Research article

Assessing pollution profiles along Little Akaki River receiving municipal and industrial wastewaters, Central Ethiopia: implications for environmental and public health safety

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ABSTRACT

Little Akaki River drains residential, industrial, and agricultural irrigation areas of Addis Ababa City Administration and is exposed to point and non-point sources of pollution. The purpose of this study was to identify sources, evaluate the levels of river water pollution, and its implications for environmental and public health. Pollution indices and multivariate statistical analyses were used to determine sources and levels of the river water pollution. Trace metals concentration was determined using inductive coupled plasma optical emission and spectrophotometer (ICP-OES). The average concentrations of COD, BOD, TDS, NO3–N, NH3–N, SO42− and PO43− ranged from 40.33 ± 5.13 to 425 ± 8.00 mg/L; 12.34 ± 0.11 to 188 ± 7.07 mg/L; 48.00 ± 0.83 to 915.57 ± 1.27 mg/L; 1.56 ± 0.10 to 66.50 ± 6.36 mg/L; 0.15 ± 0.08 to 42.83 ± 11.43 mg/L; 20.50 ± 10.61 to 77.50 ± 17.68 mg/L; and 0.35 ± 0.33 to 37.95 ± 0.92 mg/L, respectively. The average concentrations of Zn ranged (0.048–0.037 to 0.158 mg/L); Cr (0.012–0.007 to 0.203–0.199 mg/L); Cd (<0.014 to 0.007 to 0.02 to 0.001 mg/L) and Pb (0.031 ± 0.008 to 0.124 ± 0.034 mg/L). The comprehensive water pollution index values varied from 0.84–13.32, indicating that at all sampling sites (except for sampling site S1), the river water was heavily polluted (CPI >2.01). Heavy metal pollution index values further demonstrated potential environmental and public health implications. The principal component analysis revealed a total of 88.99% variation in the dataset, mainly contributed by organic matter, nutrients, dissolved salts, and trace metals that originated from anthropogenic sources. Contamination of the river water has impaired its suitability for urban agriculture, aquaculture, livestock drinking, and recreational purposes. Thus, improving the river water quality is recommended to mitigate potential adverse effects and promote sustainable use of water resources.

1. Introduction

River water is an indispensable natural resource supporting economic and social development. River and streams have largely been exploited for supplying water for human consumption, livestock drinking, aquaculture, irrigation, industries, transportation, recreation, and other purposes (Barakat et al., 2016). Despite these benefits, in developing countries, rivers and streams are subjected to various anthropogenic and natural sources of pollution. These include expansion of urban, industrial growth, agrochemicals run-off, municipal and domestic wastes (Mustapha et al., 2013; Oketola et al., 2013). As a result, organic, nutrients, trace metals, and potentially hazardous substances are introduced into the river system, causing deterioration of river water quality.

Little Akaki River (LAR) passes through the Addis Ababa City Administration receives untreated wastes discharged from industries, residential and commercial activities. Several studies reported that poorly treated and untreated industrial wastewaters, domestic wastes, and sewerages discharged into the river resulted in pollution of rivers and streams (Melaku et al., 2007; Worku and Giweta, 2018). Yet, a significant number of the urban and peri-urban populations are depending on LAR water for irrigation, livestock drinking, washing, swimming, and fishing (Melaku et al., 2007). More importantly, during the dry season when the water supply is limited, many rural communities are using this river water for domestic purposes.

In the past, limited research has been undertaken to assess the quality of LAR water based on physicochemical parameters (Degefe

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et al., 2017), identified major ions and nutrient concentrations (Melaku, 2005). Recently, Aschale et al. (2019) have assessed the composition of trace elements in irrigation water, soil, and vegetables grown along with LAR.

Water quality index (WQI), single factor evaluation index, comprehensive pollution index (CPI), the Nemerow pollution index, fuzzy comprehensive evaluation, and comprehensive water quality identification index (CWQII) are often used to assess and evaluate water quality (Ji et al., 2016; Yan et al., 2015). Moreover, the water pollution index is considered as an important tool to assess and determine the level of surface water quality, level of pollution and identify polluted sites and communicate the results in a simple and comprehensible manner to regulatory and policymakers (Tanjung et al., 2019).

Previously, researchers such as Matta et al. (2018) have used CPI to assess the quality of the Ganga River System at Rishikesh; Ji et al. (2016) have used CPI and single factor assessment to assess the water quality Wen-Rui Tang River in China; Yan et al. (2015) have also used single factor pollution index and CPI to investigate water pollution and main factors in the Honghe River watershed of China; Zhang (2017) have applied Single Factor Evaluation Index (SFEI) and CPI and other indices to explore water quality and, identify the major pollutants in the Liao River in China. Similarly, the heavy metal evaluation index is commonly applied to assess and evaluate the combined effects of heavy metal pollution (Zhang, 2017). However, pollution indices-based studies which provide an overall pollution status of LAR water have not been undertaken to determine the levels of water pollution and generate conclusive data that can give sufficient insight to make informed decisions and policy-making processes for taking mitigation measures.

Therefore, the objectives of the study were to: (i) assess the pollution levels of LAR water using comprehensive water pollution index, heavy metals evaluation index (HEI), and multivariate statistical analysis, and (ii) identify the main source and pollutants influencing river water quality and its implications for safe and sustainable use of resources.

2. Materials and methods

2.1. Study area

The study was conducted along with LAR which drains the city of Addis Ababa Administration and is used by downstream communities for agriculture, livestock, drinking, and recreational purposes. It is located at 9° N and 38° E with an altitude ranging between 2200-2500 m above sea levels. The river originates from Entoto Mountain found in the northwest parts of Addis Ababa City as a small stream and merges with Geferssa Reservoir, flows southwest part of the city, and finally joins Aba-Samuel Reservoir after traveling a total distance of about 40 km (Worku and Giwtea, 2018). LAR is one of the two major rivers found in the Akaki catchment, experiencing temperate afro-alpine climatic conditions. The daily average temperatures range from 9.9 to 24.6 °C and the mean annual rainfall is 1254 mm. The river is exposed to point and non-point sources of pollution along its catchments. These include residential, commercial, industries, connecting the septic tank and sewage to the river, open defections, illegal solid waste disposal around riverbanks, and agrochemicals. The map of the study area and sampling sites along the river are shown in Figure 1 below.
2.2. Sampling sites and sample collection

After a preliminary survey along the river course, 10 sampling sites were selected based on accessibility, ease to identify, proximity to point, and non-point sources of pollution (Figure 1).

The water samples were collected between November–December 2019 which is typically the dry season to investigate the pollution status of the river during the dry period when downstream communities are largely using the river water for different purposes; the river is accessible and water scarcity becomes critical in the area. At each sampling site, triplicate river water samples were collected using the pre-washed and cleaned plastic bottle of 1000 ml size for physico-chemical and heavy metals analysis. Analysis for physico-chemical parameters were done immediately after transporting to the laboratory, while the samples for heavy metal analysis were preserved with 5 mL HNO₃ and kept in a refrigerator at 4 °C until they were further processed and analyzed.

2.3. Water samples analysis for physico-chemical parameters

Calibrating the instrument and field measurement of river water temperature (C) and pH were taken using pH meter (Jenway 3510), and dissolved oxygen (DO) was measured using DO meter (A1.72535, 850045 Sper. Scientific, made in Taiwan). Chemical Oxygen demand (COD) was determined by closed reflux, colorimetric method, following HACH protocols using reactor digestion and (DR/2400) Spectrophotometer. Biological Oxygen demand (BODs) was measured following Winkler’s method with azide modification (APHA, 1999). Total dissolved solids (TDS), total suspended solids (TSS), salinity, conductivity, were measured using EUTECH, Conductivity/C14/C0 Meter. The turbidity of water samples was determined using Nephelometer, model: CL52D. The concentrations of S(2), SO4 –2, NO3 –N, NH3 –N, and PO4 –3 were determined according to HACH protocols using DR/2400 Spectrophotometer as follows: sulfide was determined following methylene blue method; sulfate determined by the sulfaVer-4 method; nitrate by the cadmium reduction method; ammonia (NH3 –N) by the Nessler method and phosphate determined by the ascorbic acid method.

2.4. Heavy metals analysis

For determination of the heavy metal concentrations, the water samples were digested following standard procedures (APHA, 1999) (3030 E). The preserved water samples were well mixed and then 100 mL of samples were digested using 5 mL of conc. HNO₃ (68%). The samples were gradually heated to boil and evaporate using a hot plate in the hood (3030 E). The preserved water samples were well mixed and then 100 mL HNO₃ for 2 days, and then, thoroughly washed and rinsed with de-ionized water before use.

2.5. ICP-OES operating conditions for heavy metals analysis

The concentrations of heavy metals in digesting water samples were analyzed using inductively coupled plasma optical emission spectrophotometry (ICP-OES), Arcos -SOP-ICP-OES, Model: ARCOS FHS12, made in Germany. The ICP-OES was adjusted and calibrated according to the manufacturer’s instructions. Calibration curves were prepared using standard solution of 0.08, 0.11, 0.17, 0.56, 1.12, 1.68, 2.24 and 2.80 mg/L for Zn. For other trace elements Cr, Cd and Pb standard solution of 0.03, 0.06, 0.08, 0.28, 0.56, 0.84, 1.12, and 1.40 mg/L. The concentrations of trace elements Zn, Cr, Cd, and Pb were recorded at a wavelength of 213.856, 231.604, 267.716, and 220.353 nm, respectively. The concentration was calculated on the linear graph of the standard concentration and the corresponding intensities. The calibration curves showed linearity (R² ≥ 0.99944) for all quantified elements under this study. The recovery of each trace element was determined based on spike test and control samples. Accordingly, the recovery rates of the four trace metals were: 96.25–105.59% for Zn; 89.38–112.86% for Cr; 97.93–116.43% for Cd, and 99.74–108.75% for Pb.

2.6. Quality control and quality assurance

The digested water samples were analyzed in triplicate to take the average value of concentrations of each water sample. Blank samples were prepared and analyzed to check interference from the laboratory reagents. To validate the method, spiked samples were also prepared to ascertain laboratory performance. The recovery percentages of the four metals were: Zn = 109.65; Cr = 95.68; Cd = 89.70 and Pb = 117.84 which are satisfactory. The limits of detection (LOD) and limit of quantification (LOQ) of the elements were calculated from the blank samples based on three times and ten times the standard deviation of blank samples, respectively (Alemnew et al., 2019). Accordingly, the LOD and LOQ of trace element Zn and Cd were ranged between 0.018–0.04 mg/L and 0.06–0.16 mg/L, respectively. However, for Cr and Cd, the LOD and LOQ were not determined because their concentrations in the blank samples were below detection (Cr < 0.0005 mg/L; Cd < 0.0001 mg/L). The relative standard deviation (RSD (%)) for Zn was ranged 5.787–10.510; Cd = 0.557–10.36; Cd = < 10.607 and Pb = 2.139–11.952 which showed good precision.

All of the chemical reagents used for the experiments were laboratory grade chemicals. Moreover, glassware and bottles were soaked in water diluted with 10 mL HNO₃ for 2 days, and then, thoroughly washed and rinsed with de-ionized water before use.

2.7. Comprehensive pollution index and single factor evaluation index

A single factor evaluation index is used to evaluate the contribution of individual water quality parameters to water pollution, while CPI is applied to assess the overall status of water pollution and to classify surface water quality. To do this, the measured water quality parameters and, surface water quality standards are required. Since Ethiopia has no surface water quality standards, the standards of other countries such as the United States Environmental Protection Agency standards (USEPA) (1999), Morocco surface water standards (Barakat et al., 2016), Korean Environmental Standards for Water Quality and Aquatic Ecosystem (2020) for rivers and streams, and Japan Environmental Quality Standards for Water Pollution (2020) were used to calculate CPI and HEI. The single evaluation factor and CWPI are computed using formulas expressed in Eqs. (1) and (2) (Matta et al., 2020; Mishra et al., 2015).

Single Factor Evaluation Index \(SFEI\) = \(M_i/S_i\) (1)

Where “SFEI” stands for a single factor evaluation index for each water quality parameter; “\(M_i\)” represents the measured concentration of each parameter, and “\(S_i\)” stands for the corresponding max. permissible standards for surface water. The result is interpreted as follows: when the value of \(Pi < 1\), the water quality meets the surface water quality standards (Mishra et al., 2015). On the other hand, if the value of \(Pi > 1\), it indicates that the water quality exceeded the standards; hence, the water is polluted (Yan et al., 2015).

Comprehensive water pollution index \(CPI\) = \(1/n \sum_{i=1}^{n} \frac{M_i}{S_i}\) (2)

Where: “CPI” is a comprehensive water pollution index, “\(M_i\)” represents the measured concentration of each parameter; “\(S_i\)” is environmental quality standards for surface water; “\(n\)” denotes the total number of parameters. Based on the computed value of CPI, the water quality can be classified into five categories (Son et al., 2020) as shown in Table 1.
2.8. Heavy metals evaluation index

Heavy metal evaluation index (HEI) was employed to understand the overall quality of the river water concerning heavy metals pollution (Boateng et al., 2015) which is expressed as:

\[ \text{HEI} = \sum_{i=1}^{n} \frac{\text{He}_i}{\text{Hma}_i} \]  

(3)

Where, He -stands for measured value and Hma stands for maximum admissible concentration of each trace metal. Based on the HEI value, there are three proposed levels of pollution categories (Boateng et al., 2015). These are: (i) (HEI <10), indicate low pollution; (ii) (HEI = 10–20), medium pollution; and (iii) (HEI >20), high pollution.

2.9. Multivariate statistical methods

Principal component analysis (PCA) was employed to assess and identify significant components that explain variations in LAR water quality, source and to draw conclusive information from the measured physico-chemical and heavy metals parameters (Mishra et al., 2015). Hierarchical cluster analysis (HCA) was conducted to determine the similarities among the sampling stations and grouping the sampling stations based on similarity in the physicochemical parameters of water samples (Ling et al., 2017). Before performing the PCA, the data collected from the field are tested for normality distribution. Then, normally distributed data were standardized using Z- transformation (Gajbhiye et al., 2015) using Microsoft excel-2010. Finally, PCA was performed using Past 4.02 software (Hammer et al., 2001) Moreover, Kaiser-Meyer-Olkin (KMO) and Bartlett’s sphericity tests were performed using SPSS Version 20 for the adequacy of samples and suitability of the data for PCA (Barakat et al., 2016; Hadi et al., 2016; Ling et al., 2017).

2.10. Data analysis

Descriptive statistical analyses of water samples were performed using Microsoft Excel 2010. The correlation between water quality parameters was performed using Pearson correlation at (95 %) confidence limits using statistical package for social sciences (SPSS) software, version 20. HCA was performed by Origin Pro (2017) while PCA was performed using Paste Software Version 4.02.

3. Results and discussion

3.1. Physico-chemical characteristics and heavy metals concentrations

The results of the physical-chemical parameters and the concentrations of heavy metals in LAR water were presented in Table 2.

3.1.1. Physico-chemical characteristics of LAR

Temperature is an important physical water quality parameter that influences the amount of dissolved oxygen in water, physicochemical processes, and microbial biodegradation rate, photosynthesis activity of green plants (Khan et al., 2016). As shown in Table 2, the mean and standard deviation of the temperature of LAR water samples ranged from 19.6 ± 0.14 to 22.25 ± 1.63 °C. The highest temperature was recorded at the sampling site (S8). At this sampling size, the river receives industrial wastewater from textile and garments, tanneries, paints, plastic, rubber, and boilers which may release warm water into the river system. While lowest temperature recorded at the sampling site (S5) may be due to shading effects from riverine bamboo plants growing around the river-banks. In downstream, there is a slight temperature variation which may be due to variation in altitude that increases solar radiation and varied level of water pollution (Matta et al., 2015). Comparable findings were also reported for Kenaba River (17–21 °C) (Benito, 2016) in Addis Ababa city and Modjo River (21.50–24.93 °C) (Mulu et al., 2013) in Ethiopia. However, lower values reported for Hindon River, India (15.6–34.70 °C) (Rizvi et al., 2016) and Garra River (28.70–31.1 °C) in India (Khan et al., 2016).

![Table 2: Physico-chemical parameters and heavy metal concentrations (Mean ± SD) in LAR water.](image)
Like temperature, PH is a physical water quality parameter that can influence chemical and biochemical reactions, metabolic activities, the toxicity of metals to aquatic life, and the suitability of water for different uses (Bakan et al., 2010; Matta et al., 2015). In the present study, the average pH values ranged between 7.07 ± 0.24 to 8.09 ± 0.04. The highest value recorded at sampling site (S8), indicating slightly alkaline river water, may be due to the discharge of untreated industrial wastewaters into the river from tanneries, textiles, rubber that may contain detergents and soap (Bakan et al., 2010; Khan et al., 2016) factories operating in the area. The lowest pH value was detected at the sampling site (S2) which is attributed to relatively low anthropogenic influence. Literature showed that the pH value of water is closely associated with the concentration of carbon dioxide (CO₂) and alkalinity substances (Tanjug et al., 2019). The higher the value of pH indicates a higher the alkalinity and the lower the concentration of CO₂. Moreover, other factors such as temperature, photosynthesis, the concentration of oxygen, available anions, and cations can affect pH value (Tanjug et al., 2019). The optimum pH that supports aquatic life ranged from 6.5–8.2 (Matta, 2014).

The pH of values of LAR water samples is comparable with the reported value for Nile River (pH = 7.3–8.5) in Egypt (Abdel-Satar et al., 2017) and Jakarta River (pH = 6.2–7.9 °C) in Malaysia (Mustapha et al., 2013) and Garra River water (pH = 7.10–8.30) in India (Khan et al., 2016). The measured pH values of LAR water samples were within permissible limits (6.5–8.5) of the World Health Organization (WHO) (2011) and Federal Ministry of Water Resources (FMoWR) (2001) for drinking water. Thus, the pH of LAR water was not affected by river pollution.

3.1.2. Concentrations of organic pollutants

The chemical oxygen demanding, biological oxygen demanding, and dissolved oxygen are important water quality indicators. COD measures the amount of oxygen needed to oxidize soluble and particulate organic matter found in water (Matta et al., 2020). The value of BOD indicates the amount of DO required for microorganisms to degrade and mineralize organic matter under aerobic conditions, while the value of DO indicates the total quantity of dissolved oxygen in the water for respiration and metabolic activities (Tanjug et al., 2019).

As shown in Table 2, the average concentrations of COD, BOD, and DO ranged from 40.33 ± 5.13 to 425 ± 8.0 mg/L; 12.34 ± 10.11 to 188 ± 7.07 mg/L and 3.25 ± 0.77 to 7.17 ± 0.09 mg/L, respectively. The highest concentrations of COD (425 mg/L) and BOD (188 mg/L) were recorded at the sampling site (S4), indicating a high organic load to the river, and the river water quality is deteriorating compared to the control site (S1). The major input for organic pollutants in the sampling site (S4) include Addis Ababa City Abattoir (Worku and Leta, 2017), domestic wastes, sewage line connected to the river, manure from cattle and sheep market and shed, individual septic tanks connected to the river, and application of fertilizers like urea for irrigated vegetable growing generate high organic and nutrient. Thus, it has been observed that the high organic load recorded at the sampling site (S4) has greatly affected the river water quality, changed the color of the water to black, and reduced the aesthetic value of the river due to odor bad.

The highest DO concentration was recorded at the sampling site (S1) while the lowest at the sampling site (S4). High concentration of DO may be attributed to low oxygen inputs from surrounding farmlands and low turbidity and suspended solids, photosynthetic activity of the green plants (Matta et al., 2015), whereas low DO in sampling site (S4) is mainly attributed to high organic load from anthropogenic point and non-point sources that have caused a reduction in the amount of DO in water.

The concentrations of BOD and COD in LAR water samples were lower than the reported value for Modjo river (BOD = 84.00–265.66 mg/L) and COD (295–1080 mg/L) in Ethiopia (Mulu et al., 2013); but higher than the reported value (BOD = 11.40–82.76 mg/L) and COD = 16–192 mg/L) for Hindon River, in India (Rizvi et al., 2016). Even if the Lower BOD and COD are recorded as compared to Modjo River, the organic load to LAR water is high enough to cause river water pollution due to diverse anthropogenic sources of organic inputs. For instance, in all sampling sites (except S1), the average concentrations BOD (89.08 mg/L) and COD (238.97 mg/L) have exceeded the guideline limit values of Australia and New Zealand (2000) (BOD < 15 mg/L, COD < 40 mg/L) for aquaculture. This result indicates that LAR water was highly contaminated with organic pollutants, and it can pose an adverse effect on the survival of fish.

The concentrations of DO in analyzed water samples were lower than the reported DO values for Ganga River (DO = 10.05–12.53 mg/L) in India (Meher et al., 2015) and Nile River (DO = 4.1–13.2 mg/L) in Egypt (Abdel-Satar et al., 2017), but slightly higher than the reported value (2.90–5.08 mg/L) for Ogun River in Nigeria (Okeotu et al., 2013). Thus, results indicated that LAR water is polluted with organic pollutants that have consumed and minimized the amount of DO in the river water. Dissolved oxygen is often considered a key factor for the survival of aquatic life (Bakan et al., 2010). The average concentrations of dissolved oxygen (DO) at some sampling sites (S2, S3, S4, S5, S6, and S8) were lower than European Union (EU) (1998) (5 mg/L) may be due to aerobic decomposition of organic matter, respiration of aquatic organisms and chemical oxidation. Hence, the concentrations of DO in some sampling sites (S2, S3, S4, S5, S6, and S8) were also lower than the guideline value (Boyd, 1998) (5–15 mg/L) of water quality for aquaculture. Boyd and Pillai (1984) have reported that fish do not feed or grow well when dissolved oxygen concentrations become lower than 5 mg/L. Thus, the study results should that pollution of river water with organic pollutants has adverse impacts on the fish and affect the livelihood of many farmers. Communicating the findings of this study becomes necessary to mitigate pollution-related problems.

3.1.3. Concentrations of nutrients and dissolved salts

The presence of an excess concentration of nutrients such as nitrate, ammonia, and phosphate can affect surface water quality in many ways. For instance, ammonia is toxic to aquatic biota when its concentration exceeded the permissible level; high nitrate and phosphate concentrations in water cause eutrophication (Tanjug et al., 2019). Excess phosphate in surface water causes algae blooms and eventually decreases DO in water, which may rise water temperature, kill fish and aquatic life (Bakan et al., 2010).

As shown in Table 2, the average concentrations of NO₃–N ranged from 1.56 ± 1.01 to 66.50 ± 6.36 mg/L; NH₄–N ranged from 0.15 ± 0.08 to 42.83 ± 11.43 mg/L; S²⁻ ranged from 63.67 ± 12.70–717.00 ± 14.73 μg/L; SO₄²⁻ ranged from 20.50 ± 10.61–77.50 ± 17.68 mg/L, and PO₄³⁻ ranged: 0.35 ± 0.33 to 37.97 ± 0.92 mg/L.

The highest concentrations of NO₃–N and NH₄–N were detected at the sampling site (S4) and the lowest at the sampling site (S1). The highest concentrations of nitrate and ammonia may be attributed to nitrogen inputs from point sources such as Addis Ababa Abattoir, cattle manure, cattle feed wastes, sewage, domestic wastes, septic tank connected river system, and non-point source such as chemical fertilizers used for irrigated vegetables in the area. The highest concentration of nitrate and ammonia at the sampling site (S1) is due to low anthropogenic inputs of nitrogen from chemical fertilizers used by local farmers for growing crops.

Compared to other studies, the concentration of NO₃–N in LAR was lower than the reported value (NO₃–N = 3.10–133.8 mg/L) for Hindon River, India (Rizvi et al., 2016). Mulu et al. (2013) have reported (10.15–212.33 mg/L) of HN₃–N for Modjo River which is higher than the present findings for LAR. However, the concentrations of both NO₃–N and HN₃–N in LAR water samples were higher than the reported value for the Nile River (HNO₃–N = 0.021–3.403 mg/L) and NO₃–N (0.008–0.55 mg/L) (Abdel-Satar et al., 2017), indicating LAR river water pollution with nutrients due to human activities.

At the sampling site (S2), the highest concentration of PO₄³⁻ was recorded. In this sampling station, the major sources of phosphorus input include shoe, soap, and garment factors, washing clothes and bathing,
domestic wastewater, and agrochemicals used for large irrigated vegetable production. Tanjung et al. (2019) described that almost all NO₃⁻ and PO₄³⁻ in river water generated from agricultural, industrial, and household wastes. Phosphate is an important nutrient that stimulates the growth of aquatic plants like algae and plankton that serve as food for fish. However, excess concentration of phosphate in water results in overgrowth aquatic plants and algae that rapidly consume and decrease the concentration of dissolved oxygen levels in water and kills aquatic life (Khan et al., 2016).

The highest concentration of SO₄²⁻ was recorded at the sample site (S8) due to the discharge of untreated wastewater from tanneries and leather processing factories established in the Akaki Kalti industrial zone. However, the highest concentration of SO₄²⁻ was detected at the sampling site (S3) due to the influx of wastes generated from the Addis Ababa Tannery established nearby the bank of the river. Sulfate can also be generated from agricultural fertilizers, detergents and soaps, and pulp factories (Khan et al., 2016). Mulu et al. (2013) have reported SO₄²⁻ generated from agricultural fertilizers, detergents and soaps, and pulp factories. Sulfate can also be generated from agricultural fertilizers, detergents and soaps, and pulp factories.

When compared to national and international guideline limits, the concentrations of NH₃–N were higher than the maximum permissible value of the Federal Ministry of Water Resources (FMoWR) (2001) (1.5 mg/L) for drinking water. The concentration of PO₄³⁻ was also exceeded WHO’s (2011) guideline limit value (0.5 mg/L) for drinking water. High concentrations of nutrients in river water cause eutrophication of surface water (Vadde et al., 2018), reduce aquatic species diversity and eventually increase fish mortality (Oktola et al., 2015). Thus, excessive load of nutrients in the river water may affect the end use of river water for different purposes. The average concentration of nitrate (19.84 mg/L) in LAR water was also exceeded the recommended value of the United States of America, National Academy of Science (NAS) (2001) (<10 mg/L) for livestock drinking. The excessive concentration of nitrate in the drinking water of livestock can interfere with the nitrogen-transporting capacity of hemoglobin causing respiration problems or asphyxiation when nitrate is reduced into nitrite in the animal body (NAS, 2001).

TDS, salinity, and TSS can affect surface water quality. Excess concentration of TDS affects water taste and palatability, high salinity affects the suitability of water for irrigation, and high TSS affects light transmission and affects aquatic life (Howladar et al., 2017). The average concentrations of TDS, TSS, and salinity of water samples were varied from 48 ± 0.83 to 915.57 ± 1.27 mg/L; 17 ± 4.58 to 387 ± 4.36 mg/L and 48.12 ± 1.26 to 918.10 ± 4.97 mg/L, respectively (Table 2).

The highest concentration of TSS, TDS, and salinity were recorded at the sampling site (S4) while their lowest values were obtained at the sampling site (S1). The highest concentration of TDS, TSS, and salinity may occur due to dissolved and suspended solids input into the river system from human activities; these are Addis Ababa City abattoir wastes, domestic and sewerage generating wastewaters containing detergents and salts, metal works, garages, surface drainage for irrigated vegetables and canals carried soil and agrochemicals (Melaku et al., 2007); hence, higher pollution load of TDS and TSS as compared control sample site (S1). In this regard, Matta (2014) reported that high TDS in river water may originate from salt and organic matter indicating discharge of sewerage into the river system.

Compared to other study reports, the concentration of TDS in LAR water samples was higher than the values reported for Kebena River (40.43–640 mg/L) (Benito, 2016) in Addis Ababa City, Ethiopia, and Garra River (43–263 mg/L) in India (Khan et al., 2016), exhibiting higher contamination of LAR water with dissolved solutes and ionized substances. However, the TDS in LAR water samples is lower than Ogun River (120–1240 mg/L) (Oktola et al., 2013) in Nigeria and Hindon River (243–1031 mg/L) (Rizvi et al., 2016) may be due to varied sources and amount of solids inputs.

In most sampling sites (except for site S1 and S2), the concentrations of TDS surpass the permissible limits for drinking water (500 mg/L) WHO (2011) and maximum concentration level (MCL) (500 mg/L) of United State of America, Environmental Protection Authority (USEPA) (2009). The presence of high TDS in water affects the taste and palatability of water (Howladar et al., 2017), while high concentrations of suspended solid can influence the normal functions of an aquatic ecosystem through decreasing light penetration, increasing water temperature, and photosynthetic activity of aquatic plants (Tan et al., 2017).

The average concentration of TSS (137.5 mg/L), NO₃–N (19.84 mg/L), SO₄²⁻ (54.62 mg/L) and PO₄³⁻ (15.90 mg/L) in the LAR water samples were also surpasses the United Nations, Food and Agriculture Organization (FAO) (1985) guideline limit values (NO₃–N = 0–10 mg/L; SO₄²⁻ = 0–20 mg/L; PO₄³⁻ = 0–2 gm/L) of water quality for irrigation. Excess concentration of TSS in irrigation water samples may have adverse effects, these include the formation of surface crust that inhibits water percolation into the soil, affects aeration of the soil, suspended particles may cover plant leaves, and reduces the photosynthetic activity of plant (South Africa, Department of Water Affairs and Forestry) (DWAF, 1996).

High turbidity reduces sunlight reaching phytoplankton found in the bottom of the water by scattering and obstructing incoming light by suspended particulate matter such as mud, algae, detritus, and fecal material clay, finely organic matter. During this study, the results obtained for conductivity and turbidity ranged from 0.15 ± 0.00 to 3.36 ± 0.01 mS and 38.57 ± 4.31 to 140.33 ± 3.21 NTU, respectively.

The highest conductivity was obtained at sampling site (S6) located in proximity, alcohol factories, garages, electrical wires damped open spaces, solder, fuel station, commercial and domestic wastes, agrochemicals leached from irrigated vegetables, and water draining canals. The highest turbidity was detected at the sampling site (S3) may be due to discharge pig husbandry wastes, washing chemical and powder bags and plastic containers, domestic wastes, sewage, algae growth, soil laden irrigation canal. Matta et al. (2020) described that water turbidity can be caused by clay and silt, fine inorganic and organic matters, algae, and microorganism. The value for the conductivity of LAR water samples is comparable to that of Modjo River (1.57–2.93 mS) (Mulu et al., 2013) but higher than Jakarta River (1.17–1.49 mS) in Malaysia (Mustapha et al., 2013) and Nile River (0.26–0.81 mS) in Egypt (Abdel-Satar et al., 2017).

The average turbidity of LAR water (106.24 NTU) was also exceeded the guideline limits of Health Canada (2012) (50 NTU) and British Columbia (2017) (50 NTU). High concentrations of suspended solids and turbidity impair the effort to use river water for recreation as they reduce visibility/ clarity within the water body, affect the safety and esthetic attraction of the water used for recreation (Health Canada, 2012).

3.1.4. Concentrations of trace metals and their implications for various uses

Contamination of river water with heavy metals is a serious environmental and public health concern due to its toxicity, persistence, bioaccumulation, and bio-magnification properties. High concentration of heavy metals that exceeded allowable limits in river water may affect...
the suitability of river water for irrigation due to its soil pollution and phytotoxicity to plants affects the quality of soil and crops and threatens aquatic life and human health through the food chain (Boateng et al., 2015; Matta et al., 2018). In this study, the average concentrations of Zn ranged from 0.048 ± 0.037 to 0.318 ± 0.158 mg/L; Cr from 0.012 ± 0.007 to 0.203 ± 0.199 mg/L; Cd from <0.014 ± 0.0007 to 0.02 ± 0.001 mg/L; and Pb from 0.031 ± 0.008 to 0.124 ± 0.034 mg/L (Table 2).

The maximum concentration of heavy metals detected at various sampling sites might be due to the amount of metal inputs from various sources. For instance, the highest concentration of Zn was recorded at the sampling site (S10) which is attributed to the influx of up-river industrial wastewaters and widespread use of agrochemicals such as fertilizers and pesticides (Boateng et al., 2015; Wuana and Okieimen 2011). In this respect, Sardar et al. (2013) reported that pesticides like fungicide which is widely applied in agricultural crop protection contain Pb, Zn, Cu, Mn, and Hg.

The maximum Cr concentration was recorded at the sampling site (S3) due to untreated tannery industry wastewaters. The highest concentration of Cd occurred at the sampling site (S5) and Pb at the sampling site (S4). The major anthropogenic inputs of Pb are vehicle batteries, battery maintenance, cable covers, pigments, solder, garage wastewaters, fuel stations, and agrochemicals used for irrigated vegetables (Boateng et al., 2015; Matta and Gjyli, 2016). Cd is usually originated from Ni–Cd batteries, cadmium coating of vessels and vehicles, pigments, stabilizers, alloys, phosphate fertilizers, and detergents (Wuana and Okieimen, 2011).

A comparison of the results obtained from sample analysis with other river study reports indicated that the concentration of Zn in LAR water higher than the reported value for Nile River (0.01–0.115 mg/L) in Egypt (Abdel-Satar et al., 2017) and Ogun River (0.01–0.07 mg/L) in Nigeria (Oketola et al., 2013). Similarly, the concentration of Cr in LAR water was higher than the reported value for Jakarta River (0.01–0.04 mg/L) in Malaysia (Mustapha et al., 2013). However, the concentration of Cd in LAR river water samples was lower than the reported value for Jakarta River (0.01–1.00 mg/L) in Malaysia. Mustapha et al. (2013) have reported the concentration of Pb (0.01–0.04 mg/L) in Jakarta River which is lower than results obtained for LAR water samples. Generally, the comparison made indicated that there is variability in the amount of heavy metals concentration in river water due to varied sources and amount of metals inputs. The concentration of Zn, Cr, and Pb in LAR water needs attention. An elevated concentration of heavy metals in surface water beyond allowable limits may cause severe effects on plants, animals, humans and ultimately impairs the beneficial uses of water for various purposes (Sardar et al., 2013). Comparing with national and international guidelines limit values, the concentrations of Cr at sampling sites (S2); (S3); (S4); (S8); (S9) and (S10) exceeded the permissible limit provided by WHO (2011), FMoWR (2001), and Northern Ireland Environmental Agency (NIEA) (2014) (0.05 mg/L) for drinking water. Moreover, in all sampling sites, the concentration of Cd exceeded the maximum permissible limits (0.003 mg/L) of FMoWR (2001). Similarly, the concentrations of Pb at all sampling sites were surpassed the maximum permissible limits (0.01 mg/L) of FMoWR (2001) NIEA (2014), and WHO (2008) for drinking water. High concentrations of toxic trace metals like Cd and Pb have a capacity for bioaccumulation and biomagnification and may cause far-reaching adverse impacts on aquatic life and human health.

In some sampling sites, (S2), (S3), (S4), and (S8), the concentrations of Cr exceeded the guideline limits of FAO (1985), USEPA (2012), and (DWA, 1996) (0.1 mg/L) of water quality for irrigation. A high concentration of Cr in irrigation water may lead to the accumulation of trace metals in the soil and plant tissues. Sardar et al. (2013) have reported that leafy vegetables are capable to absorb and accumulate higher amounts of heavy metals in their leaves, and ultimately affect public health. Similarly, the concentration of Cr in water samples was also slightly exceeded the Canadian Council of Ministers of the Environment (CCME), (2005) (0.05 mg/L) and Oklowski (2009) (0.05 mg/L) guideline values for livestock water quality. A high concentration of Cr that exceeded guideline limits may pose toxicity in livestock, which can be manifested in the form of diseases like diarrhea, dehydración, and carcinogenic in livestock (DWAF, 1996). The concentrations of Pb in water samples surpass the CCME (2005) (0–0.01 mg/L), DWA (1996) (0.015 mg/L) and NAS (2001) (0.015 mg/L) guidelines for livestock drinking water. Lead is a toxic metal that can adversely affect the reproductive hormones of animals (Valente-Campos et al., 2014). Livestock ingests trace metals with water and accumulates in their kidney, muscles, and liver. Rubio et al. (1998) have reported that trace elements like Cd and Pb were found in cow milk. The concentrations of trace metals like Cr, Cd, and Pb that have surpassed the guidelines value deserve high attention due to their toxicity, bioaccumulation, and bio-magnification properties of trace metals and the impacts they may cause on livestock health and human food safety.

The average concentration of trace elements Zn, Cr, Cd and Pb in water sample were found to be higher than the Australia and New Zealand (2000) (Zn < 0.005 mg/L; Cr < 0.02 mg/L; Cd < 0.0002–0.0017 mg/L), CCME (2007) (Zn = 0.03 mg/L; Cr = 0.001 mg/L) and DWA (1996) (Zn = 0.03 mg/L; Cr = 0.002 mg/L; Pb = 0–0.01 mg/L) guideline limits of water quality for aquaculture. According to Svobodová et al. (1993), lead toxicity in fish may cause gill damage, kills fish with suffocation, and damage the nervous system. A high concentration of Cd in water can be absorbed through the gastrointestinal tract and cause liver necrosis and mortality in fish (National Academy of Science, 1993). Consumption of fish contaminated with toxic metals may pose a potential health risk to humans (Asare-Donkor et al., 2016). Hence, LAR water quality is not fit for fishery production due to metal toxicity and public health concern.

The concentrations of Cr, Cd and Pb in water samples were also higher than the Australia and New Zealand (2000) (Cr = 0.05 mg/L; Cd = 0.005 mg/L; Pb = 0.05 mg/L) and IRMA (2018) (Cr = 0.05 mg/L; Cd = 0.005 mg/L; and Pb = 0.01 mg/L) guideline limits of water quality for recreation. This result indicates that LAR water quality is deteriorated and not fit for primary and secondary recreation purposes due to safety and public health implication. The comparison made with national and international guidelines and standards showed that the concentration of some heavy metals in the river water samples surpasses allowable limits and affects the suitability of the water for drinking, irrigation, livestock drinking, and recreation. This information is essential for creating awareness among environmentalists, regulatory bodies, and local communities as well as the population of Addis Ababa City Administration so that due attention and synergetic approaches to mitigating heavy metal pollution and contribute to preserving the river water quality.

3.2. Comprehensive pollution index and single factor evaluation index

To understand the overall status of LAR water pollution and identify the major parameters contributing to the pollution, a comprehensive water pollution index (CPI) and single factor evaluation indices were applied (Mishra et al., 2015). Water quality assessment is usually a very complex process that involves various kinds of pollutants that exist in the river water. The comprehensive pollution index is commonly applied to water quality assessment across the world, and it is a relatively strong assessment tool that provides comprehensive information about the status of water quality (Ji et al., 2016). According to (Yan et al., 2015) both a single factor pollution index and CPI are tools to be applied to explore major water pollutants and to evaluate the level of water pollution. In this study, the results of CPI and single factor evaluation are presented in Table 3, and the trend of CPI downstream is presented in Figure 2.

As shown in Table 3, in some sampling sites, the value of single factor evaluation (PI) for COD at sampling sites (S4, S5, S8), BOD at sampling sites (S4, S5, S8); NH₃–N at sampling sites (S2, S3, S4, S5, S6, S7, S8, and S9), PO₄³⁻ at sampling sites (S2, S3, S4, S5, S6, S7, S8, S9, and S10), Zn at sampling sites (S2, S4, and S10) and Cr at sampling site (S3) exceeded a
The CPI values of LAR water samples varied between 0.85–13.32 with an average value of 7.08. As indicated in Table 3, CPI values varied among sampling sites, implying that all sampled sites experienced different levels of pollution. However, the highest CPI was recorded at the sampling site (S4) as compared to the control sample site (S1). This may be attributed to high load of organic, nutrients, TDS, and TSS inputs from Addis Ababa city Abattoir, cattle manure, domestic wastes, sewerage, septic wastes; while heavy metals are generated from garages, vehicle battery maintenance shops, factory, and agrochemicals used for irrigated vegetables. Thus, the highest CPI was recorded at this site as compared to the control site (S1).

As shown in Figure 2, CPI showed an increasing trend in the upper course at the sampling site (S2) and then decreasing. In sampling site (S2), BOD, COD, NH₃, and PO₄³⁻ Zn and Cr have contributed higher CPI value as compared to the control sample site (S1). This may be attributed to organic, nutrients, and heavy metals generated from soap and shoe factories, Addis Ababa Tannery wastewaters, domestic wastes, septic tanks, and latrine-connected river systems. The graph showed increasing trends and reached a maximum at sampling site (S4) and thereafter, gradually decreasing trends along the lower course of the river may be due to decreasing input of pollutants load and effects of self-purification of the river downstream.

Based on the water quality classification described in (Son et al., 2020), the CPI values obtained showed that in all sampling sites (except control sample site (S1), the river water quality fall in class V (CPI > 2.01); hence, the river water quality is classified as heavily polluted. Thus, in all sampled sites (except S1), the river water was polluted by cumulative/comprehensive/effects of pollutants. This result reflects that LAR water quality along with all sampling stations (except control) highly deteriorated.

A comparison of the CPI value obtained for LAR water with similar studies in other countries, showed that the value of CPI achieved for LAR was higher than the reported CPI values (1.25–8.52) for Henwal River, India (Matta et al., 2020), indicating that the LAR water was more heavily polluted. Matta et al. (2018) have also reported comprehensive pollution index value ranged 0.54–2.47 for Ganga River at Rishikesh which is lower than the present findings. Son et al. (2020) reported the CPI value ranged 0.50 to 1.57 with an average value of 1.08 for Cau River which is lower than the value obtained for LAR. The comparison made showed that the overall quality of the LAR water highly deteriorates indicating that this index is a useful tool to identify and communicate the overall status of river water quality to decision-makers.
3.3. Heavy metals evaluation index

Heavy metal is an important pollutant that can affect water quality. Nationally or globally, much attention is given to heavy metal pollution due to its adverse environmental impacts and multiple health repercussions (Moyel et al., 2015). The suitability of surface water for various purposes such as drinking, agricultural irrigation, and aquaculture can be determined by assessing and evaluating the content of trace metals in the water (Rezaei et al., 2019). Thus, the index is an important tool to assess and evaluate the combined effects of heavy metals on water quality (Zhang, 2017). There are several water quality indices developed to assess and interpret metal pollution, these include heavy metal pollution index (HPI), metal pollution index (MPI), heavy metal evaluation index (HEI), and degree of contamination (Cd) (Boateng et al., 2015; Edet and Offiong, 2003; Moyel et al., 2015). However, Edet and Offiong (2003) have described that the computation of Cd and HPI are cumbersome, and they have suggested that HEI is preferred for monitoring heavy metals contamination. Moreover, HEI is important not only for evaluating the overall pollution status of water quality concerning heavy metals content but also used for easy interpretation of the pollution index (Rezaei et al., 2019).

The overall status of LAR water quality with regards to the content of heavy metals is presented in Figure 3. The HEI value ranged from 5.39 to 16.32 with an average value of 9.60. The highest HEI value recorded at the sampling site (S10) may be due to a non-point source of metals mainly from agrochemical inputs. Lowest HEI occurred at the sampling site (S7) where domestic solid transfer site and irrigated vegetable growing below Behre-Tsegaye Park. In this area, the presence of dense bamboo growing on riverbanks might have contributed to the low concentration of (sequestered metals released to river water) heavy metals. Based on proposed water quality criteria indicated in Boateng et al. (2015), 60% of the sampling sites (S1, S3, S6, S7, S8, and S9) fall within the low pollution category (HEI < 10) may be due to low metals load in these sites. However, 40% of the sampling sites (S2, S4, S5, and S10) fall within the medium pollution (HEI = 10 – 20) category. In the sampling site (S2), the major inputs of metals include tanneries, domestic wastes, and agrochemicals. For sampling sites (S4) and (S5) the main sources for heavy metal inputs include metal workshops, garages, vehicle batteries, paints and pigment, fuel stations, and agrochemicals, while for sampling sites (S10) is mainly from influx from up-river and agrochemicals used for irrigated vegetables growing. This result showed a warning signal that at all sampling sites, the river water was polluted with trace metals contamination because trace amounts of metals especially Cr, Cd, and Pb can be very toxic to plants and animals. More importantly, the availability of trace metals with smaller concentrations than their corresponding maximum allowable concentration in water, but close to the respective permissible maximum allowable concentration (MAC) values may affect the overall water quality owning to additive or combined effects (Tamasi and Cini, 2004). Hence, using such toxic metal-loaded river water for irrigations, domestic, livestock drinking, and fishery may have environmental and public health implications.

The average HEI obtained from this study is lower than the reported value of 7.56–83.49 for Ismailia Canal Water, Egypt (Goher et al., 2014). Edet and Offiong (2003) reported that 65.5% of the sampled sites were classed as low while 34.5% classed as a medium for the Akpabuyo-Odukpani river basin in Nigeria. Rezaei et al. (2019) reported the HEI values ranged from 0.22 to 3.65 with a mean value of 1.2, which is lower than the current findings. Generally, the results of LAR water analysis indicate that the overall status of LAR water pollution with heavy metals is alarming given the toxic properties of heavy metals. Thus, attention should be given, and regulatory monitoring is necessary to informing policy and decision-makers and local communities about river water contamination with toxic heavy metals and its implications for agricultural soil, plants, aquatic life, and human health.

3.4. Pearson correlation

Pearson correlation analysis was performed to evaluate whether a linear correlation exists between pairs of water quality parameters (Barakat et al., 2016), identify sources, describe their pathway and behavior (Bhuyan et al., 2018; Yang et al., 2016). The result of the Pearson correlation of LAR water is presented in Table 4.

The correlation coefficient (r) indicated a significant positive correlation between water sample pH- temp. (r = 0.632) at (P < 0.05) and strong association between BOD – COD (r = 0.940) at (P < 0.01). These paired parameters might have originated from common sources and exhibiting similar behavior in their pathway (Yang et al., 2016). The significant positive correlation recorded between TDS – COD (r = 0.727); TDS – BOD (r = 0.668) at (P < 0.05), TSS – COD (r = 0.814); TSS – BOD (r = 0.883) both at (P < 0.01), and TSS – TDS (r = 0.730) (P < 0.05). These associations may indicate that organic pollutants, suspended solid and dissolved solids may originate from common sources such as domestic, sewerage, municipal and industrial wastes (Melaku et al., 2007; Oketola et al., 2013). A significant association were also found between EC – COD (r = 0.772); EC – TSS (r = 0.649) (P < 0.05); as well as, EC – TDS (r = 0.935) and EC – salinity (r = 0.950) at (P < 0.01), indicating that organic pollutants and ionized substance and salts were originated from the similar sources such as industrial effluents, abattoir, domestic wastes (Bhuyan et al., 2018).

A positive correlation recorded between turbidity- COD (r = 0.638); turbidity – BOD (r = 0.662); turbidity – TSS (r = 0.659); turbidity – EC (r = 0.676) at (P < 0.05), turbidity -TDS (r = 0.772) and turbidity -salinity (r = 0.773) at (P < 0.01). This result implies that the organic matter, TSS, TDS constituent of water samples may directly influence water turbidity. A positive correlation recorded for paired SO$_4^{2-}$ -BOD (r = 0.658); SO$_4^{2-}$ -TDS (r = 0.676); SO$_4^{2-}$ -TSS (r = 0.686), SO$_4^{2-}$ – salinity (r = 0.668) at (P < 0.05), and SO$_4^{2-}$ - Turbidity (r = 0.831) at (P < 0.01) may indicate that sulfate, organic pollutants, dissolved and suspended solids were originated from common sources such as tanning industries. A significant negative correlation recorded between NH$_3$ –N -temp (r = -0.671) at (P < 0.05) and pairs of trace metals (Cd–Cr) (r = -0.693) suggesting that paired variables were originated from dispersed sources. A strong association between NH$_3$ –COD (r = 0.828); NH$_3$–N BOD (r = 0.776) indicating common sources for organic and nutrients. High inputs of organic matter to river water under an anaerobic situation may cause the formation of ammonia and organic acids (Ling et al., 2017). There was a significant positive association between NO$_3$ –N–PO$_4^{3-}$ (r = 0.681) at (P < 0.05) exhibiting that nutrients in water samples may originate from common anthropogenic sources such as domestic wastewaters, detergents, sewerage, industries, agrochemicals such as fertilizers (Oketola et al., 2013). Zn–Cr (r = -0.232) showed a low negative association indicating that they were originated from dispersed sources.

![Figure 3. Trace metals and HEI values along LAR water.](image-url)
Table 4. Pearson correlation of physicochemical parameters and heavy metals of LAR water.

|       | Temp | PH   | COD  | BOD  | DO   | TDS  | TSS  | Salinity | Cond  | Turbid | Sulfide | SO\textsubscript{4}\textsuperscript{2-} | NO\textsubscript{2} | NH\textsubscript{3}-N | PO\textsubscript{4}\textsuperscript{3-} | Zn    | Cr    | Cd    | Pb    |
|-------|------|------|------|------|------|------|------|----------|-------|--------|---------|----------|----------|----------|-------------------|-------|-------|-------|-------|
| Temp  | 1    |      |      |      |      |      |      |          |       |        |         |          |          |          |                   |       |       |       |       |
| PH    | 0.632|      |      |      |      |      |      |          |       |        |         |          |          |          |                   |       |       |       |       |
| COD   | -0.611| -0.186| 1    |      |      |      |      |          |       |        |         |          |          |          |                   |       |       |       |       |
| BOD   | -0.546| -0.170| 0.940**| 1    |      |      |      |          |       |        |         |          |          |          |                   |       |       |       |       |
| DO    | 0.016| 0.002| -0.614| -0.531| 1    |      |      |          |       |        |         |          |          |          |                   |       |       |       |       |
| TDS   | -0.465| 0.305| 0.727**| 0.668*| -0.364| 1    |      |          |       |        |         |          |          |          |                   |       |       |       |       |
| TSS   | -0.575| -0.002| 0.814**| 0.883**| -0.353| 0.730*| 1    |          |       |        |         |          |          |          |                   |       |       |       |       |
| Salinity | -0.479| 0.285| 0.744**| 0.674*| -0.390| 0.998**| 0.736*| 1        |       |        |         |          |          |          |                   |       |       |       |       |
| Cond. | -0.497| 0.184| 0.727**| 0.620| -0.423| 0.935**| 0.649*| 0.950**| 1    |        |         |          |          |          |                   |       |       |       |       |
| Turbid | -0.342| 0.173| 0.638*| 0.662*| -0.481| 0.772**| 0.659*| 0.773**| 0.676*| 1    |         |          |          |          |                   |       |       |       |       |
| Sulfide | 0.454| 0.362| 0.251| 0.262| -0.316| 0.039| 0.012| 0.033| -0.041| 0.247| 1        |          |          |          |                   |       |       |       |       |
| SO\textsubscript{4}\textsuperscript{2-} | -0.101| 0.314| 0.585| 0.658*| -0.476| 0.676*| 0.653*| 0.668*| 0.559| 0.831**| 0.439| 1        |          |          |          |                   |       |       |       |       |
| NO\textsubscript{2}\textsuperscript{1} | -0.319| -0.247| 0.578| 0.623| -0.411| 0.264| 0.550| 0.259| 0.183| 0.044| 0.019| 0.321| 1        |          |          |          |                   |       |       |       |       |
| NH\textsubscript{3} | -0.671*| -0.086| 0.828**| 0.776**| -0.424| 0.767**| 0.888**| 0.782**| 0.723*| 0.722*| -0.004| 0.699*| 0.468| 1        |          |          |          |                   |       |       |       |       |
| PO\textsubscript{4}\textsuperscript{3-} | -0.258| -0.301| 0.278| 0.363| -0.029| 0.152| 0.128| 0.127| 0.085| -0.122| -0.054| 0.048| 0.681*| -0.002| 1        |          |          |          |                   |       |       |       |       |
| Zn    | -0.309| 0.042| 0.184| 0.224| 0.340| 0.085| 0.325| 0.305| -0.183| -0.243| -0.336| 0.177| -0.060| 0.536| 1        |          |          |          |                   |       |       |       |       |
| Cr    | 0.282| 0.077| 0.076| 0.290| -0.381| 0.050| 0.080| 0.023| -0.088| 0.320| 0.340| 0.486| 0.342| -0.068| 0.475| -0.232| 1        |          |          |          |                   |       |       |       |       |
| Cd    | 0.017| 0.356| -0.189| -0.283| 0.369| 0.054| -0.020| 0.057| 0.030| -0.218| -0.246| -0.479| -0.382| -0.121| 0.479| -0.693*| 1        |          |          |          |                   |       |       |       |       |
| Pb    | -0.582| -0.502| 0.61| 0.708*| -0.271| 0.295| 0.53| 0.284| 0.192| 0.227| -0.097| 0.16| 0.729*| 0.364| 0.752*| 0.41| 0.408| -0.28| 1        |          |          |          |                   |       |       |       |       |

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).
This result is in line with the findings of Bhutan et al. (2018) who have reported a strong positive relation between COD – BOD (r = 0.994) for the Brahmaputra River in Bangladesh. The present findings were also in line with Liou et al. (2004) who have reported a positive correlation between NH$_3$-N, BOD (r = 0.6618) for Keya River in Taiwan, and Barakat et al. (2016) who have reported a positive correlation between NO$_3$-N, COD (r = 0.73) for Oum Er Rabia River in Morocco.

3.5. Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is employed for grouping closely resembled sample sites based on similarity in water quality parameters and to identify the similarity and differences between sample sites for a better understanding of the water quality status along the river (Barakat et al., 2016; Son et al., 2020). The result of HCA is presented in Figure 4.

Cluster-1: encompasses sampling sites: S2, and S3. It represents the upper parts of the LAR course just below the control sampling point (S1). In this cluster, sampling sites S2 and S3 are closely resembled each other and exhibit similar physico-chemical parameters as they received pollutants from tanneries, soap and shoe factories, wood processing, metal processing, domestic, sewerage, and commercial wastes established around the river banks. Consequently, the quality of water samples at sites (S2) and (S3) were influenced by anthropogenic sources of pollutants. As a result, the highest values of PO$_4$-P (S2) and Cr (S3) were recorded in this cluster. However, compared to other clusters, this cluster is relatively encompassed less polluted cities. The sampling site (S1) located at the Gefersa Reservoir (S1- control) is surrounded partly by eucalyptus plantation and partly by agricultural lands with limited human impacts. As the CPI result indicated, the reservoir water quality is slightly polluted and its quality is not much affected; hence, not clustered with other sample sites found in the upper course.

Cluster-2: this cluster consists of sampling sites: (S4, S5, S6, and S7) located in the mid-course of the river. In this cluster group, (S5) and (S6) are very closely resembled as they were linked at a low distance. The sampling site (S4) was found to be more closely resemble site (S5) and (S6) than site (S7). Owing to its location, the sampling site (S4) receives pollutants from Addis Ababa City abattoir, garages, vehicle battery maintenance shops, sheep and cattle pens, fuel stations, and agrochemicals from irrigated vegetable farms. Thus, the highest COD, BOD, and salt concentrations (TDS, TSS, Salinity, EC, turbidity, NO$_3$-N, and Pb) were recorded at the sampling site (S4). The sample site (S5) is received pollutants from surrounding the National Alcohol Factory and irrigated vegetable farms. Sample sites (S6) and (S7) received wastes from upriver and surrounded by irrigated vegetables grown using the river water. Compared to other clusters, this cluster represents the most polluted sites.

Cluster-3: it encompasses sample sites (S8) and (S9) which are located in the lower course of the LAR system. The sampling site (S8) is typically located in the proximity of the Akaki-Kalti Industrial Zone where old industries are established. These include textile and garments, tanneries, paints, and plastic and discharging poorly treated wastewater into the river. The sampling site (S9) receives an influx of wastes from

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**Table 5. Principal component analysis of LAR water samples.**

| Parameters | Components | PC1  | PC2  | PC3  | PC4  | PC5  |
|-----------|------------|------|------|------|------|------|
| Temp.     |            | -0.19995 | 0.36465 | 0.13405 | 0.3072 | 0.087693 |
| PH        |            | -0.00884 | 0.35187 | -0.20772 | 0.45628 | -0.04028 |
| COD       |            | 0.32795 | -0.08595 | 0.01734 | -0.01469 | 0.27637 |
| BOD       |            | 0.32992 | -0.05411 | 0.1237 | -0.02547 | 0.16066 |
| DO        |            | -0.20092 | -0.17305 | -0.14315 | 0.016283 | -0.29381 |
| TDS       |            | 0.30174 | 0.023572 | -0.24761 | 0.19603 | -0.16725 |
| TSS       |            | 0.23474 | -0.06221 | -0.04218 | -0.19504 | 0.17916 |
| Salinity  |            | 0.30357 | 0.02229 | -0.25532 | 0.17341 | -0.1452 |
| Cond      |            | 0.28024 | 0.000778 | -0.29262 | 0.11117 | -0.13911 |
| Turbidity |            | 0.27893 | 0.23509 | -0.11538 | -0.07089 | -0.09118 |
| S$^{-2}$  |            | 0.058226 | 0.3263 | 0.18627 | 0.26284 | 0.48845 |
| SO$_4^{2-}$ |            | 0.27377 | 0.32205 | 0.057852 | -0.01611 | -0.16016 |
| NO$_3$-N  |            | 0.201 | -0.19664 | 0.3399 | 0.039916 | 0.03056 |
| NH$_3$-N  |            | 0.31265 | -0.00589 | -0.13853 | -0.23521 | 0.047903 |
| PO$_4$-P  |            | 0.1017 | -0.30118 | 0.3622 | 0.29808 | -0.31261 |
| Zn        |            | 0.043638 | -0.40649 | -0.13433 | 0.49333 | -0.03782 |
| Cr        |            | 0.090898 | 0.19769 | 0.44161 | 0.135 | -0.31781 |
| Cd        |            | -0.1222 | -0.25191 | -0.23113 | 0.27211 | 0.44207 |
| Pb        |            | 0.23797 | -0.18601 | 0.32449 | 0.11544 | 0.17325 |
| Eigenvalue|            | 8.05863 | 3.03714 | 2.64778 | 1.73772 | 1.11132 |
| % of Variance |            | 43.215 | 16.287 | 14.199 | 9.3187 | 5.9596 |
| Cumulative % |            | 43.22 | 59.51 | 73.71 | 83.03 | 88.99 |
upriver; effluent released from municipal wastewater treatment plant and surrounded by irrigated vegetable farms. Thus, this cluster represents the second polluted site. The sampling site (S10) is located at the lower tip of the river, received up-river wastes and agro-chemicals washed out from surrounding agricultural crop and irrigated vegetable farms. However, the concentration of pollutants at this sampling site was low, which may be due to natural aeration, microbial degradation of wastes, and dilution (Bu et al., 2010). Thus, cluster analyses help to identify sources of pollutants and pollution load along the river. More importantly, it can be used to establish permanent monitoring sites for long-term monitoring and follow-up of the river pollution to take appropriate measures.

### 3.6. Principal component analysis

Principal component analysis (PCA) is commonly applied to assess and evaluate water quality and identify the most important parameters that describe the entire data set by reducing and summarizing the bulk of data with minimal loss of original information (Ji et al., 2016). Hence, PCA involves the conversion of original variables into new and unrelated variables called the principal components.

In this study, the PCA is used to identify sources of pollutants and to describe the variations in water quality (Boateng et al., 2015; Oketola et al., 2013). The result of PCA including retained components, their loadings, eigenvalues; percent variance, and the cumulative percentage is presented in Table 5. The number of PCs to be retained was selected based on eigenvalues and scree plot (Howladar et al., 2017; Liou et al., 2004). Accordingly, the principal component with eigenvalue (λ > 1) was retained (Ouyang, 2005).

The extracted eigenvectors of PCA of the water samples revealed that the first five principal components covered 88.99% variance of the total data set. As shown in Table 5, 43.22% of the variance was explained by principal component (PC1), 16.29% of the variation contributed by PC2; 14.20% of variation contributed by PC3; 9.32% variation contributed by PC4, and 5.96% of variation contributed by PC5 with eigenvalue of 8.06, 6.04, 2.65, 1.74 and 1.11, respectively. According to Boateng et al. (2015), the positively loaded parameter influences water quality while the negatively loaded parameter is not.

PC1 showed a positive loading on COD, BOD, TDS, Salinity, and NH3-N. This result can be interpreted as organic matter, dissolved salt, and nutrient were the major factors responsible for contamination of the river water. In an anaerobic situation, high inputs of organic matter to river water may cause the formation of ammonia and organic acids (Ling et al., 2017). Anthropogenic sources of organic and nutrient pollutants were domestic, industrial, abattoir wastewaters, sewage, and agrochemicals. PC2 has positive loading on temp., pH, S−2 and SO42−, but negative loading on PO43− and Zn. Sulphide and sulfate were the main pollutants that may be generated from industries such as tanneries (Tadesse et al., 2016) and agrochemicals such as fertilizer and fungicide contain sulfate and phosphorous (Comero et al., 2014). Temperature and pH are important physical water quality parameters that influence biological and chemical reactions. Increased surface water temperature may enhance degradation of organic matter, facilitating dissolved salts and trace metals, and mineralization of organic nitrogen into NH4−N.

PC3 showed a positive loading on NO3−, PO43−, Cr, and Pb indicating nutrients and trace metals were dominant factors responsible for the change in river water quality. High loading of nutrients and trace metals may originate from untreated domestic wastes, sewages, detergents, industrial wastes, and fertilizers (Barakat et al., 2016). Trace metal like Cr may originate from tanneries, textile, metal works, electroplating, and paint factories (Melaku et al., 2007); whereas Pb may be generated from the vehicle battery, pigments, fossil fuels, and phosphate fertilizers (DWAf, 1996; Medaiba et al., 2004; Svobodova et al., 1993). PC4 depicted a positive loading on Zn. Thus, Zn represents a dominant factor for river water contamination. Positive loading on Zn may be attributed to human activities such as the use of Zn for galvanizing materials in steel and metals productions, application of Zn oxide in rubber manufacturing industries to activate the vulcanization process (Maurya and Malik, 2016), and is originated from the influx of industrial effluents and from of agrochemicals such as pesticides and fertilizers used in irrigated vegetable farms found in the proximity of river banks (Boateng et al., 2015). PCs was mainly contributed by positive loadings on S−2 and Cd, and by negative loadings on Cr and PO43−. Thus, it represents trace metal and sulphide as dominant source factors for river water pollution. Sulphide may be generated from various industries such as tanneries and textiles (WWAP, 2017) whereas Cd may be released from textile and leather industries, electroplating, pigments, thermoplastic stabilizers, vehicle batteries (Svobodova et al., 1993).

Generally, the PCA results showed that COD, BOD, TDS, Salinity, NH3-N, trace metals (Cr, Pb, and Cd) were found to be the most dominant pollutants responsible for contamination of LAR water. Thus, organic, nutrients, dissolved solid and minerals and trace metals are important parameters explaining the variations in the river water quality. This is in line with Ling et al. (2017) reports’ indicating that organic pollutants, nutrients, and salt were the most important pollutants contributing to water quality variation in the Wen-Rui Tang River watershed, China. Hence, positive loadings of organic and nutrient may indicate that water quality variations are associated with anthropogenic inputs that have influenced the river water quality. PCA is an important technique not only to understand source factors and variation in water quality but also to support efforts exerted towards conservation and management of river of water.

### 3.7. Science communication

In urban areas, river water pollution becomes a key problem affecting the environment and human health. To address this issue, generating conclusive information and communicating research findings are necessary. The results of this study are widely disseminated to end-users and decision-makers using different mechanisms. Information on the pollution status, major sources, and ways of mitigating water pollution is needed for local people (direct users), local government and regulatory body, industrial managers, environmental advocators, and media peoples to address LAR water contamination and sustainably use water resources. Science and knowledge communication is necessary to create awareness on the issue and increase the scientific understanding for preventing water pollution. Awareness for urban dwellers is necessary to change the practices of dumping domestic and commercial wastes into the river and open areas and to avoid connecting latrine and septic tank to the river system. Sharing science-based information with local industrial managers and regulatory bodies will assist in improving water quality and preserve a healthy aquatic ecosystem by treating wastes at the source. Addis Ababa University has already initiated science and technology promotion activities through its FM 99.4 Radio programme using local language to put scientific and technical knowledge into practice and support science and knowledge-based development. This can be used as one of the mechanisms to share the outcomes of the study at large to reach the general public.

### 4. Conclusion

The study revealed that the average concentrations of physicochemical parameters such as COD, BOD, TDS, EC, Turbidity, NO3−, NH3-N, PO43−, Cr, Cd, and Pb were surpassed recommended drinking water quality standards of Ethiopia (FMoWR, 2001) and the guideline value of (NIEA, 2014) and WHO (2011). This result indicates that the quality of LAR water has been influenced mainly by anthropogenic sources of pollution, such as industrial, domestic, municipal, sewage, and agrochemicals. The concentrations of heavy metals like Cr, Cd, and Pb in the river water exceeded the permissible limit value set for drinking water; Cr and Pb surpass limits set for livestock drinking water, Cr, Cd and Pb
were also surpasses guidelines limits of aquaculture, agriculture, and recreational water quality, hence affect the suitability of water for these development activities. A comprehensive water pollution index analysis results further confirmed that, except for Gefersa Reservoir (S1), the LAR water was heavily polluted with organic pollutants, nutrients, and trace metals. Heavy metal evaluation factor results showed that LAR water quality is classified as low to medium pollution with heavy metals. Pollution with heavy metals has far-reaching environmental and public health consequences. Pearson correlation analyses showed organic, nutrient, and some trace metals were originated from common sources like industries, abattoir, domestic, and sewerage. The principal component analyses explained 88.99% of the total variance in data sets, demonstrated that organic pollutants, nutrients, dissolved salts, and trace metals were the major source factors responsible for river water pollution. Thus, this study has shown the present status of LAR water pollution, dominant source factors, and implications for environmental and public health safety as well as the need for improving the water quality of the river for sustainable use. Therefore, to improve the river water quality, the following recommendations are made:

- Establish sampling stations for continuous monitoring on regular basis,
- Conduct further comprehensive long-term studies on biological, heavy metals, and physicochemical water quality and eco-smart river water treatment technologies with the active involvement of local people, and generate concrete data and information for the decision-maker and communities,
- Enforcing existing laws and standards related to pollution control and solid waste management and promote waste reduction at sources,
- Promoting afforestation with phytoremediation plants along the river banks and establishing buffer zone with strip grass around irrigated vegetable farms found nearby the riverbank may reduce agricultural runoff and leaching of toxic metals into the river system, and
- Awareness creation regarding river pollution and the need for multiple barrier approach at large.

To this effect, the findings from this study may provide invaluable information and concrete scientific data for government, policymakers, and environmentalists.

Declarations

Author contribution statement

Deshu Mamo Mekuria, Seyoum Leta Asfaw & Alemnew Berhanu Kassegne: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Kassegne: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Data availability statement

No additional information is available for this paper.

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