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Research article

Spatio-temporal variability and potential health risks assessment of heavy metals in the surface water of Awash basin, Ethiopia

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ABSTRACT

Increasing urbanization and industrialization are impacting on water quality globally. In the Awash River basin, Ethiopia, these drivers are impacting on water quality with further impacts created due to changes in water management releasing geogenic contaminants. The resulting water quality has potential to cause significant ecological and human health impacts. The physicochemical and heavy metals saptio-temporal variability and their associated risks to human health and ecology were assessed across twenty sampling stations in the Awash River basin. Over twenty-two physicochemical and ten heavy metals parameters were analyzed using different instruments including inductively coupled plasma mass spectrometer (ICP-MS). Elevated levels of heavy metals (As, V, Mo, Mn, and Fe) were detected in the surface water, surpassing the drinking water quality standards set by the World Health Organization (WHO). Seasonal variation was evident with peak concentration of As, Ni, Hg, and Cr were recorded in the dry season. A water quality index, hazard quotient, hazard index, heavy metal pollution index and heavy metal evaluation index were formulated to assess the potential risks to both human health and the environment. The highest values of heavy metal pollution index (HPI) above the threshold (>100) were observed in stations at Lake Beseka with HPI values ranged from 105 to 177. Similarly, the highest values of the heavy metals evaluation index (HEI) were observed in stations situated at cluster 3. The evaluation of health risk that is not related to cancer through hazard quotient demonstrated that in the case of both dermal and ingestion contact, cluster C3 > C1 > C4 > C2 and C3 > C4 > C2 > C1 were observed in children and adults, respectively. Overall, measures to reduce potential pollution risks must be taken in accordance with the standards in the river basin. Nevertheless, further research on the toxicity of heavy metals that pose risks to human health is also necessary.

1. Introduction

Globally, surface water for potable water supply is subject to numerous severe threats and stresses at both a national and

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international level, all of which are primarily caused by human and natural activities [1–3]. Notably, contamination of surface water by heavy metals (HMs) has emerged as a major environmental challenge worldwide [4,5]. The effect of HMs contamination, which can be induced by chemical or biological processes [6], on the environment and human health are noteworthy [7]. The presence of high concentrations of HMs such as aluminum, cobalt, copper, iron, lead, manganese, nickel, and zinc have been found to pose water hazards [8]. Thus, consistent exposure to HMs beyond their safe limits in humans and animals can have detrimental effects and result in non-carcinogenic risks such as neurological disorders, and liver and kidney diseases [9].

The Awash River basin (ARB) is one of the river basins in Ethiopia. Specifically, tributary rivers near factories have been receiving untreated wastewater, which makes them less safe to use and drink from directly or indirectly. For example, there are numerous factories located on the banks of the upstream Koka that manufacture products such as textiles, beer, soft drinks, alcohol, meat, and paint, all of them discharge effluents that has either been inadequately or partially treated into the tributary rivers. Consequently, degrades the receiver water bodies, because the wastewater drained potentially contains a large number of undesirable chemicals, suspended materials, and dissolved substances such as HMs, which have resulted in environmental issues. This is predominantly caused by unregulated levels of pollution resulting from factors such as industrial and population expansion, as well as insufficient sewerage and storm water infrastructure, which mainly degrade inhabitants and the environment. However, those who live in the basin use the river for irrigation, drinking water, fishing, and watering livestock are highly exposed and might be affected for environmental problems, and their wellbeing, and also become water insecure as well [10,11].

Nonetheless, there are three water supply systems are diverting the river water for domestic water supply and have got difficulties to treat well and enough due to the rise in pollutants load from the upstream catchments. But also, geogenic (Natural activities) factors significantly alter the water quality (WQ) of Lake Beseka (LB) and indirectly affect the river Awash downstream of the lake after the LB mix [12,13]. With the exception of a few research works, the majority of studies have concentrated on examining the physicochemical features of the surface water in the basin. Regrettably, analyzing these particular physicochemical factors does not accurately reflect the condition of the ecosystem as a whole [14]. Nonetheless, in recent times, a small number of investigations have been carried out to evaluate the human health and ecological impacts in Awash basin. Pollution of water with HMs is a widespread issue, and therefore, their distribution, concentrations, and sources gained global attention. The existence of HM contaminants in water bodies has raised significant concerns due to their well-known adverse effects on human health and ecosystem conditions. The examination was based on data obtained from 20 sampling stations located along the river's course. Unfortunately, the levels of V, Mo, Fe, Mn, Cr, Ni, Cu, Zn,

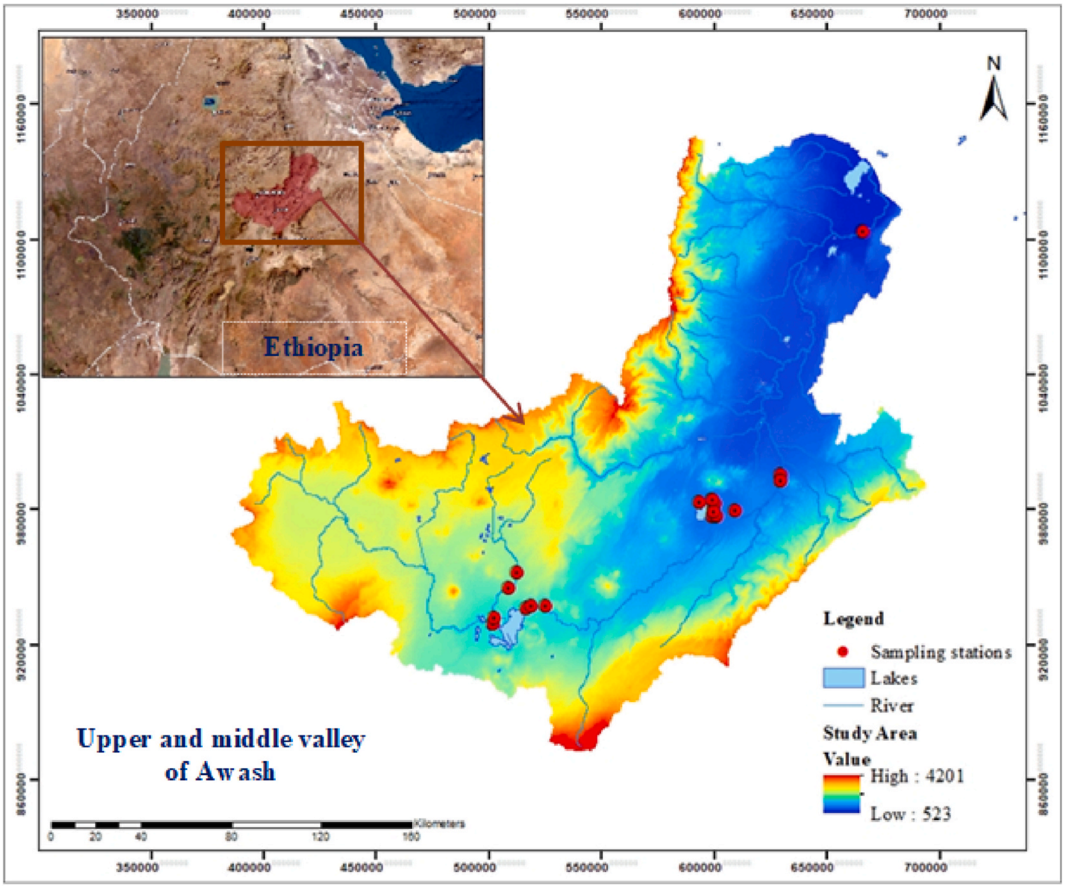

Fig. 1. Map of the study area and sampling stations of the Awash Basin, Ethiopia.

As, and Hg were not measured in the collected samples at these sites.

In this research, the background value technique was utilized. In reality, one of the three selections of the background value technique was employed. The control value of surface sediment samples gathered from the research area, which served as an uncontaminated reference, was utilized. In fact, there is still ambiguity when comparing different techniques, and there is no globally recognized methodology. However, so far, diverse methods have been suggested to evaluate the ecological hazard of water quality in the surroundings by utilizing distinct viewpoints of chemical, biological, and toxicological indicators. Thus, this investigation employed various literature sources, sediment quality guidelines (SQGs), permissible values, and uncontaminated water quality data for selected chemical substances to determine the background value for the research area. This research primarily aimed to evaluate a spatio-temporal examination of the variation in HMs concentrations in the surface water of ARB and to determine the potential risks of human exposure to polluted surface waters caused by HMs and their effects on the environment and human well-being. Overall, the study's results offer a comprehensive understanding of the concentration of HMs, the risks that water bodies pose to ecosystems.

2. Materials and methods

2.1. Description of the study area

The ARB is the fourth largest river basin in Ethiopia. It ranks seventh from the twelve river basin of the country in terms of surface water resources. The basin is placed between 7053′42″ to 12007′20″ North and 370 56′ 56″ to 430 17′ 04″ East. The river Awash originates from central highlands of Ethiopia and travelling a distance of 1280 km and eventually reaching and discharging into Lake Abbe near Djibuti boarder. The total area of the basin is about 114,123 square kilometer [15]. The basin is a heavily exploited and polluted basin. The basin has a multitude of businesses, over 50% of industries such as textiles, paints, slaughterhouses, soft drinks, spirits, breweries and pharmaceuticals are located on the banks of the Awash River and its tributaries.

Over the past 20 years, the Ministry of Water and Energy (MoWE) has attempted to evaluate river water on a regular basis using a variety of different ways. Yet, the basin Awash has been abused, developed and polluted. Accordingly, water pollution and drought directly or indirectly affect more than 18 million people in the Awash basin. As seen in Fig. 1, sampling sites were selected based on accessibility, availability of stable riverbeds, pollution load, and disturbance, safety, and characteristics. In order to obtaining more reliable data and to increase the representativeness of water resources and dynamics, samples were collected in April, June, August, and October. Thus, the selected stations were subject to extreme climate variations, i.e. the dry season (April and June) and the rainy seasons (July and October) were taken into account.

2.2. Sampling stations and sample collection

Water quality data is sparse in Ethiopia with limited data base. In Ethiopia, sampling and monitoring of surface water and industrial wastewater assessment carried on in different basins unregularly. For instance, the basin mainly focused on water quality parameters like physicochemical level. Nonetheless, the HMs and emerging pollutants weren't noticed. However, in order to evaluate the water quality and associated risks to human health and ecology, a total of seventy surface water samples were collected for one year (April, June, August, and end of October), from the twenty sampling stations (Fig. 1). Samples were collected from different water bodies such as from tributaries, the Koka Dam, LB, and also from gauged and ungagged stations along the main Awash River basin (Fig. 1). Samples were often taken in the middle month using grab sampling techniques. The plastic bottles used were rinsed to minimize the risk of contamination. Depending on spatial and temporal variability of the basin, the sampling frequency was performed four times a year for physicocohemical analysis (22 WQ parameters) and twice a year for HM analysis (10 HMs).

2.3. Analytical methodology and quality control

In order to accomplish the aim of the study, the WQ of the basin was assessed using various approaches including physical, chemical, and HMs analysis [16]. To maintain the quality of the data obtained in the investigation, proper sterilization of equipment aseptic procedures, control media, blank measurements, and triplicate analysis were used. In the study, physicochemical parameters were analyzed using in-situ multi-meters at sampling sites via Waterproof 800 multi-meter for the analysis of temperature/EC/TDS/pH; photometer 7100 for TH, alkalinity, SO_4^{2-}, PO_4^{3-}, Cl^-, F^-, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, NO_3^-, NO_2^-, NH_4^+, and NH_3 analysis; FAAS for Na and K analysis at EARI and ICP-MS/OES were used for HMs analysis at Oxford University. Following sample collection, samples were acidified, allowed to equilibrate overnight to allow any precipitates or materials that had adhered to the bottles to dissolve, and then shipped to Oxford University in the UK.

A PerkinElmer NexION 2000B instrument, ICP-MS was used to examine the levels of HMs. Conditions including instrumental selection were set to validate and regulate the quality of data, accuracy and stability of calibration. The instrument was calibrated using the external calibration technique, in which the concentrations for the measured sample set were extrapolated using linear regressions made from raw counts per second data from a number of standards. In order to normalize any general instrument drift, all blanks, standards, and samples were spiked with 1 μg/L Rh, In, and Ir. Dilutions were made using a 2% HNO_3 solution, prepared using in-house distilled HNO_3 and 18.2 Mohm DI water.

2.4. Water quality and pollution indices

Different WQ and pollution indices have been used to assess the health, and suitability of water. The water quality indices (WQIs) are one of the most effective and supportive tools to assess information on the quality of any water body [17]. Both the relative weight and WQI were computed using Eq. (1) and Eq. (2), respectively. Where, R_{Wi} represents the relative weight.

$$R_{Wi} = \frac{Wi}{\sum_{i=1}^{n} Wi} \tag{1}$$

$$WQI = \sum_{i=0}^{n} Wi * \frac{Ci}{Si} * 100 \tag{2}$$

The assessment of HMs pollution was an important aspect of most WQ assessment programs. For instance, the Global Environment Monitoring System (GEMS) program comprises ten metals: Al, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn, and others also use As and Se. Whereas, the US-EPA considers eight trace elements as high priority: As, Cd, Cu, Cr, Pb, Hg, Ni, and Zn [18]. Therefore, some others use the same metals in their priority lists. Others use some highly toxic metals such as Be, T, V, Sb, and Mo should be monitored where they are likely to occur. The HPI is one of the effective tools to analyze and convey data (raw environmental information) to the public, technicians, managers, and decision-makers. The heavy metal pollution can be examined by determining the quality index of HMs pollution index methods. It rates the aggregate influence of individual HMs on the overall WQ and is useful in getting a composite influence of all the metals on overall pollution [19]. Equation (4) was used to how the weightage of each parameter to compute HPI.

$$Qi = \frac{\sum_{i=1}^{n} |\boldsymbol{Mi}\ (-)\ \boldsymbol{Ii}|}{(\boldsymbol{Si} - \boldsymbol{Ii})} * 100 \tag{3}$$

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} \boldsymbol{WiQi}}{\sum_{i=1}^{n} \boldsymbol{Wi}} \tag{4}$$

Where Mi is the concentration of HMs monitored in μg/L, Qi is the sub-index of the ith parameters (calculated using Eq. (3)), Wi is the unit weightage of the ith parameter and n is the number of parameters considered. In the equation, unit weightage (Wi) is unit weightage is taken as a value inversely proportional to the recommended standard (Si) of the corresponding parameter. Similar to HPI, the heavy metal evaluation index (HEI) was used to evaluate (Eq. (4)) the concentration of heavy metals and metalloids in the water quality of the basin water bodies for different uses like domestic uses [20,21]. It is calculated using Eq. (5). Where, H_c and H_{Mac} are the concentration of HMs analyzed and the maximum admissible concentration of the ith parameter, respectively.

$$\mathrm{HEI} = \frac{\sum_{i=1}^{n} \boldsymbol{Hc}}{\sum_{i=1}^{n} \boldsymbol{H_{Mac}}} \tag{5}$$

2.5. Contamination factor (Cf) and Modified contamination degree (mCd)

The surface water contamination level by HMs can be expressed in terms of the contamination level of surface water. As shown in Eq. (6) and Eq. (7) it is a ratio obtained by dividing the concentration of each HM in the water by the upper permissible value or its background value [22].

$$\text{Contamination factor (Cf)} = \frac{\text{Concentration of water sample (Ci)}}{\text{Concentration of background sample (Cb)}} \tag{6}$$

$$C_f^i = \frac{C_A^i}{C_N^i} - 1 \tag{7}$$

Modified contamination degree (C_d): Modified contamination factor (mCf) the new method, sometimes called contamination degree (C_d) [23]. As shown in Eq. (9), the contamination degree (C_d) is defined as a sum of all contamination factors ($\sum C_f$). This is the well-known pollution indicator index developed by the Geological Survey of the Slovak Republic and used to evaluate the water quality of the basin. It is computed using Eq. (8).

$$C_d = \sum_{i=1}^{n} C_f^i \tag{8}$$

Contamination degree (Cd) is defined as a sum of all contamination factors (Cf) and is expressed

$$mCd = \sum_{I=1}^{n} Cf^{i} \Big/ n \tag{9}$$

2.6. Ecological risk assessment

Human health and ecological risks assessment cannot be carried out completely and accurately because they contain many estimations and uncertainties. The health of surface water bodies such as rivers and lakes can be assessed using ecological risk assessment indices. Nontheless, there exist diverse techniques for evaluating the risk of heavy metals, among which the approach of computing the entire concentration is extensively employed and recommended [24,25]. The ecological risk assessment indices (ERAI) are used to assess the ecological risk that might be posed during the discharge of domestic and industrial wastes on surface water bodies. The risk was computed using the following formulae (Eq. 10 and Eq. (11)).

$$\boldsymbol{E_r^i} = \boldsymbol{T_r^i} * \boldsymbol{C_f^i} \ldots\ldots\ldots \left(\boldsymbol{C_f^i} = \frac{\boldsymbol{C_i}}{\boldsymbol{C_n}} - 1 \right) \tag{10}$$

$$\boldsymbol{ERAI} = \sum_{i=1}^{n} E_r^i \tag{11}$$

Where $\boldsymbol{E_r^i}$ is the individual potential ecological risk factor of HMs, $\boldsymbol{T_r^i}$ is the biological toxicity factor of heavy metals, $\mathbf{C_i}$ is the measured mean concentration of heavy metals in μg/L, and $\mathbf{C_n}$ is the geochemical background value of HMs [26,27], in the surface water of ARB, driven from maximum allowable WHO standard [28].

2.7. Human health risk assessment

Risk assessment is a predictive estimate of potential health impacts, which might be ecological and human health risks. It mainly focuses on the existing situation and the future of water bodies in the Awash River Basin, Ethiopia.

2.7.1. Non-carcinogenic and carcinogenic risk assessment

Most researchers used to assess human health risk assessment using different terminologies including health hazard, risk, and exposure. In fact, risk assessment is the process of estimating the potential impact of a hazard (often chemicals) on a specific human population under a specific set of conditions and for a specific time frame. In the study, the authors tried to assess human health ($\mathrm{CDI_{ingestion}}$ and $\mathrm{CDI_{dermal}}$) [29,30] and ecological risks using the following equations (Eq. 12, Eq. (13), Eq. (14), and Eq. (15)).

$$\mathrm{CDI_{ing}} = \frac{Csw * \ IRsw * EF * ED}{Bw * AT} \tag{12}$$

$$\mathrm{CDI_{derm}} = \frac{Csw * SA * Kp * ABS * ET * CF * EF * ED}{Bw * AT} \tag{13}$$

Whereas, $\mathrm{CDI_{ingestion}}$ is an average daily intake of heavy metals from ingestion; $\mathrm{CDI_{dermal}}$ = an average intake of heavy metals from dermal contact; Csw = heavy metal concentration in the surface water (μg/L/day); IRsw = ingestion rate for SW (Liter/day); CF = conversion factor (L/$\mathrm{cm^3}$); ED = exposure duration (years); BW = bodyweight of the exposed individual (Kg); AT = time period over which the dose is averaged (days); EF = exposure frequency (days/year); SA = exposure skin surface area ($\mathrm{cm^2}$); Kp = permeability (cm/hr), and ABS = dermal absorption factor (unit-less) (indicated in Table 5).

2.7.2. Hazard quintet (HQ) and hazard index (HI)

The hazard quintet and the hazard index are indicators for assessing the non-carcinogenic risk [37]. According to USEPA [38], non-carcinogenic hazards are characterized by a risk quotient (HQ), which is a risk assessments parameter and is expressed as the probability than an individual will suffer an adverse effect. Conversely, the risk index is used to assess the overall potential for non-carcinogenic side effects caused by more than one heavy metal (HM). The HI computed the overall sum of all calculated HQs for each HM (Eq. (16)).

$$\mathrm{HQ_{ingestion}} = \frac{\mathrm{EXPingestion}}{\mathrm{RfDingestion}} \tag{14}$$

$$\mathrm{HQ_{dermal=}} \frac{\mathrm{EXPdermal}}{\mathrm{RFDdermal}} \tag{15}$$

$$\mathrm{HI} = \sum \mathrm{HQi} \tag{16}$$

The probability of developing cancer using polluted river water during a lifetime was estimated by multiplying ADI values with the cancer slope factor (SF) [38]. The carcinogenic risk was estimated both for an individual method (Risk-i) and multiple methods (Risk factor) and was calculated using Eq. (17) and Eq. (18) respectively.

$$\text{Carcinogenic Risk Individual} = \text{ADI} * \text{SF} \tag{17}$$

$$\text{Carcinogenic Risk Total} = \sum_{i=1}^{m} \sum_{i=0}^{n} Risk\ ij \tag{18}$$

Whereas, CDI, the lifetime cancer risk can be calculated using Eq. (13) and in this study, $\text{Risk}_{\text{ingestion}}$ and $\text{Risk}_{\text{dermal}}$ are considered as risk contributors through water media [39].

2.8. Analytical tools

The results of the water quality test were analyzed and evaluated by descriptive analysis using the statistical software SPSS version 23, origin lab 23, and Minitab [40]. The relationship between HMs and physicochemical concentrations was compared and Pearson's correlation coefficient test (two-way) [41] was used, differences were also considered at $p < 0.05$. Correlation, principal component, and cluster analyses were used to assess sources of HMs pollution and address problems and issues.

3. Results and discussions

3.1. Physicochemical analysis

The concentration of physicochemical water quality parameters in the samples of Awash basin measured at particular 20 stations. The seasonal variation of physicochemical results of the basin are shown in Figures (from Fig. 2a to d) and Fig. 3 were compared with the correlation analysis explained in Table 2 and also the mean and standard deviation were computed as shown in Table 3. The concentration of electrical conductivity, EC ranged from 3650 μS/cm to 172.4 μS/cm with a mean value of 1019 μS/cm. These high values indicate the presence of large number of ions within the surface waters. Studies have shown that high salt concentrations can cause eye irritation in humans and chlorosis in plants.

As illustrated in Fig. 3, the highest values of pH, electrical conductivity, total dissolved solids, alkalinity, bicarbonates, carbonates, and chloride and also the lowest turbidity and total hardness were exhibited in cluster three. These high values might be due to organic and inorganic constituents released from geogenic interactions. The pH values varied from 9.65 to 6.59 with an average of 8.2. The pH can affect the formation of metal complexes due to the complexing ability of dissolved organic carbons. At most of the stations sampled, the recorded turbidity values were above the WHO-specified 5 NTU tolerance. Because of high precipitation and urban and

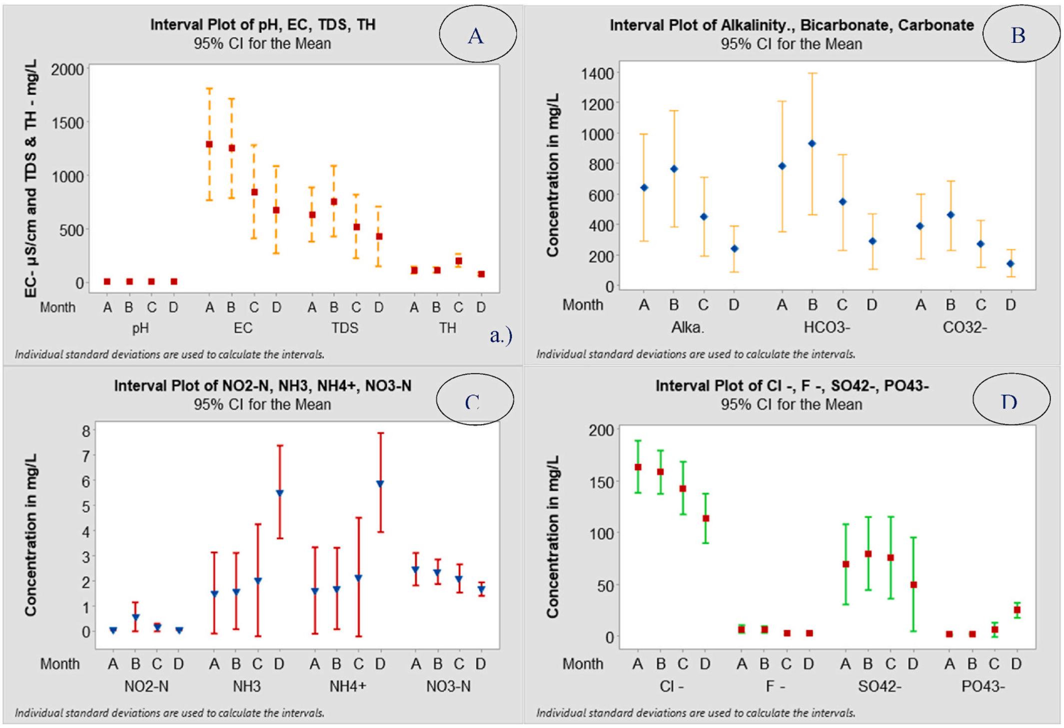

Fig. 2. Seasonal variation of some physicochemical parameters in the Awash basin.

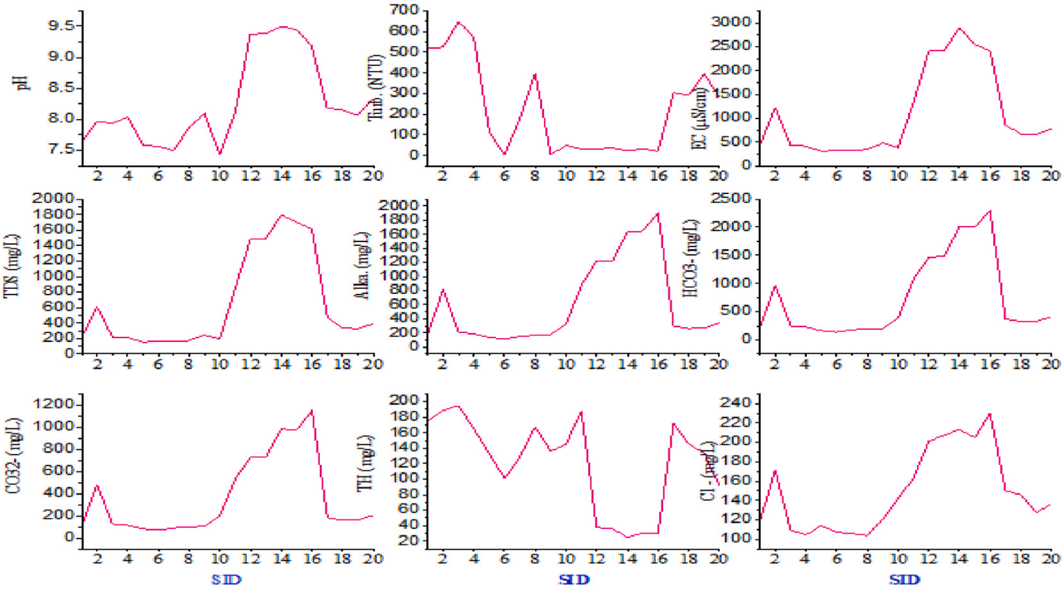

Fig. 3. Spatial variation of physicochemical parameters and at all sampling stations.

Table 1

The comparisons of heavy metals mean concentration in different countries.

River/basin	Country	V	Cr	Mn	Ni	Cu	Zn	As	Mo	Fe	Hg	References
Sisa River, Kumasi	Ghana	–	70	47.5	–	1075	193	–	–	2525		[41]
Honghu Lake	China	–	0.65	–	–	0.2	4.03	3.99	–	–	0.004	[43]
Patancheru district	India	–	16.8	72.9	26.7	–	98.6	29.2	–	162	–	[44]
Songhua River	China	–	12.0	–	1.68	4.27	64.3	–	–	–	–	[45]
Kolong River	India	–	–	–	–	0.05	0.13	–	–	–	0.59	[5]
Uglješnica	Serbia	–	–	935	–	438	1308	1.5	–	453	1.05	[46]
Odra River	Poland	–	–	353	–	54.6	535	–	–	1861	–	[47]
Nairobi River	Kenya	–	–	4300	–	50	480	–	–	25.60	–	[48]
Lorestan province	Iran	–	31	30	27	29	39	–	–	56	–	[49]
Awash basin	Ethiopia	26.6	3.3	67	2.3	108.5	55.6	23	31.2	221	0.6	This study
	WHO	20	50	500	20	1300	3000	10	70	300	2	[28]

Table 2

Correlation matrix and level of significance of selected heavy metals of surface water in the Awash basin.

Heavy Metals	V	Cr	Mn	Ni	Cu	Zn	As	Mo	Fe	Hg
Vanadium (V)	1									
Chromium (Cr)	−.142	1								
Manganese (Mn)	−.076	.740**	1							
Nickel (Ni)	−.327*	.614**	.764**	1						
Copper (Cu)	−.280	.245	−.115	.023	1					
Zinc (Zn)	−.274	−.117	−.062	.045	−.097	1				
Arsenic (As)	.755**	−.114	.062	−.200	−.403*	−.223	1			
Molybdenum (Mo)	.933**	−.191	−.086	−.358*	−.284	−.262	.760**	1		
Iron (Fe)	.389*	−.189	−.145	−.029	−.250	−.084	.103	.304	1	
Mercury (Hg)	.663**	.021	.115	−.005	−.170	−.203	.672**	.770**	.016	1

*. Correlation is significant at the 0.05 level (2-tailed). Bold values are highly correlated.

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

agricultural runoff in rainy season high values in turbidity observed.

Fig. 2A shows graphs of EC, TDS and TH ranges; Fig. 2B introduces alkalinity, bicarbonates and carbonates; Fig. C describes nitrate, ammonia, ammonium and nitrate; and Fig. D shows levels of chloride, fluoride, sulfate, and phosphate). N.B: Dry and wet seasons; A = April 2021, B = June 2021, C= August 2021, and D = October 2021.

As shown in Table 2, alkalinity in river water is positively correlated with HCO3-, CO32, pH, and EC. This may reflect the chemical relationship of water and the forces of hydrogen (pH), HCO3- and CO32-. This may be due to the volcanic activity (ash) that occurred

Table 3
Mean (ẍ) and standard deviation (SD) of heavy metals in the surface water collected from different sampling stations of the Awash Basin (N = 40).

SID	V-51	Cr-52	Mn-55	Fe-56	Ni-60	Cu-63	Zn-66	As-75	Mo-98	Hg-202
SW1	8.0 ± 5.1	5.5 ± 5.0	14.3 ± 2.5	125.5 ± 84.0	4.0 ± 2.1	156.9 ± 89.1	56.0 ± 32.7	5.0 ± 4.6	2.7 ± 1.4	1.0 ± 0.9
SW2	12.7 ± 2.8	23.2 ± 12.9	626.8 ± 618.4	30.5 ± 7.5	5.8 ± 4.6	131.5 ± 88.8	23.0 ± 3.9	10.9 ± 9.7	6.0 ± 2.4	0.8 ± 0.5
SW3	15.9 ± 0.4	5.3 ± 0.4	99.7 ± 90.5	29.9 ± 3.5	2.3 ± 0.7	208.8 ± 173.1	25.5 ± 6.3	6.2 ± 4.7	4.4 ± 0.8	0.1 ± 0.0
SW4	18.4 ± 4.8	11.4 ± 11.2	8.3 ± 1.1	26.3 ± 14.8	2.6 ± 0.4	215.0 ± 183.6	29.1 ± 5.2	5.4 ± 4.3	4.5 ± 0.8	0.0 ± 0.0
SW5	3.2 ± 0.0	3.1 ± 2.7	13.3 ± 5.0	209.1 ± 29.5	3.2 ± 0.4	311.0 ± 274.8	44.3 ± 0.9	3.0 ± 2.4	4.4 ± 1.2	0.1 ± 0.1
SW6	7.1 ± 2.0	0.8 ± 0.5	4.4 ± 1.7	14.6 ± 4.2	1.9 ± 0.1	98.4 ± 66.8	67.4 ± 8.0	2.1 ± 1.6	5.5 ± 1.2	0.1 ± 0.0
SW7	5.1 ± 0.1	0.5 ± 0.1	7.4 ± 1.5	185.0 ± 138.8	2.3 ± 0.8	50.5 ± 25.0	25.4 ± 8.6	3.0 ± 2.3	5.1 ± 0.8	0.1 ± 0.0
SW8	8.2 ± 2.2	0.8 ± 0.04	21.1 ± 15.7	379.6 ± 207.5	2.9 ± 0.5	81.3 ± 54.4	45.7 ± 28.1	3.5 ± 2.6	4.0 ± 0.4	0.1 ± 0.1
SW9	8.0 ± 2.1	0.4 ± 0.2	6.8 ± 1.0	74.4 ± 30.8	1.7 ± 0.3	58.8 ± 37.6	468.8 ± 21.2	3.0 ± 2.5	5.7 ± 1.8	0.1 ± 0.0
SW10	26.4 ± 21.1	0.6 ± 0.0	173.5 ± 54.5	344.0 ± 303.3	2.8 ± 1.4	119.3 ± 89.0	100.8 ± 78.3	10.2 ± 3.9	35.9 ± 32.5	0.0 ± 0.0
SW11	12.7 ± 7.0	0.4 ± 0.1	132.8 ± 114.1	52.1 ± 17.4	1.7 ± 0.3	119.2 ± 81.2	25.2 ± 2.8	23.8 ± 22.7	15.1 ± 11.1	0.6 ± 0.4
SW12	69.9 ± 1.2	1.4 ± 0.5	23.0 ± 1.1	631.3 ± 227.0	1.5 ± 0.2	54.3 ± 29.3	21.4 ± 1.8	57.2 ± 38.4	88.9 ± 5.2	1.2 ± 0.3
SW13	72.8 ± 0.9	1.5 ± 0.5	19.0 ± 6.7	598.7 ± 300.5	1.5 ± 0.3	49.6 ± 29.1	11.5 ± 1.6	43.4 ± 24.3	91.0 ± 5.2	1.8 ± 0.8
SW14	71.3 ± 1.4	1.1 ± 0.7	12.7 ± 9.2	459.4 ± 382.6	1.3 ± 0.3	45.5 ± 20.6	8.1 ± 3.8	35.1 ± 16.0	116.7 ± 30.1	2.5 ± 1.6
SW15	62.0 ± 5.0	0.6 ± 0.2	7.5 ± 4.4	108.7 ± 87.3	1.2 ± 0.1	58.4 ± 38.2	8.1 ± 1.5	45.6 ± 20.9	111.7 ± 3.2	1.4 ± 0.2
SW16	94.2	1.9	7.91	150.7	0.8	15.6	8.2	61.2	92.0	0.97
SW17	9.6 ± 1.3	0.7 ± 0.4	89.5 ± 81.2	262.6 ± 94.5	2.4 ± 0.2	52.5 ± 36.8	24.1 ± 1.0	17.7 ± 15.5	20.2 ± 11.0	0.2 ± 0.0
SW18	15.0 ± 9.6	0.6 ± 0.0	16.4 ± 10.2	273.0 ± 161.6	2.2 ± 0.7	65.6 ± 46.2	25.9 ± 3.9	12.0 ± 11.3	13.0 ± 9.4	0.1 ± 0.0
SW19	18.5 ± 8.5	0.6 ± 0.0	13.8 ± 6.2	239.7 ± 94.5	2.2 ± 0.6	62.7 ± 43.0	42.4 ± 21.7	9.9 ± 9.03	11.4 ± 7.4	0.1 ± 0.0
SW20	23.8 ± 10.0	0.5 ± 0.1	11.5 ± 5.8	198.3 ± 89.4	1.1 ± 0.1	169.4 ± 152.1	28.0 ± 1.6	10.9 ± 9.2	16.4 ± 6.5	0.0 ± 0.0
Max	94.2/SW16	36.1/SW02	1245.2/SW02	899.2/SW13	10.4/SW02	585.8/SW05	490.0/SW09	95.6/SW12	146.7/SW14	4.2/SW14
Min	2.9/SW01	0.2/SW04	2.7/SW06	10.5/SW06	0.8/SW16	15.6/SW16	4.4/SW14	0.4/SW01	1.3/SW01	0.0 (BDL)
Range	91.3	35.9	1242	888.7	9.6	570.2	485.6	95.2	145.4	4.2
Mean	26.5	3.1	67.0	221.4	2.3	108.5	55.6	17.4	31.2	0.6
WHO 2011	20 μg/L	50 μg/L	500 μg/L	300 μg/L	20 μg/L	1300 μg/L	3000 μg/L	10 μg/L	70 μg/L	2 μg/L

N.B: All units are in ppb (μg/L); BDL below the detection limit.

while, bicarbonate ions were predominantly observed in the water chemistry of LB between pH 9.54 and 9.65. These values are high, so which becomes unsuitable for most aquatic environments and organisms. Similarly, basic ions such as HCO3-, and CO32- ions may contribute to the presence of high alkalinity at stations SW12, SW13, SW14, SW15, and SW16. Ions like, Ca and Mg contents are essentially important factors in the effect of hardness on the toxicity of natural waters, but their effects were not significant in LB.

Industrialization and uncontrolled household waste continue to degrade WQs, which can directly or indirectly affect human health, water availability, and sustainability for the poor. That is the main reason, affecting scarce water resources. As explained in Table 2, the statistical distributions of several physicochemical parameters and selected HMs from the dry and wet ARB. The pH value was between 7.2 and 9.5 during the dry and wet seasons. High pH values (>8.5) exceeding WHO limits were recorded in both seasons. Similarly, the values recorded for the dry and wet seasons ranged between 432 μS/cm to 3650 μS/cm and 172 μS/cm to 2290 μS/cm, respectively.

3.2. The concentration of heavy metals

The average values found in this study were found to be reasonably acceptable when the level of heavy metals in the surface water of various nations was computed, as shown in Table 1. On the basis of the measured concentration of individual heavy metals, their minimum, maximum, and mean values were calculated. As explained in Table 3, the average levels of As (95.60 μg/L), Mo (146.73 μg/L), Hg (4.18 μg/L), and V (94.19 μg/L) exceeded the WHO's (2011) limit of 10 μg/L, 70 μg/L, 2 μg/L, and 20 μg/L respectively. This is possible due to both human activities and natural occurrences, which have led to a rise in the concentration of HMs in the water of Beseka. Consequently, consumption of contaminated water with HMs such as Cd, Cr, Mn, Hg, Zn, As, and Mo can cause neurosis and chlorosis due to their persistent nature and prolonged biological half-lives within the human body [42].

The average level of iron in the surface water of Awash is 246 μg/L. Although iron is an essential heavy metal, exceeding the recommended limit can lead to severe damage. At station SW13, the concentration of iron was found to be high (almost three times higher than the WHO limit), which can negatively impact human health. This may lead to increased hypertension and congestion, which can further increase the respiration rate. During the study, it was observed that the concentration of Cr was lower than the WHO limit (50 μg/L) throughout the study area. The values of Cr ranged from 0.2 to 36.1 μg/L and 0.5 to 22.5 μg/L during dry and wet seasons, respectively. The highest value of Cr (36.12 μg/L) was observed in cluster 1. The Cr is a well-known carcinogenic substance, and the highest concentration was observed in areas with a high number of tanneries located in the upstream Koka catchment. The highest Hg levels, 4.18 μg/L were observed in the study areas, which could be attributed to organic and inorganic chemicals or substances used in industries like paint, textile, and tanning, which mix with water when wastewater is released. Research on As issues in Africa primarily focuses on pollution characterization and quantification, with limited studies on human health risks and treatment systems.

In the dry season, high As concentrations ranged from 3.7 to 95.6 μg/L, while in the wet season, concentrations were greatly reduced to 0.4 to 24.7 μg/L due to strong dilution effects. Drinking water containing high levels of As can lead to severe health issues in humans [50]. Similarly, the surface water in the Awash Basin exhibited elevated Ni levels (0.8–10.4 μg/L) during the dry season and lower levels (1.2–3.5 μg/L) in the wet season. The highest Ni concentration (10.41 μg/L) was recorded during the dry season. Ni is known to trigger allergic reactions and some of its compounds are potentially carcinogenic. Moreover, nickel exposure has been linked to various health issues in humans, including renal, cardiovascular, reproductive, and immunological effects [51]. Cluster 1 had a high level of Zn, primarily due to the improper disposal of industrial and household waste, such as car tires and motor oil.

As seen in Fig. 4, high concentrations of V, As, Mo, Hg, and Fe were observed in C3, which might be highly related to the rift features and the sedimentary properties (because of volcanic ash and weathering of rocks). The level of V ranged from 94.19 to 0.91 μg/L with a mean value of 26.45 μg/L, which exceed the permissible limit by four times. Natural activities like surface weathering and volcanic ash in the LB might be a cause for HMs. Similarly, high concentrations of Cr, Mn, Ni, and Cu were observed in C1 from industrial waste containing tanneries (five or more tanneries are located along the Little Akaki). These have been increased the level of HMs in surface water, which might cause toxic and detrimental effects on aquatic organisms, human health, and the environment. This may be due to chemical fertilizers from upland farmlands remaining in the environment and enriching Fe in rivers.

Even though the concentration of pollutants decreases throughout the downstream courses due to sedimentation, turbulence, adsorption, precipitation, and transformation effects at Koka Dam. The statistical graphic concentration shows C4, which is downstream of LB, was affected by the upstream discharge or fluxes. Due to the discharge of LB, a high concentration of As was observed in C4, which is relatively higher than cluster two and cluster one (highlighted by blue color) (Fig. 4). Exposure to elevated concentrations of HMs, such asCr, Hg, Pb, As, and others might cause cancer, retard human development, and productivity, and can cause severe health and environmental effects and in extreme cases, death [52,53]. The highest concentrations of V, Cr, Mn, Fe, Cu, Zn, As, Mo, and Hg with values of 94.16 μS/cm, 36.12 μS/cm, 1245.18 μS/cm, 899.15 μS/cm, 10.41 μS/cm, 585.83 μS/cm, 489.96 μS/cm, 95.6 μS/cm, 146.7 μS/cm and 4.18 μS/cm were measured respectively at separate stations. About 50% of the analyzed HMs including As (95.6 μg/L, Mo (146.7 μg/L), V (94.2 μg/L), Mn (1245 μg/L), and Fe (899 μg/L) exceeded about nine-folds, two-folds, four-folds, two and half-folds, and three-folds of the WHO limits respectively.

As explained in Table 2, the Pearson correlation coefficient was utilized to assess the potential analogous origins of metals in the surface water. A person's correlation matrix for r-values analysis that there was a strong positive correlation between As and V, As and Mo, Mo and V, Ni and Mn, Ni and Cr, Hg and V, Hg and As, and Hg and Mo with a high r-value of 0.933, 0.760, 0.755, 0.764, 0.614, 0.663, 0.672, and 0.770 respectively ($p < 0.001$). According to Table 2, the correlation matrix for individuals revealed that As and V, as well as As and Mo, have a strong correlation with r-values of 83.2% and 77.4%, respectively. In sum, discharge of industrial wastewater

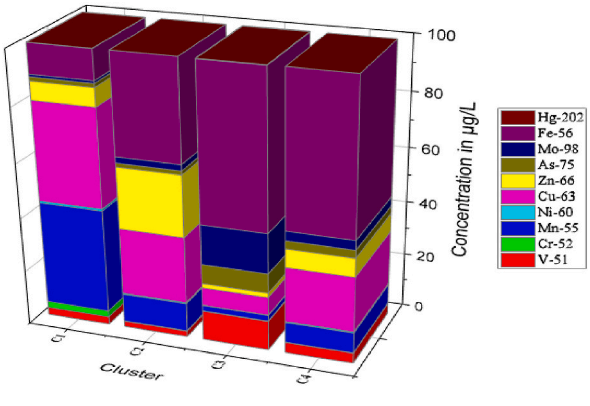

Fig. 4. The average concentration of heavy metals in the cluster stations of the study area. N.B: **C1**= Cluster 1 stands Awash upstream Koka; **C2**= Cluster 2 stands upstream LB; **C3** =Cluster 3 stands stations on LB, and **C4** =Cluster 4 Awash River after Lake Beseka mix.

reserved for months in ponds, sewage treatment plants, and lagoon polluted water bodies during the rainy season. Nonetheless, during the dry season, the potential for river dilution or mass conservation effects was weak due to the quantity and volume limitations of the expected relatively freshwater sources high pollution exhibited.

The metal Hg is an extremely hazardous heavy metal that is present in the biosphere. As indicated in Fig. 5a and b, a significant proportion of the samples exhibit high levels, especially in the middle valley (cluster three) of the study area, where the concentration of Hg was high. This can transform into a highly toxic methylmercury when in contact with aquatic sediments. The metal Cr is also a toxic and carcinogenic element [54]. Nonetheless, in case the amount of HMs surpasses the acceptable limit in aquatic systems, they become perilous as they accumulate in living beings, including As, Cr, and Cu. These metals transform into toxic and cancer-causing agents that contaminate ecosystems. The pollution caused by heavy metals is persistent, subtle, and enduring. As metals are not biodegradable and have a lengthy half-life, they remain in various body parts and the environment, leading to health risks.

3.3. *Cluster analysis*

Cluster 1 is comprises stations SW1, SW2, SW3, SW4, and SW10. The stations grouped in this cluster are substantially the upstream side of Koka except for station SW10, indicating parallels in heavy metals essence content including Cr, Mn, Ni, and Cu in Awash and its tributary rivers water sample. Therefore, the potential source in this cluster has been anthropogenic factors such as urban waste, industrial waste, and the like. However, the associations of these stations can also be seen in the figure in plots in plot Fig. 5b. Cluster 2 is represented by stations SW12, SW13, SW14, SW15, and SW16. This cluster is unexpectedly affected by groundwater-surface water interactions and the presence of these HMs is largely associated with the geogenic nature of the lake catchment. Cluster 3 includes SW5, SW6, SW7, SW8, SW9, and SW11, indicating their sources of HMs content similarity to that of the control samples.

Therefore, the heavy metal content of the River Awash in these stations was not affected significantly by geogenic exertion and could be attributed to anthropogenic sources. This result is harmonious with that of the score plot, plot 5b. The fourth cluster is made up of SW17, SW18, SW19, and SW20 are associated with the discharge of Lake Beseka's water into Awash River, indicating that the cluster is affected by the accretive impact of geogenic (the lake water discharge) and anthropogenic sources. The sources of HMs in the study sites are highlighted by the cluster analysis in Fig. 5a and b. For instance, the statistical studies revealed a significant link between the Hg, Mo, V, As, and Fe depicted in Table 3. It indicates that geogenic activities inside the research region, which were weathering impacts of the geology, rather than their anthropogenic activities in the LB, were what caused the degree of contamination of these metals.

In conclusion, all of the clusters generated were based on known associations between metals and surface water samples. The cluster analysis (Fig. 5a and b) illustrates that cluster 1 contains only Fe, which appeared due to industrial and domestic wastes. Cluster 2 consisted of Mn, Cu, and Zn, which might be from the irrigation runoff, industrial wastes, and unregulated application of chemicals and fertilizers and vehicle wastes like tires, batteries, and oils. Cluster 3 contained Mo, As, V, Cr, Mn, and Ni, which is the weakest of the three clusters and the one with the highest concentration of HMs, for this group, there is a strong indication of a natural source from geogenic material decomposition, volcanic interaction, and burning of substances containing these metals.

3.4. *The water quality index (WQI)*

The WQI was employed to evaluate the condition of water quality and its appropriateness analysis. According to the investigation, the entire WQI score amounted to 316.7, indicating severely contaminated water. Turbidity can harm aquatic habitats and influence marine life by intensifying spawning and decreasing food systems [55]. As explained in Table 4, the turbidity measurements may impact the WQI of a reservoir. The values demonstrate that the greatest levels of turbidity and As have an impact on the WQ of the waterways.

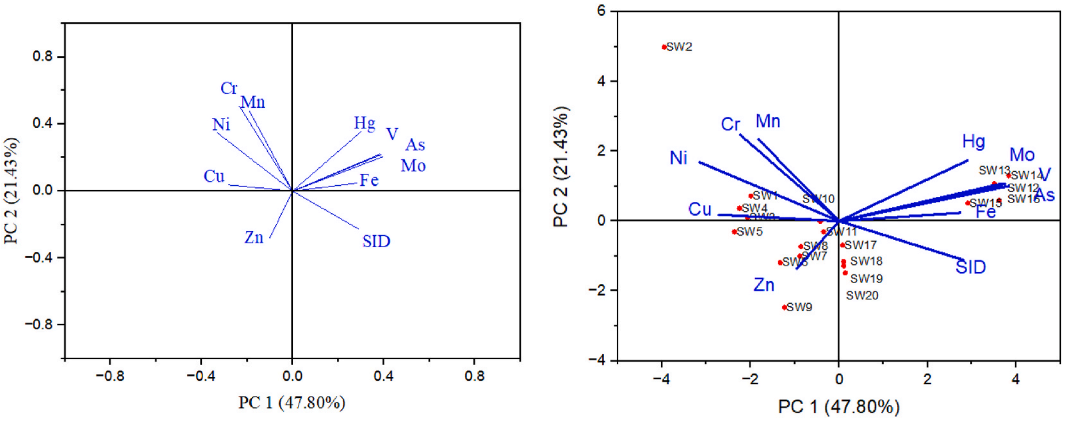

Fig. 5. A PC biplot showing heavy metal concentration, ratios and possible sources (5A) and a combination of score and loading plots (5B). NB: N.B: Variables and observation (axes D1 and D2 69.23% after varimax rotations).

Table 4
Basic statistics of heavy metals and the water quality index (WQI).

Parameters	Min	Max	Mean (Ci)	WHO, 2017 (S_i)	Weight (W_i)	Relative weight (R_{Wi})	C_i/S_i	WQI
pH	6.59	9.65	8.2	6.5–8.5	4	0.071	1.03	7.32
EC - µS/cm	172.4	3650	1016	750	3	0.054	1.36	7.26
TDS- mg/L	86	2482	599.3	500	3	0.054	1.19	6.42
Turbidity-NTU	1.52	1050	230.5	5	3	0.054	46.1	246.96
Vanadium- µg/L	2.91	94.19	26.45	20	4	0.071	1.32	9.45
Chromium- µg/L	0.22	36.12	6.84	50	5	0.089	0.14	1.22
Manganese- µg/L	2.71	1245.2	203.61	500	4	0.071	0.41	2.91
Nickel- µg/L	0.81	10.41	1.69	20	5	0.089	0.09	0.75
Copper- µg/L	15.64	583.83	127.98	1300	4	0.071	0.09	0.70
Zinc- µg/L	4.37	489.96	102.18	3000	4	0.071	0.03	0.24
Arsenic- µg/L	0.38	95.6	23.02	10	5	0.089	2.30	20.55
Molybdenum- µg/L	1.31	146.73	41.46	70	3	0.054	0.59	3.17
Iron- µg/L	10.46	899.15	246.43	300	4	0.071	0.82	5.87
Mercury- µg/L	0.01	4.18	0.87	2	5	0.089	0.44	3.88
					$\sum = 56$	$\sum = 1.00$		316.72
WQI: < 50		50 < WQI ≤100		100 < WQI ≤200		200 < WQI ≤300		>300
WQ Excellent		Good water		Poor water		Very poor water		NRU

N.B: N = 70 for variable pH, electrical conductivity (EC), total dissolved solids (TDS), and turbidity. (N.B NTU).

Table 5
Parameters used to calculate human exposures.

Health index Parameter	Symbol	Unit	Human exposure		References
			Child	Adult	
Body Weight	BW	kg	14	54.1	[31]
Exposure frequency	EF	Days/years	365	365	[32]
Exposure duration	ED	years	7	70	[33]
Ingestion rate	IR	Liter/day	1.3	2.2	[34]
Exposed skin surface area	SA	cm^2	7422	18000	[32]
Exposure time	ET	hr/day	1	0.58	[35]
Permeability	Kp	cm/hr	–	–	[32]
Conversion factor	CF	L/cm^3	0.001	0.001	[32]
Dermal absorption factor	ABS	Unit-less	0.03	0.03	[36]
Skin adherence factor	AF	$mg.cm^2$	0.02	0.07	[36]
Average time (Carcinogens)	AT	days	365*70	365*70	[36]
Average time (Non-carcinogens)	AT	days	365*ED	365*ED	[34]

N.B: Average body weight (M = 56.5 Kg & F = 51.6 Kg) adopted from the WorldData.info (March 27, 2022) [35].

3.5. Heavy metal pollution indices (HPI)

The HPI serves as a highly beneficial instrument for assessing the overall contamination of water sources concerning HMs pollution in surface water [56]. As depicted in Fig. 6, a considerable HPI score exceeding 100 was detected in twenty-five percent of water

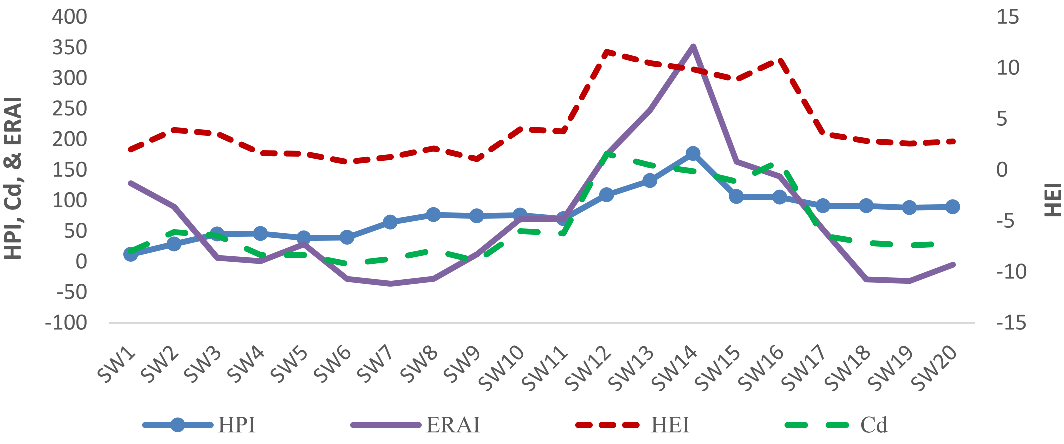

Fig. 6. The distribution of heavy metal pollution and evaluation indices in water samples of Awash basin.

samples, including stations SW12, SW13, SW14, SW15, and SW16 with corresponding HEI values of 109.2, 132.3, 176.7, 106.3, and 105.3, respectively [57]. During the investigation, maximum admissible concentration were employed, namely 10 μg/L, 50 μg/L, 5000 μg/L, 300 μg/L, 50 μg/L, 2 μg/L, 1300 μg/L, 40 μg/L, 500 μg/L, and 70 μg/L for As, Ni, Zn, Fe, Cr, Hg, Cu, V, Mn, and Mo respectively. The majority of stations exhibited HEI values ranging from over one to under 20. With the escalation of industrial waste and erosion, the concentration of HMs has increased in the SW bodies, posing a threat. The values discovered indicate the severity of the problem that will arise in the near future.

Most highly toxic heavy metals, including As, Cr, Ni, and Hg are frequently found in both natural activities and individual operations, and can cause significant environmental pollution. The concentration of As in the study area exceeded the limit (10 μg/L) due to geogenic factors, and it poses a serious threat to human health as it is a well-known geotoxicant HM that can cause cancer in humans [58]. Very high HPI values were observed at stations SW12, SW13, SW14, SW15, and SW16, with higher values recorded at stations SW12, SW13, and SW16. This is likely due to the rapid development of industrialization and urbanization in the study area (upper Koka), which significantly increases HMs contamination in the basin.

3.6. Hazard quintet (HQ) and hazard index (HI)

Sampling stations were grouped into four major spatial clusters, C1, C2, C3, and C4 to characterize the catchment using the HQ index. The variability of HMs concentration was clearly observed due to the flux sources difference and showed significant spatial variability of HQ index was observed as per the following order C3 > C4 > C1 > C2. In all aforementioned clusters, except HQ dermal, the HQ values were found above the allowable limit and might impact the child's health. Extremely high HQ ingestion values were recorded in C3 at 10.75 and 11.44 in adults and children respectively.

Similarly, the high values of HQ dermal were shown at 31.65 and 7.17 in both age groups. Obviously, the value found was unexpected, even though; the rift geology has a significant impact and deteriorates the lake water. In this study high concentration of hazard quotient (HQ), $HQ_{ingestion}$ was computed in both age groups using Eq. (14), Eq. (15), and Eq. (16) (adults and children) in Fig. 7a and b. For instance, a hazard quotient dermal (HQ_{dermal}) contact value for adults was seen in the cluster order of C3 > C1 > C4 > C2, whereas this cluster order somehow varied in children in the order of C3 > C4 > C2 > C1, the range lies in both age groups under the recommendable limit (HQ < 1).

On contrary, extremely high values of hazard quetiont ingestion ($HQ_{ingestion}$) were observed in cluster three (C3), in stations SW12, SW13, SW14, SW15, and SW16 in both age groups, nonetheless, the order in the adult group looks like C3 > C4 > C1 > C2 while the exposure of the SW ingestion for the child was in the order of C3 > C4 > C2 > C1. The HQ_{dermal} values in both age groups were recorded below one, but the untreated water ingestion direct use of the surface water of Awash was could not recommended (in all clusters) (Fig. 8b). As shown in Fig. 8a, the HI or the exposure of both age groups shows a high positive correlation with 95% linearity.

As illustrated in Fig. 8b, the elevated HI values of non-carcinogenic hazards were observed to be more prevalent in children than in adults. The diagrams further indicate that metal contamination affects children more acutely than adults. Non-carcinogenic health effects are unlikely if the values are less than 1 (HI < 1). However, if the values exceed 1 (HI > 1), negative impacts such as non-carcinogenic health effects may arise [32].

3.7. Cancer risk assessment

In the study, the carcinogenic risks of elements were computed, and found the possibility of appearing high risks of cancer-causing chemicals has been increasing in the surface water of the basin because of the discharge of industrial and domestic wastes including geogenic impacts as well. For instance, the Ni and Cr cancer-causing properties were computed in both age groups, and the CR values of Cr and Ni were computed in both age groups and found 0.0028 for adults and 0.0063 for children and 0.0000046 for adults and 0.00000097 for children respectively. It means that the possibility of sixty-three children per ten thousand and twenty adults per ten thousand people might be vulnerable to the adverse effect of chromium toxicity might be for genotoxicity or cytotoxicity if the community ingests the river water without any prior treatment of the basin water.

3.8. Risk assessment: ecological risk assessment

As seen in Fig. 9, the investigation revealed that elevated levels of the aforementioned substances were observed at all monitoring sites, particularly at stations belonging to cluster one and cluster three, which posed significant ecological hazards related to Cu, Zn, As, and Hg. In this study, Hg, As, and Cu have a negative impact on the condition of surface water and the ecology of the basin. For instance, cluster three, which encompasses stations SW12, SW13, SW14, and SW15, is primarily affected by Hg, As and Fe has the potential to harm the health of LB. Station SW1, situated along the ARB before it enters Koka dam, was found to be heavily polluted by industrial waste from Addis Ababa, and stations SW3 (East Africa tannery) and SW4 (downstream of all tanneries) were found to be contaminated points by tanneries and other firms waste.

As explained in Table 3, certain stations had the highest potential ecological risk levels of heavy metals (or metalloids), including $\sum R_r^i$ and ERAI, with the greatest spatial variability. Figs. 6 and 9 also reveal extremely high values of these elements, ranging from 160 to 360, with SW12, SW13, SW14, and SW15 stations having values of 174.78, 247.7, 351.8, and 163.5, respectively.

Notably, SW1 and SW16 stations had significant values of $\sum R_r^i$, ranging from 80 to 160, with values of 128.25 and 139.34, respectively. This increase in values could be attributed to the geogenic nature and presence of volcanic ash in the study area. In conclusion, the study determined that the water in LB, the Modjo River, and some stations along the River Awash were unsuitable for

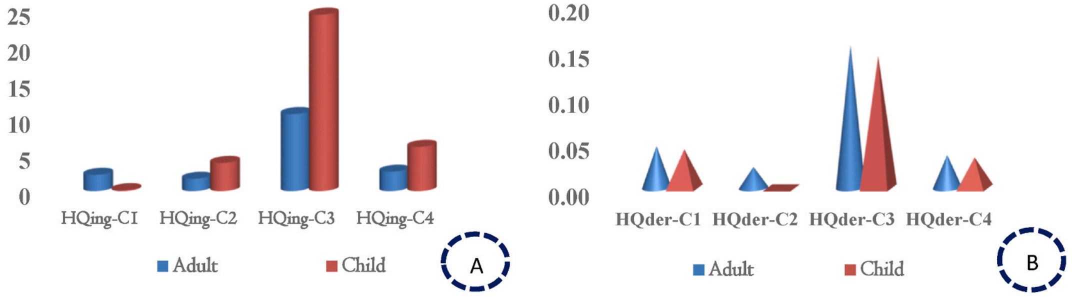

Fig. 7. The health quotient analysis in both age groups and pathways through ingestion (Fig. 7A) and dermal (Fig. 7B) in the surface water of Awash River basin.

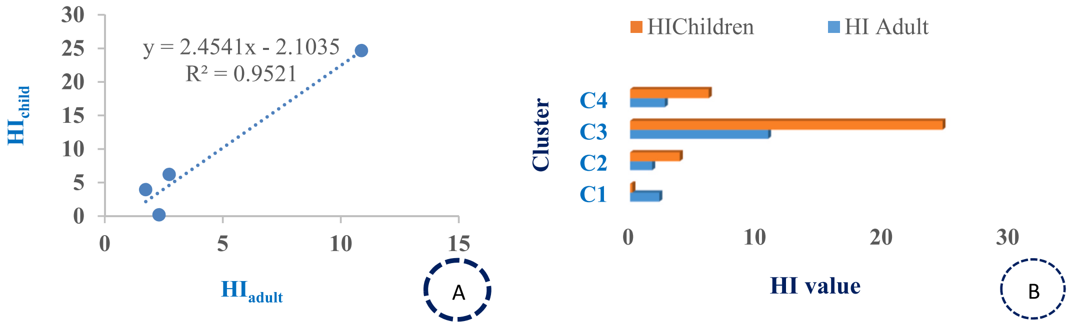

Fig. 8. Linearity of hazard index (HI) between child and adult and their positive associations (Fig. 8A) and also showing the hazard index values at four different cluster stations in the Awash River basin (Fig. 8B).

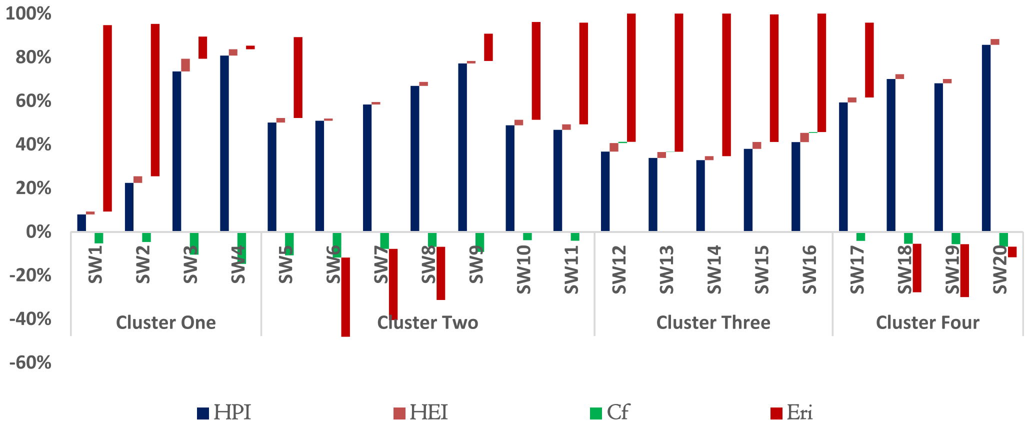

Fig. 9. The values of heavy metal pollution index (HPI), heavy metal evaluation index (HEI), and Cd values (**NB: C1** stands from surface water (SW) station SW1 to SW4; **C2** from station SW5 to SW11; **C3** stands from SW12 to SW16; and **C4** stands from SW17 to SW20).

domestic and agricultural purposes. In general, in underdeveloped nations such as Ethiopia, inadequate wastewater management has led to a significant issue of heavy metal pollution. Despite, the Federal Democratic Republic of Ethiopia has tasked the utilization, distribution, and safeguarding of water resources like rivers and lakes but due several factors, they were not well secured. Thus, due to multiple factors, the contamination of water resource in developed and utilized basin like Awash is escalating harshly. The primary reason for this issue is mainly due to uncontrolled pollution levels caused by factors like industrial and population growth [42], inadequate sewage, and storm water infrastructure, which severely impacts both the environment and the people living in the area. Consequently, they are highly susceptible to environmental concerns, which can negatively impact their overall health and well-being. Also, this can lead to water insecurity issues.

4. Conclusion

The current investigation aimed to examine the water quality of Awash basin, with particular emphasis on variations of HMs, as well as their potential risks on human health and ecology. Several pollution indices, such as WQI, HQ, HEI, and HPI, were intended to determine the extent and levels of ten HMs; as well as the possibility of exposure to contaminated surface water, human health risks in both age groups were evaluated. Risks to the environment were described. The results revealed significant differences in values between sampling stations and seasons, with notable variations in concentrations. For instance, the statistical examination disclosed that geogenic activities were the primary source of certain HMs, namely As, Hg, Fe, and V, while human activities contributed to the presence of Cu, Cr, Mn, Ni, and Zn. The occurrence of these HMs (Cu, Cr, Mn, Zn, and Ni) could also be attributed to the natural origin erosion of lithological and geological units, including volcanic ash.

The computation of contamination indicators (HPI) revealed that a great number of the stations were severely (SW12, SW13, SW14, & SW16) impacted, whereas certain stations were moderately (SW1, SW3, SW5, SW9, SW10, SW18, SW19, & SW20) and heavily (SW4, SW6, SW7, SW8, SW11, SW15, & SW17) impacted. Thus, these differences in concentrations were primarily attributed to alterations in locations and seasonal variations. This suggests that the surface water was polluted and unsuited for consumption; in essence, the basin water was not fit for drinking. Furthermore, the computation of heavy metal levels and pollution indices indicated that around fifty percent of the samples surpassed the threshold values. This not only rendered the water unfit for consumption but also posed a threat to the well-being of individuals living downstream. High risks of cancer-causing HMs such as Ni and Cr cancer-causing were computed for both age groups, and the CR values of Cr and Ni were computed in both age groups and found 0.0028 (for adults) and 0.0063 for children and 0.0000046 (for adults) and 0.00000097 (for children) respectively. Thus, from health standpoint, exposure to HMs is becoming a pressing concern for downstream users.

In this particular investigation, it is crucial to consider the enduring consequences of HMs buildup caused by spatial and temporal inconsistency in contamination. This is because human societies in the basin highly rely on various activities such as domestic chores, animal husbandry, and crop irrigation, which are all affected, either directly or indirectly, by substandard wastewater control. In conclusion, the investigation reveals that the river is contaminated, and a majority of constituents surpass the WHO's recommended thresholds due to inadequate management of wastewater and water resources. Accordingly, the outcomes of hazard evaluations indicate an imminent threat if prompt action is not taken. Therefore, it is crucial to safeguard our water sources and maintain them for livestock watering, domestic uses, and ecology. Both governments and private sectors also should adhere to environmental laws to prevent any potential contamination.

Author contribution statement

Yosef Abebe: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Dr. Tena Alamirew, Prof. Paul Whitehead and Prof, Katrina Charles: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Prof. Dr. Ing. Esayas Alemayehu: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Data availability statement

Data will be made available on request.

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.

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