2-}	NH_3	Cl^-	S^{2-}	References
Ethiopia	Ayka Addis Textile	—	—	—	28	—	—	[17]
	Meta Abo Brewery	—	—	—	68	—	—	
	Balezaf Alcohol and Liquors	—	—	—	60	—	—	
	Hafde Tannery	—	—	—	670	—	—	
	Sabata Agroindustry	—	—	—	28	—	—	
India	Textile industries	—	—	—	—	819–4780	—	[13]
Ethiopia	DH-GEDA Textile Factory	8.50 ± 2.90	1.99 ± 1.45	72 ± 33	2.94 ± 2.56	—	2.29 ± 1.84	[40]
	NOYA Textile Factory	9.55 ± 0.05	0.40 ± 0.10	ND	0.50 ± 0.10	—	0.80 ± 0.01	
	ALMHADI Textile Factory	10.55 ± 8.05	0.56 ± 0.26	6.0 ± 4.0	2.23 ± 0.53	—	0.13 ± 0.09	
	ALSAR Textile Factory	19.8 ± 11.1	10.85 ± 3.15	143 ± 42	13.63 ± 1.38	—	0.22 ± 0.18	
Nigeria	Paint Industries	—	—	—	—	63.8–733.8	—	[6]
Palestine	Leather Industries	—	—	—	19.4	43,100	—	[47]
Ethiopia	Liquor Factory	—	—	2500 ± 8.9	—	—	—	[45]
India	Vapi Industrial Area	2.0–345	7–87	125–2789	—	156–4400	—	[38]
India	Engineering Factory	—	—	—	—	167–218	—	[48]
	Paper Factory	—	—	—	—	125–181	—	
	Chemical Factory	—	—	—	—	162–241	—	
	Dye Factory	—	—	—	—	190–273	—	
	Paint Factory	—	—	—	—	200–245	—	
	Pharmaceutical Factory	—	—	—	—	205–261	—	
	Textile Factory	—	—	—	—	218–250	—	
	Petrochemical Factory	—	—	—	—	181–241	—	
Nigeria	Various Industrial Effluents	—	—	2.8–34.3	—	—	—	[35]
Nigeria	Chemical Producing Industries	—	—	—	—	66.84–1321	0.01–1.94	[36]
Nigeria	Pharmaceutical Industries	1.52–3.31	0.08–0.16	7.0–14	—	10—18	—	[37]

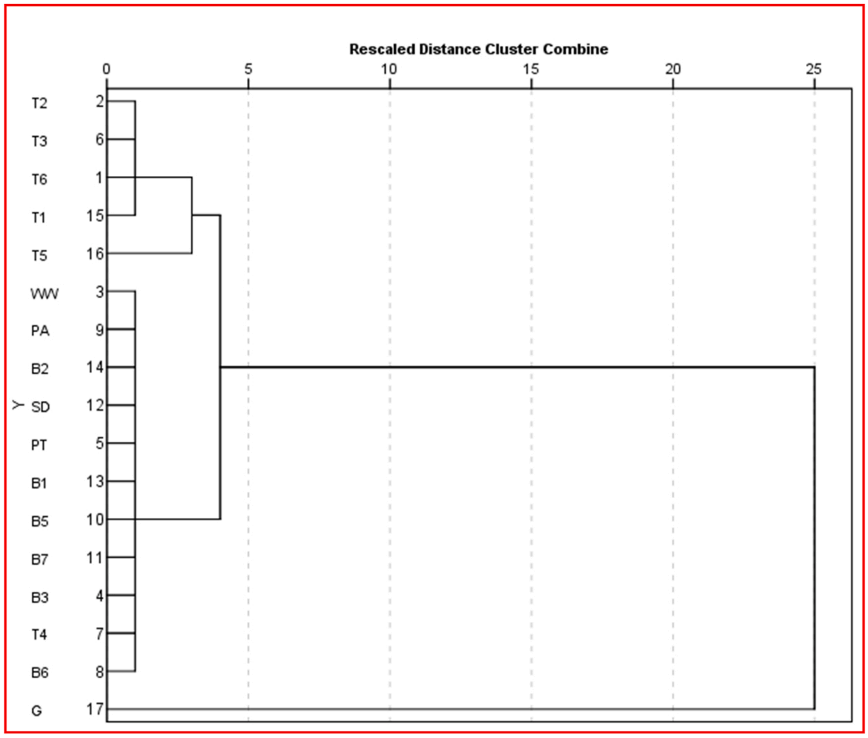

Fig. 2. Dendrogram obtained from hierarchical cluster analysis of the studied factories based on the physicochemical characteristics of their wastewater effluents.

status, with respect to the physicochemical properties and concentrations of nutrients present in their wastewater. As shown in the dendrogram (Fig. 3), the factories can be categorized into three groups, as tanneries, other factories and the bleach factory (G, Ghion Berekina). Out of the six tanneries included in the study, five showed similar characteristics in their wastewater, while one tannery (Abissinia Tannery (T1)) behaved similarly as the other types of factories.

3.3. Discriminant analysis

Linear discriminant analysis (LDA) was performed on the three groups identified in the cluster analysis, in order to identify those physicochemical characteristics and nutrients that best discriminate among the groups. As shown in the scores plot in Fig. 4a, 100% of the wastewater samples were correctly classified into the three groups of factories. Two discriminant functions were computed (Table 8a), and the first function discriminated the bleach from the tanneries and other factories. This function is more influenced by EC and TDS, which loaded more to the negative side of the function. Hence, the bleach factory is differentiated from the tanneries and other factories (Fig. 3a) due to the higher EC and TDS in their wastewaters.

The second discriminant function created distinctive separation of tanneries from the other factories. This function is highly influenced to the positive side by TDS and EC (Table 8a). Hence, comparing Table 8a and Fig. 4a, it can be concluded that wastewater discharged from tanneries is characterized by higher TDS and EC than the other factories,

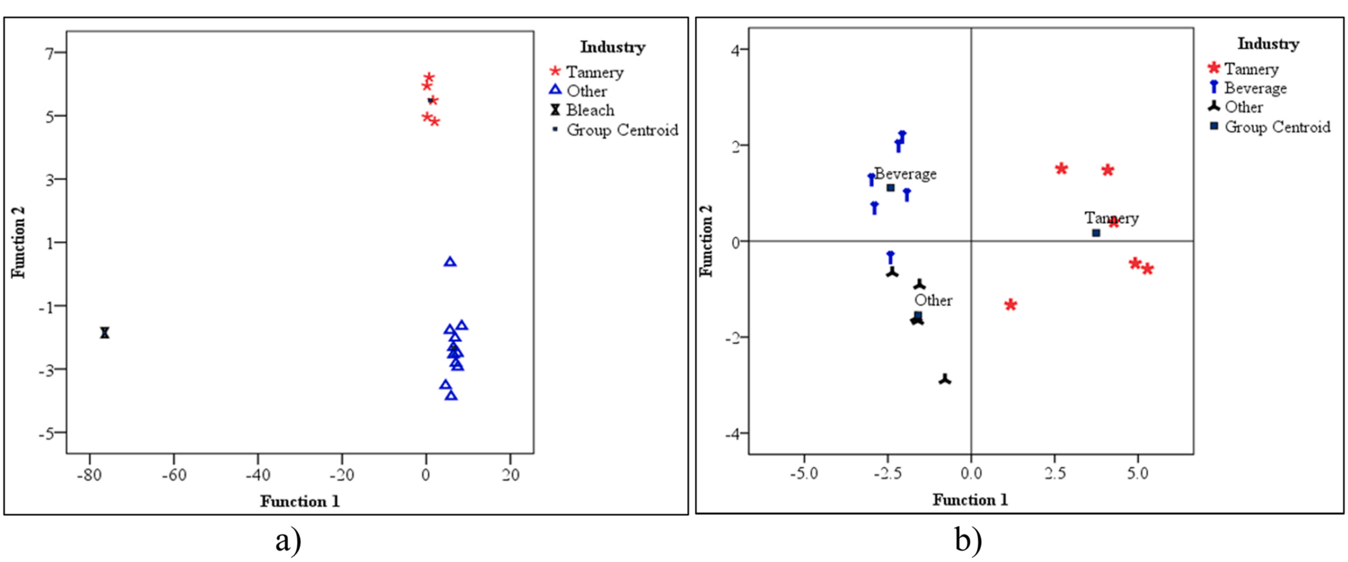

Fig. 3. Scatter plot of the wastewater samples on the plane of the two discriminant function scores obtained from the linear discriminant analysis of the different factories based on the physicochemical characteristics and nutrients (a) and heavy metals (b) in their wastewater effluents.

Table 8
Canonical function coefficients obtained from the linear discriminant analysis of the three groups of factories based on the physicochemical (a) and heavy metal (b) characteristics of their wastewater effluents.

Parameters	a		Parameter	b	
	Function			Function	
	1	2		1	2
pH	-0.089	-0.082	Cr	0.509	0.186
TDS	-0.144	0.382	Pb	-0.257	-0.232
EC	-0.144	0.379	Mn	0.150	0.057
SO_4^{2-}	-0.002	0.208	Fe	-0.100	0.582
NH_4^+	-0.015	0.182	Cu	0.007	0.373
NH_3	-0.010	0.181	Ni	0.092	0.331
TH	0.002	0.137	Zn	-0.060	0.287
S^{2-}	0.005	0.128	–	–	–
Cl^-	-0.009	0.115	–	–	–
PO_4^{3-}	0.006	-0.063	–	–	–
Temp.	0.015	-0.053	–	–	–
NO_2^-	-0.005	0.049	–	–	–
NO_3^-	0.000	-0.026	–	–	–
T.A	-0.014	0.015	–	–	–

Temp. (°C) and EC (μs/cm), all physicochemical parameters are in mg/l and heavy metals in μg/l; T.A = total alkalinity; T.H = total hardness.

except the bleach factory.

3.4. Concentrations of elements

The concentrations of the elements Fe, Mn, Cr, Co, Ni, Cu, Zn, Cd, Pb and As were also determined in the wastewater samples (Table 9). Serious pollution by the potentially toxic elements was observed in the discharges from the Addis Ababa Tannery (T1) and the Dire Tannery (T5). Wastewater from these two factories contained significantly high concentrations of Fe, Zn, Mn, Cu and Cr, above the maximum limits set by the ETHEPA and USEPA. This, especially compared to the other tanneries, may be explained from the wastewater treatment facilities of the two factories, which were not functional during the time of sampling.

Batu Tannery (T2) for Mn, New wing Addis Tannery (T6) and Ghion Berekina (G) for Cr also violated the maximum limits of the ETHEPA and USEPA standards. Despite the presence of a functional tertiary level treatment plant, the wastewater discharge from the BGI Brewery (B5) violated the maximum standard limits of the ETHEPA and USEPA in Fe, Mn and Cu concentrations. Additionally, the effluents from the BGI Brewery contained the highest levels of Ni (45.4 ± 0.13 μg/l) and Pb (40.4 ± 1.1 μg/l), but all of them were within the upper limits of the ETHEPA and USEPA. The other brewery included in the study, the Heineken Brewery (B3), which was also using wastewater treatment at the tertiary level, did not show such pollution problems in its wastewater discharge. Among the studied trace metals Cd, Co and As were not detected in any of the wastewater samples.

The highest concentrations of Cu, Fe and Zn were found in wastewater effluents from the Dire Tannery (T5), and Mn from the Batu Tannery (T2). These trace metals are toxic when they are ingested into living organisms in a relatively high concentration or bio-accumulate in the human organ system [19,58–60]. Out of the six sampled tanneries, the wastewater discharge from the Addis Ababa Tannery (T1), the Dire Tannery (T5) and the New Wing Addis Tannery (T6) as well as Ghion Berekina (G), were found to be highly contaminated with Cr metal, which is commonly used in tanning, where all of them were found to be above the upper limit of the ETHEPA industrial wastewater discharge (2.0 mg/l). Chromium is highly toxic to living organisms including humans [19,61].

4. Conclusions and recommendation

In this study, the physicochemical parameters, nutrients and concentrations of selected heavy metals in industrial discharges were investigated. All of the factories included in this study, violated the regulatory limit for one or more pollutants set by the Environmental Protection Agency of Ethiopia, the Environmental Protection Agency of USA and the United Nations Food and Agricultural organization. Some of the factories were found to release wastewater that is high in EC, TDS, pH and total hardness. Among the nutrients, only a few samples contained NO_3^-, PO_4^{3-} and SO_4^{2-} with values above the maximum permissible limits set by the USEPA and ETHEPA. The Addis Ababa Tannery (T1) and the Dire Tannery (T5) contained Fe, Mn, Cr, Cu and Zn with concentrations exceeding the maximum limits of the standards. Levels of Fe, Mn and Cu in the BGI Brewery (B5) were also above the limits set by the USEPA and/ or ETHEPA. Considering the results of this study and the likely presence of toxic organic solvents, which were not included in the study, there is a need for serious action from all stakeholders, including regulatory bodies, to enforce rules and regulations relating to permissible discharges, and for industries to control their pollution with appropriate treatment systems. Such needs to be complemented by systematic sampling and monitoring campaigns in rivers and waterbodies to understand and quantify the levels of pollution, and to better target management and mitigation measures. To this effect, the findings

Table 9
The concentrations of some trace metals (μg/l) determined in the wastewater effluent samples from the studied factories. Values are mean ± standard deviation.

Code	Fe	Mn	Cr	Co	Ni	Cu	Zn	Cd	Pb	As
T1	**17810.2 ± 4.36**	**6279.1 ± 4.49**	**2007.0 ± 8.32**	–	38.07 ± 0.09	**2132.0 ± 0.51**	**5130.3 ± 0.78**	–	6.32 ± 0.74	–
T2	2431.0 ± 1.36	**8235.0 ± 35.33**	1347.2 ± 2.11	–	17.26 ± 0.11	30.50 ± 0.12	177.60 ± 0.31	–	13.44 ± 2.3	–
T3	801.9 ± 2.34	807.8 ± 4.79	634.0 ± 3.6	–	18.82 ± 0.18	49.63 ± 0.39	293.9 ± 1.13	–	16.69 ± 0.654	–
T4	5414.0 ± 27.90	246.6 ± 3.40	1332.0 ± 7.32	–	27.12 ± 0.146	170.90 ± 1.80	771.10 ± 3.75	–	6.74 ± 1.73	–
T5	**20570.1 ± 3.25**	**7069.2 ± 2.60**	**2010.0 ± 6.52**	–	30.09 ± 0.04	**2215.0 ± 0.77**	**5170.7 ± 0.91**	–	4.15 ± 0.79	–
T6	2959.1 ± 4.36	579.2 ± 3.59	**2015.0 ± 7.62**	–	31.08 ± 0.08	112.0 ± 0.49	497.6 ± 0.90	–	5.12 ± 0.84	–
B1	1285.0 ± 16.82	55.65 ± 0.196	36.01 ± 0.345	–	17.05 ± 0.127	28.52 ± 0.11	160.7 ± 0.39	–	5.45 ± 0.68	–
B2	9749.0 ± 7.05	541.70 ± 4.06	34.84 ± 0.17	–	18.23 ± 0.04	30.70 ± 0.12	1960.3 ± 0.29	–	20.97 ± 0.46	–
B3	9875.0 ± 38.65	88.20 ± 0.52	87.42 ± 9.70	–	16.74 ± 0.126	47.57 ± 0.08	220.1 ± 0.77	–	11.50 ± 0.60	–
B5	**10,410.0 ± 25.58**	**5187.7 ± 2.46**	120.8 ± 0.58	–	45.39 ± 0.134	**2059.2 ± 1.43**	1866.0 ± 18.17	–	40.41 ± 1.11	–
B6	1100.0 ± 8.46	54.25 ± 0.15	31.10 ± 0.12	–	19.98 ± 0.17	57.95 ± 0.11	357.9 ± 0.69	–	29.49 ± 0.285	–
B7	9530.0 ± 16.35	257.60 ± 0.23	180.20 ± 9.12	–	31.87 ± 0.03	352.60 ± 2.45	2040.0 ± 15.16	–	< 0.01	–
SD	500.0 ± 2.32	44.23 ± 0.24	42.79 ± 1.19	–	16.10 ± 0.07	40.65 ± 0.21	457.9 ± 0.70	–	26.07 ± 0.55	–
PA	508.5 ± 2.08	207.9 ± 0.85	45.13 ± 0.154	–	19.19 ± 0.237	62.40 ± 0.17	420.50 ± 2.64	–	39.94 ± 0.57	–
WW	899.6 ± 3.74	354.8 ± 1.18	68.03 ± 3.89	–	18.11 ± 0.11	27.64 ± 0.27	298.3 ± 0.92	–	17.32 ± 0.45	–
PT	272.1 ± 0.55	66.98 ± 0.86	33.67 ± 1.49	–	11.95 ± 0.19	22.05 ± 0.13	134.70 ± 1.10	–	17.32 ± 0.50	–
G	570.5 ± 3.44	55.32 ± 0.29	**2054.0 ± 1.20**	–	24.10 ± 0.17	851.56 ± 0.31	477.9 ± 0.85	–	25.28 ± 0.65	–
ETHEPA	*10000*	*5000*	*2000*	*1000*	*3000*	*2000*	*5000*	*1000*	*500*	*250*
USEPA	*10000*	*10000*	*2000*	–	*1000*	*2000*	*5000*	*300*	*1000*	*500*

ETHEPA, Environmental Protection Agency of Ethiopia: industrial wastewater discharging standards applied for all effluents. USEPA, USA Environmental Protection Agency. – = Co < 0.003, Cd < 0.004 and As < 0.198. Values in bold are above the guideline limits.

from this study may provide invaluable information and concrete scientific data for government, policy makers, and environmentalists.

Author statement

The work does not involve the use of human or animal subjects, and hence ethical consideration is not required. As corresponding author, I confirm that the manuscript has been read and approved for resubmission by all the named authors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Author contributions

All authors contributed to the work presented in the manuscript.

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