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

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Handling Editor: Dr. Lawrence Lash

Keywords:
Addis Ababa
Effluents
Heavy metals
Nutrients
Photometer 7500
ICP-OES

ARTICLE INFO

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
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 discharges 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 on risk 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°040 E and covers around 1500 km². 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 area [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%), HNO₃ (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% HNO₃ 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 (NH₃, NO₂, NO₃, PO₄, SO₄²⁻, 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 solutions were made in a 0.5% HNO₃ using high-purity water (18.2 MΩ/cm).
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 varied 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 treatment plant | Status of treatment plant |
|-----------------|------|-------------|--------------------------|--------------------------|
| New wing Addis Tannery | T6 | 474790.9 988794.9 | Secondary | Functional |
| Batu Tannery | T2 | 473428 987287.1 | Secondary | Functional |
| Akaki Kality wastewater Tannery | WW | 473124.1 986011.5 | Tertiary | Functional |
| Heineken Brewery | B3 | 471447.5 994821.7 | Tertiary | Functional |
| Kadisco Paint Factory | PT | 473415 986989 | Secondary | Functional |
| Ashwa ELICO Tannery | T3 | 473964.8 989395.3 | Secondary | Functional |
| Abisnisia 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 Factory National | SD | 465312.7 992601.4 | NTP | — |
| Alcohol & Liquor Factory Balezaf | B2 | 460058 985902 | Primary | Functional |
| Alcohol Factory 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 |
|-----------|-----------|-----------------|
| NO₃ | Diazonium- reduction of nitrate to nitrite and react with sulphonic acid in the presence of N-(1-naphthyl)-ethylenediamine | Reddish dye |
| NO₂ | Nitrite react with sulphonic acid and couple with N-(1-naphthyl)-ethylenediamine | Reddish dye |
| Alkalinity | Colorimetric method carbonates/bicarbonates/ hydroxides/borates/phosphates/silicates etc. react with alkalophot indicator. | Blue |
| Hardness | Colorimetric method calcium and magnesium ions react with hardicol indicator. | Purple |
| NH₃ | Ammonia reacts with salicylate in the presence of chlorine. | Green blue |
| Cl⁻ | Chlorides react with silver nitrate to produce turbid insoluble silver chloride | Turbid |
| PO₄³⁻ | Phosphate reacts with ammonium molybdate, under acidic environment, to form phosphor-molybdic acid. Then it is reduced by ascorbic acid | Blue |
| SO₄²⁻ | Barium reacts with sulphate to form turbid insoluble barium sulphate | Turbid |
| S²⁻ | 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) | 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      | 206             | 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      | 232             | 0.003      | < 0.003      | —            | —            |

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 Olugbuyojo [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
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 CaCO3 equivalent per liter, signifies the quality of water mainly in terms of Ca2+ and Mg2+ (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
3.2. Concentrations of nutrients in the industrial wastewaters

As was the case for physicochemical characteristics, the concentrations of nutrients found in the wastewater discharges 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 for the 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 the effluent samples, except from the Heineken Brewery, were 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 intestine 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 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) 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$_4^+$ in water is expected to be present as NH$_3$ rather than as NH$_4^+$. However, as the pH of the wastewater samples were in slightly basic conditions, 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$_3^-$ | NO$_2^-$ | 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 | 0.06 ± 0.011 | 185 ± 11.163 | 0.05 ± 0.009 | 0.05 ± 0.001 | 44 ± 2.622 | 0.09 ± 0.001 |
| T4   | 3.28 ± 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 ± 0.176 | 185 ± 8.073 | 0.05 ± 0.038 | 0.05 ± 0.047 | 34 ± 2.940 | 0.06 ± 0.005 |
| PA   | 0.14 ± 0.01 | Trace | Trace | 11.7 ± 0.410 | 15.5 ± 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 ± 0.133 | 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 ± 1.169 | 0.58 ± 0.011 | 0.62 ± 0.022 | 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 | 20 | 1000 | 2 |
3.2.3. Phosphate

The amount of \(\text{PO}_4^{3-}\) 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 \(\text{PO}_4^{3-}\) 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 \(\text{PO}_4^{3-}\) 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 \(\text{PO}_4^{3-}\) are 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 the mineralization of fresh waters [55]. Ingestion of high levels of phosphorus in human diet can give rise to adverse health effects to humans [56]. Chloride 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 the biological treatment systems to remove \(\text{SO}_4^{2-}\) before discharging to the environment.

Levels of \(\text{SO}_4^{2-}\) 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 \(\text{SO}_4^{2-}\) 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 sulfate 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 \(\text{SO}_4^{2-}\). 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

| 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|            |
| Ethiopia        | DH-GEDA Textile Factory         | 6.50 ± 2.90 | 1.99 ± 1.45 | 72 ± 33    | 819–4780|       |        | [13]       |
|                 | NOVA Textile Factory            | 1.00 ± 0.05 | 0.40 ± 0.10 | 819–4780   |         |       |        |            |
|                 | ALMIHADI Textile Factory        | 10.55 ± 8.05 | 0.56 ± 0.26 | 819–4780   |         |       |        |            |
|                 | ALSAR Textile Factory           | 9.55 ± 10.11 | 13.85 ± 3.15 | 819–4780   |         |       |        |            |
| Nigeria         | Paint Industries                |         |             |             | 19.4    | 43,100|        | [6]        |
| Palestine       | Leather Industries              |         |             |             |         | 43,100|        | [17]       |
| 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    |         |             |             |         |       |        | [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]       |
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.

![Dendrogram](image1.png)

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

![Scatter plots](image2.png)

**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.
Serious pollution by the potentially toxic elements was observed in the two factories, which were not functional during the time of sampling. Except the bleach factory, the three groups of factories based on the physicochemical and heavy metal characteristics of their wastewater effluents.

### 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.

### Table 9

| 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 ± 3.16 | 8235.0 ± 35.33 | 1347.2 ± 2.11 | – | 17.26 ± 0.11 | 30.50 ± 0.16 | 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 ± 0.65 | – |
| T4   | 5414.0 ± 27.90 | 246.6 ± 3.40 | 1332.0 ± 7.32 | – | 27.12 ± 0.146 | 170.90 ± 0.80 | 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 | 497.60 ± 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 | 1906.3 ± 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 ± 2.4 | 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 | 31.0 ± 0.12 | – | 19.98 ± 0.17 | 57.95 ± 0.11 | 357.9 ± 0.69 | – | 29.49 ± 0.285 | – |
| B7   | 9330.0 ± 16.35 | 257.60 ± 0.92 | 180.20 ± 9.12 | – | 31.87 ± 0.03 | 352.60 ± 2.45 | 2040.1 ± 15.16 | – | < 0.01 | – |
| SD   | 500.0 ± 2.32 | 44.23 ± 0.24 | 42.79 ± 3.19 | – | 16.10 ± 0.07 | 40.65 ± 0.21 | 457.9 ± 0.70 | – | 26.07 ± 0.55 | – |
| PA   | 5065.0 ± 20.8 | 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 | 603.8 ± 3.89 | – | 18.11 ± 0.11 | 27.64 ± 0.27 | 298.3 ± 0.92 | – | 37.12 ± 0.45 | – |
| PT   | 2721.0 ± 0.55 | 69.48 ± 0.86 | 33.67 ± 1.4 | – | 11.95 ± 0.19 | 220.05 ± 1.13 | 134.70 ± 1.10 | – | 17.32 ± 0.5 | – |
| G    | 570.0 ± 3.44 | 53.55 ± 0.29 | 2054.0 ± 1.20 | – | 24.10 ± 0.17 | 851.56 ± 0.31 | 477.9 ± 0.85 | – | 25.28 ± 0.65 | – |
| ETHEPA | 1000.0 | 5000 | 2000 | 1000 | 3000 | 2000 | 5000 | 1000 | 500 | 250 |
| USEPA | 10000 | 10000 | 10000 | 10000 | 10000 | 10000 | 10000 | 10000 | 10000 | 10000 |

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 organism [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 NO₃, PO₄ and SO₄ 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
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.

Acknowledgements

This work was supported by the Water Security and Sustainable Development Hub which is funded by the UK Research and Innovation’s Global Challenges Research Fund (GCRF), grant number: ES/S008179/1.

Author contributions

All authors contributed to the work presented in the manuscript.

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