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Research article

Sources and level of heavy metal contamination in the water of Awetu watershed streams, southwestern Ethiopia

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ABSTRACT

The present study aimed to investigate the contamination source, level, and spatial distribution of globally alarming trace metals from Awetu watershed streams, southwestern Ethiopia. Surface water samples were collected from 20 sampling sites in December 2019. Water samples were collected in 500 ml polyethylene bottles previously washed with deionized water and rinsed with the sample to be collected from different stretches and acidified with 5 ml concentrated nitric acid. The samples were digested with open acid digestion and the contents of the metal were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES) ranged from 18 - 351 μg/L for As, 5–19 μg/L for Cd, 232–421 μg/L for Cr, 314–920 μg/L for Pb and 10–16 μg/L for Hg. The highest concentrations of As were detected at K3, Cd at K2, Pb and Cr at D4, and Hg at D5. Analysis of variance results revealed that the Cd concentrations were statistically significant among all the streams except for Boye. Streams found at the center of Jimma city with effluents emanated from Jimma University, garage maintenances, car-wash and agricultural areas had higher values than the streams in the periphery. This study concluded that a higher concentration of trace elements is associated with the type of waste entering the streams. Trace elements concentration in the watershed is to the level that can pose a risk to downstream users. Public awareness creation to establish waste management systems and river quality monitoring should be implemented to minimize the public health risk and deterioration of the aquatic ecosystem.

1. Introduction

The natural flow of water bodies drained contaminants into one-point collection sites, dams, and reservoirs that can serve as a sink (Ahmed et al., 2009; Gómez-Hortigüela et al., 2013). The unplanned urbanization and industrialization of Ethiopia have adverse effects on the water and sediment quality, as well as the diversity of aquatic fauna. The dumping of municipal waste, untreated waste from various factories and agro-chemicals has reached an alarming situation in open water bodies and streams that continually increases the quantity of metals and deteriorates the quality of water (Abegaz, 2007; Ali et al., 2016). Due to their non-biodegradability and persistent nature, trace metals accumulate in aquatic ecosystems, leading to pollution and accumulation to the top consumers through the food chain (Zeng et al., 2014; Akele et al., 2016).

Pollution of aquatic ecosystems with trace elements is a global problem (Kumar et al., 2019). Least developed countries lack both the equipment and technical capabilities to detect and monitor water quality and are therefore exposed to heavy metal pollution (Nagajyoti et al., 2010; Woldetsadik et al., 2017). Trace amounts of trace elements are always present in surface waters from terrigenous sources such as weathering of rocks resulting from geochemical recycling in the eco-systems (Mohod and Dhote, 2013; JI and JN, 2016) However, excess trace elements in the water environment might occur through various processes and pathways by anthropogenic activities besides the natural processes (Pekey, 2006; Yuan et al., 2013; Kumar et al., 2020).

Due to poor management and the absence of solid and liquid waste treatment technologies in developing countries, the waste generated from anthropogenic activities could be dumped into the nearby water bodies and rivers crossing cities and their boundaries (Giridharan et al., 2008; Kaufman et al., 2012). Water bodies receive and absorb trace elements mainly caused by rapid urbanization and industrialization (Du Laing et al., 2009; Rango et al., 2013; Saha and Paul, 2016). A study conducted in Ethiopia showed that stream water pollution with trace elements sourced from industrial, residential, and agricultural wastes gets higher downstream when it enters Addis Ababa city (Abegaz, 2007; Woldetsadik et al., 2017; Yohannes and Elias, 2017). A similar study

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conducted in Slovenia, Kazakhstan and Nile Delta Lagoons shows the quantity of river water can reach alarming levels due to rapid urbanization, insufficient adherence to municipal and industrial wastewater generation, and pollutants from agricultural fields or industries. The increment of trace metals in the water bodies due to uncoordinated rapid urbanization with a lack of awareness in the urban rivers also have a serious concern for the sustainable development of the city. The concentration of trace elements in surface waters becomes relatively high due to significant anthropogenic metal loadings carried by tributary rivers (Li et al., 2011; Gergen and Harmanescu, 2012). Thus, metal pollution in the aquatic environment has owed to its environmental traces, abundance, and persistence (Rango et al., 2013; Ali et al., 2016; Zhang et al., 2016, 2018). Moreover, water quality characteristics, such as dissolved oxygen, pH, and organic matter content also affect the mobility and availability of these trace elements in the aquatic environment (Sim et al., 2016).

Trace elemental concentrations in stream water compartments can reveal local and regional pollution (Sekabira et al., 2010). Bottom stream sediments are also sensitive indicators for monitoring contaminants as they act as a sink and a carrier for pollutants in the aquatic environment (Benson and Etesin, 2008). Thus, water analyses play an essential role in evaluating the aquatic environment's pollution status (Moore et al., 2011; Gergen and Harmanescu, 2012). The behavior of metals in natural water is also a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry (Suresh et al., 2012; Islam et al., 2015).

Most urban and semi-urban settings in developing countries have no proper waste management system (Khan et al., 2005). For instance, Jimma city, which has more than 300,000 population, has no waste management system, where open dumping of solid waste and discharge of untreated wastewater is a daily practice. Previous studies (Ambelu et al., 2013; Alemneh et al., 2017) indicated that the solid and liquid waste dumping had affected the Kitto and Boye water bodies in the Awetu watershed.

Awetu watershed is a considerably large drainage catchment area of land on the southwestern part of Ethiopia, covering numerous streams used as domestic water sources. However, the watershed has experienced extensive agriculture and rapid urbanization in recent years, potential sources of heavy metals pollution. The studied streams receive untreated effluents from agro-chemicals, pesticides, car repair garages, car-wash, metal plating, laboratories, waste discharge from Jimma University, and other sources. The high concentration of trace elements such as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) are discharged into the Awetu watershed streams.

Surface water pollution with trace elements is a significant concern that requires immediate attention through source identification. However, most of the studies conducted on stream pollution focus on the investigation of mainly organic and common metals, thereby lacking information about the level of trace elements at a spatial scale along the course of the urban and semi-urban environment. This is highly relevant to devise a pollution control strategy. Despite the widespread environmental deterioration of the urban and semi-urban environment in most low-income countries such as Ethiopia, the identification of pollution sources of trace elements and their level is hardly available. Hence, this study investigates the pollution sources, spatial distribution, and pollution dynamics of trace elements in the Awetu watershed surface water in southwestern Ethiopia.

2. Materials and methods

2.1. Study area and sampling sites

The study area is located in the urban and semi-urban parts of Jimma city, Southwestern Ethiopia. Jimma city is the largest city in the region, located at 7°40′ N 36°50′ E. It has an altitude of 1,780 m above sea level, with an average temperature of 18.9 °C and a mean annual precipitation of 1624 mm (Getahun et al., 2012; Yasin et al., 2015). Awetu watershed mainly contains four streams, of which Awetu is the largest one, which divides Jimma city into two while Dololo, Kitto, and Boye streams are tributaries of Awetu stream. Major anthropogenic activities at each sampling site along the course of the Awetu watershed are described in Table 1. Samples of surface water were collected from Awetu (A1, A2, A3, A4, A5, and A6), Dololo (D1, D2, D3, D4, and D5), Kitto (K1, K2, K3, K4, and K5), and Boye (B1, B2, B3, and B4) streams. Samples collected from A1 (upstream) was considered as background concentrations of the study area since it is assumed to be free from known anthropogenic heavy metal sources (Figure 1).

2.2. Sample collection and processing

Triplicate water samples were collected from 20 sampling locations in December 2019 across the Awetu watershed streams (Figure 1). Each sample was collected by submerging the sample container into the stream at about 100–300 mm below the surface and 1m away from the edge after rinsing the bucket with an open end facing against the current flow direction (Taylor and Governor, 2015). A1000 mL polyethylene (PET) bottles pre-cleaned with nitric acid (10 %) for 24 h and rinsed three times with deionized water were used to collect surface water samples. Samples were labeled, immediately transported to the laboratory using a cold box maintained at 4 °C and filtered through a 0.45 μm Millipore membrane filter and kept acidified with nitric acid (pH ~2) until metal concentrations were determined. The physicochemical properties of the water samples, such as pH, electric conductivity (EC), dissolved oxygen (DO), and turbidity were recorded in-situ, using a calibrated portable multiparameter probe (Hanna LP.2000). Geographic coordinates of each sampling site were recorded using a GPS device (Garmin GPS60).

2.3. Sample extraction and determination of trace elements

A portion of the digested filtrate samples was sent for As, Cd, Cr, Pb, and Hg analyses using inductively coupled plasma optical emission spectrometry (ICP-OES) (ARCOS FHS12, Germany) (APHA/WEF/AWWA, 1989). The absorption wavelength and detection limits of each trace elements were as follows: 193.7 nm and 0.05 mg/L for As; 226.5 nm and 0.005 mg/L for Cd; 205.6 nm and 0.005 mg/L for Cr; 253.6 nm and 0.05 mg/L for Hg; 220.3 nm and 0.05 mg/L for Pb, respectively. The metal content analyzed is referred to as the acid extractable metals constituting dissolved and weakly sorbed metals on particulates.

2.4. Quality control and quality assurance

Quality control (QC) and quality assurance (QA) was operated using procedural blanks and duplicates run in each batch of ten samples. A thousand milligrams per liter standard solutions of each metal were prepared from nitrate salts, supplied from BDH (Poole, England), and used for calibration purposes. Mixed working standard solutions containing all metals were prepared by dilution inappropriate procedures using double-distilled deionized water. Measurement for each resolution was done in triplicate, and the average was taken (APHA/WEF/AWWA, 1989). The analytical method accuracy was evaluated by drawing calibration curves and the simultaneous performance of analytical blanks (Sekabira et al., 2010).

2.5. Statistical analyses

The means and standard deviations of the metal concentrations in water were calculated. The differences of heavy metal concentrations and physicochemical properties among the streams in the watershed were analyzed with a one-way ANOVA, followed by posthoc Tukey tests. The statistical analysis was performed using SPSS version 20 statistical software and a significance level of 0.05 ($p < 0.05$) was considered statistically significant. The relationship between the variables was evaluated

Table 1. Description of Awetu watershed streams with their major anthropogenic activities in the sampling sites.

Stream Name	Sampling Code	Major anthropogenic activities of the site
Awetu	A1	Agricultural activities and grazing
	A2	Agricultural activities, grazing, washing clothes, and bathing
	A3	Horticulture, recreational, residential and commercial, vehicle traffic and agricultural runoff
	A4	Washing, swimming and fetching water for household consumption
	A5	Vehicle traffic, washing, car washing, and seedling plantation
	A6	Crossing asphalt road, high vehicle traffic, residential area and small scale industries of the town enters into this stream before it.
Dololo	D1	Public institutions, domestic activities, vehicle traffic, hospital, chemical and biological laboratories, and construction sites.
	D2	Car washing, small scale enterprises like garages, woodwork, and vehicle traffic.
	D3	Commercial area, high vehicle traffic, garages, gas/petrol station and seepage
	D4	Car washing, gas/fuel station, garages, residential and commercial and seepage
	D5	Commercial, recreational, vehicle traffic, bus park, gas/petrol station, cement stores, metal works and fabrications, and seepage
Kitto	K1	Institutional wastes, waste stabilization pond, wood and metalwork enterprise, garage, car washing, agricultural activities, and bridge.
	K2	Residential, commercial, garage, seepage and agricultural activities
	K3	Residential, commercial, seepage, agricultural activities, and airport
	K4	Grazing, agricultural activities and small scale enterprises like garages
	K5	Solid waste dump sites, horticulture, residential and vehicle traffic
Boye	B1	Car washing, vehicle traffic, residential and commercial area
	B2	Agriculture runoff, irrigation, and residential area
	B3	Irrigation, agricultural runoff, slaughterhouse, and residential area
	B4	Wetland, grazing, agricultural activities, fishing and recreational

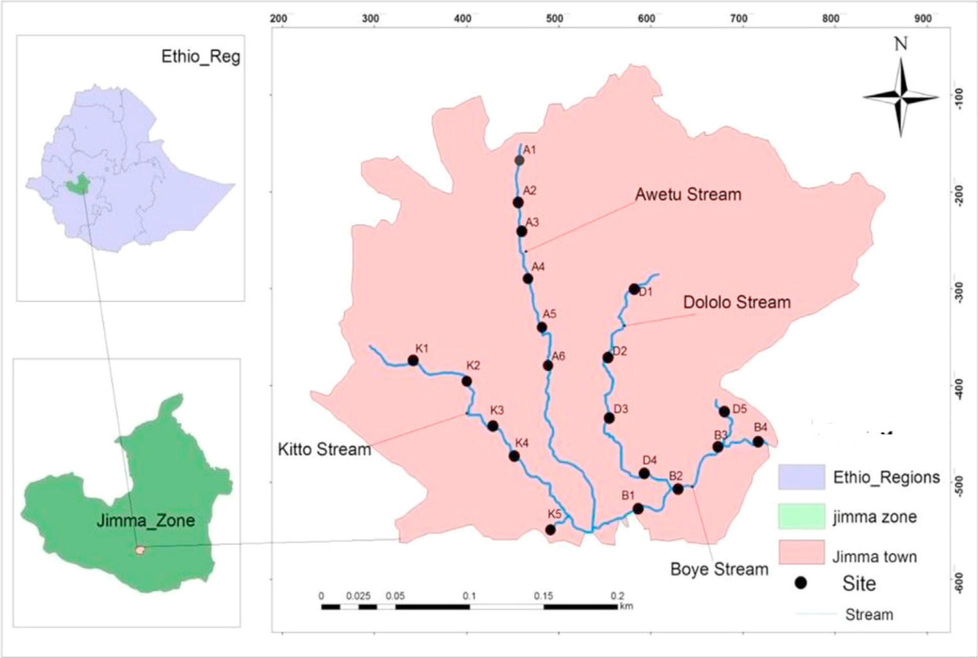

Figure 1. Sampling points along streams at Awetu watershed (Generated from ArcGIS 10.3 (ESRI, Redlands, California, USA)).

based on Pearson's correlation test. The study area and spatial distribution of the sampling sites were mapped using ArcGIS 10.3 (ESRI, Redlands, California, USA). Principal components analysis (PCA) was used as a multivariate statistical method that summarizes the variation of a data set between samples to a set of uncorrelated components. This method was performed to determine the differentiation of trace elements with physicochemical properties based on the elemental level. Since PCA results are sensitive to measurement scales, the original metal contents in water samples were transformed by log (x+1). Cluster analysis (CA) (wards method) was performed by PAleontological STatistics software (PAST Version 3.25, 1999–2019) to determine the relationships between trace elements in water and environmental variables.

3. Results and discussion

3.1. Physico-chemical properties of surface water

The physicochemical properties of the water samples from streams are presented in Table 2. EC ranges from 50.10 – 407.00 μS/cm where the maximum is registered at D1, while the DO ranges from 3.24 to 7.28 mg/L. The measured DO values at the Boye stream (B1, B2, B3 and B4), Awetu stream (A6) and Dololo stream (D1, D4 and D5) were below 4 mg/L. These show stress to most aquatic animals with severe scarcity as compared to the other sampling points. Turbidity ranges from 8.02 - 302.00 NTU with the highest values at D3 and K5. Among the studied

Table 2. Physico-chemical properties of water samples in Awetu watershed streams.

Site	Dissolved Oxygen (mg/L)	Electric Conductivity (μS/cm)	pH	Turbidity (NTU)
	(Average ±SD)	(Average ±SD)	(Average ±SD)	(Average ±SD)
A1	7.09 ± 0.03	62.30 ± 0.46	7.59 ± 0.14	50.50 ± 1.76
A2	6.71 ± 0.17	62.30 ± 0.59	7.60 ± 0.20	52.10 ± 1.50
A3	6.70 ± 0.04	66.30 ± 3.31	7.58 ± 0.02	60.70 ± 0.10
A4	7.28 ± 0.01	69.30 ± 0.83	7.42 ± 0.09	106.00 ± 0.87
A5	7.01 ± 0.04	85.60 ± 1.85	7.05 ± 0.01	71.20 ± 1.06
A6	3.33 ± 0.03	131.40 ± 2.47	7.03 ± 0.02	51.90 ± 1.54
D1	3.59 ± 0.38	407.00 ± 3.21	7.01 ± 0.005	11.97 ± 0.77
D2	4.18 ± 0.32	299.00 ± 1.84	7.43 ± 0.19	26.60 ± 1.01
D3	4.96 ± 0.52	250.00 ± 3.00	7.49 ± 0.09	302.00 ± 1.00
D4	3.80 ± 0.46	313.00 ± 1.62	7.43 ± 0.19	65.30 ± 0.56
D5	3.78 ± 0.54	343.00 ± 2.35	7.40 ± 0.15	14.73 ± 0.95
K1	6.27 ± 0.78	84.40 ± 1.34	5.82 ± 0.26	276.00 ± 1.26
K2	5.99 ± 0.69	82.10 ± 1.56	7.27 ± 0.13	189.00 ± 1.49
K3	5.25 ± 0.23	90.10 ± 2.94	7.03 ± 0.09	128.00 ± 0.87
K4	5.20 ± 0.16	201.00 ± 2.20	7.23 ± 0.09	8.02 ± 0,90
K5	4.96 ± 0.65	250.00 ± 1.80	7.49 ± 0.06	302.00 ± 0.96
B1	3.49 ± 0.51	93.40 ± 2.12	6.79 ± 0.08	54.90 ± 0.47
B2	3.24 ± 0.10	87.30 ± 1.41	6.85 ± 0.04	19.40 ± 0.60
B3	3.79 ± 0.15	87.80 ± 1.68	6.88 ± 0.08	31.80 ± 0.26
B4	3.68 ± 0.11	105.30 ± 1.77	6.78 ± 0.09	26.40 ± 0.44

SD = Standard Deviation, mg/L = milligram per liter, μS/cm = micro siemens per centimeter and NTU = nephelometric turbidity unit.

physicochemical properties, pH shows from slightly acidic to slightly alkaline (6.78–7.60) in all sampling sites except at K1 which is acidic (pH = 5.82), reflecting the availability of carbonate host in the area (Moore et al., 2011; Radulescu et al., 2014). Comparatively, the pH values from Boye stream sites are lower which might be due to the decrement in dissolved oxygen in the downstream side of the watershed. The water pH predominately controlled the solubility of heavy metals. A higher pH value can reduce the solubility while a low level enhances the dissolution

Table 3. Heavy metal concentrations in water (μg/L) were collected from each sampling site in Awetu watershed streams.

Sites	As	Cd	Cr	Pb	Hg
A1	133	16	331	314	10
A2	175	14	393	689	11
A3	18	11	355	858	10
A4	181	15	302	569	14
A5	124	6	232	524	12
A6	71	10	320	581	15
D1	253	5	386	641	10
D2	173	11	376	736	12
D3	341	8	363	464	12
D4	158	7	421	920	11
D5	303	6	404	628	16
K1	165	15	313	498	12
K2	106	19	312	338	14
K3	351	16	338	491	11
K4	151	14	363	592	13
K5	197	16	330	419	10
B1	222	11	306	689	13
B2	64	13	325	492	12
B3	23	11	315	721	11
B4	257	10	407	694	12
Mean ± SD	173 ± 95	12 ± 3.9	345 ± 45.6	593 ± 157.5	12 ± 1.7
BC	133	16	331	314	10
WRW	0.02	0.01	1	1	0.07
USEPA	1	2	11	3	1.8
TRV	150	5	11	3	2

SD is the standard deviation, BC - Background Concentration (this study), TRV - Traceity Reference Value for freshwater proposed by USEPA (USEPA, 2004), United States Environmental Protection Authority (USEPA, 2004), WRW - World River Water (Khan et al., 2005) processes and released free metal ions into the water column (Singh and Kumar, 2017). The mobility and bioavailability of most of the trace elements such as As, Cd, Cr, and Pb are principally enhanced within an acidic environment (Caruso et al., 2008). EC and turbidity are the other water characteristics that strongly affect surface water quality (De Troyer et al., 2016). The ANOVA performed for EC showed statistically significant differences between Awetu and Dololo, Dololo and Kitto, and Dololo and Boye streams ($p < 0.001$).

3.2. Heavy metal concentrations in surface water samples

The mean concentrations of trace elements in stream waters followed a decreasing Pb > Cr > As > Cd > Hg. The concentrations of trace elements were compared with world river water (Khan et al., 2005), USEPA (USEPA, 2004), irrigation water guideline values (FAO/WHO, 2001), and background concentration of the study (Table 3). The mean values of trace elements were higher than WRW (Khan et al., 2005), USEPA and TRV (USEPA, 2004), indicating severe contamination of the streams. The highest mean concentrations of As (246 ± 80 μg/L), Cr (390 ± 23 μg/L), and Pb (678 ± 167 μg/L) were detected at Dololo stream, Cd at Kitto (16 ± 2 μg/L), and Hg with very low values in all the streams. The highest concentration of Pb was observed at D4 (920 μg/L), which is much higher than the legal limits set by USEPA in WRW (3 μg/L).

In developing countries, leaded gasoline is still commonly used, which significantly increases the amount of Pb in urban soils due to its non-degradability nature (Naveedullah and Hashmi, 2013) which eventually disposed of to the nearby water bodies. Pesticides, car washing at the side of the streams, and lead pipe from the city's old and corroded water distribution line were the other causes of the elevated concentration of Pb (Sörme and Lagerkvist, 2002; Haiyan and Stuanes, 2003; Getaneh et al., 2014). Therefore, the most likely sources of Pb pollution are industrial processes, smelting and fumes from high traffic loads, and atmospheric deposition (Flora et al., 2012; Zeng et al., 2014). Because of its intrinsic chemical characteristics, Pb can also be found in association with other elemental pairs inherently linked with each other (Patrick, 2006).

The concentration of Cr ranges from 232 to 421 μg/L, with an average of 344.6 ± 45.6 μg/L. At D4, the confluence point of the Dololo and Kochi streams, the highest concentrations of Cr were detected (Figure 2). The main reasons for higher Cr are the discharge of untreated waste from chemical laboratories, construction remnants, deposition of household and municipal wastes, infrastructural encroachment, construction and demolition activities, and dust emissions from automobile exhaust fumes (Rule et al., 2006; Gergen and Harmanescu, 2012; Khan et al., 2017; Umaya, 2017). And without preliminary treatment, these wastes are directly reached by the water bodies and the values are by far greater than the world river water standards (USEPA, 2004; Rajiv et al., 2010) (Table 3). The persistence nature of Cr (VI) accumulates in the food chain, which reaches harmful levels in living things over time, resulting in severe health hazards (Jaishankar et al., 2014). The higher concentrations of Cr significantly inhibit the activity of microorganisms and pose a serious threat to the health of the environment, humans and animals (Mengistie et al., 2016; Ayangbenro and Babalola, 2017).

Cd concentrations range from 5 to 19 μg/L, with an average value of 12 ± 4 μg/L which surpass the permissible limit set by the USEPA criteria for water quality, World Rivers and FAO guideline values for irrigation water (FAO/WHO, 2001; USEPA, 2004; Khan et al., 2005). The highest concentration of Cd was detected at K2, where the area has been associated for several decades with intensive cropping with high inputs of agrochemicals such as phosphate fertilizer. Welding, fertilizer, surface runoff and deposition and solid waste disposal are the other sources of Cd, contributing to the leaching of the nickel-cadmium battery to the nearby water bodies (Sharma et al., 2015; Ayangbenro and Babalola, 2017). The Cd released from these sources reaches aquatic ecosystems that later easily affect humans through the food chain, drinking water, and breathing. Under the USEPA (2004) cancer guidelines, Cd was identified as a potential human carcinogen; acute and chronic exposure leads to adverse health effects both for humans and animals (Dokmeci et al., 2009). The ANOVA performed for trace metal concentrations showed statistically significant differences for Cd between Awetu and Dololo ($p < 0.05$), Dololo and Kitto ($p < 0.001$). The ANOVA test revealed that DO showed statistically significant difference between Awetu and Dololo, and Awetu and Boye stream ($p < 0.05$) (Table 4).

The highest concentration of As is detected at K3 (351 μg/L), D3 (341 μg/L), and D5 (303 μg/L). K3 is the area where maximum agricultural activities and extensive use of arsenic trioxide pesticides are predominantly applied which attributes for highest concentration of As (Asere et al., 2013; Wang et al., 2017). Sites D3 and D5 are located in the center of the city, where pesticides, insecticides, herbicides, pigments and the use of wood preservatives containing arsenic have contributed to environmental contamination (Khandaker et al., 2009; Bencko and Foong, 2017). At the pH value of7.49, the highest concentration of As (341 μg/L) suggests that higher pH is more conducive to the mobilization of As (Bencko and Foong, 2017). More significantly, it persists in pollution due to the persistent presence of As in water bodies, which imposes detrimental effects on different aquatic and terrestrial species and eventually affects human health (Chatterjee et al., 2017).

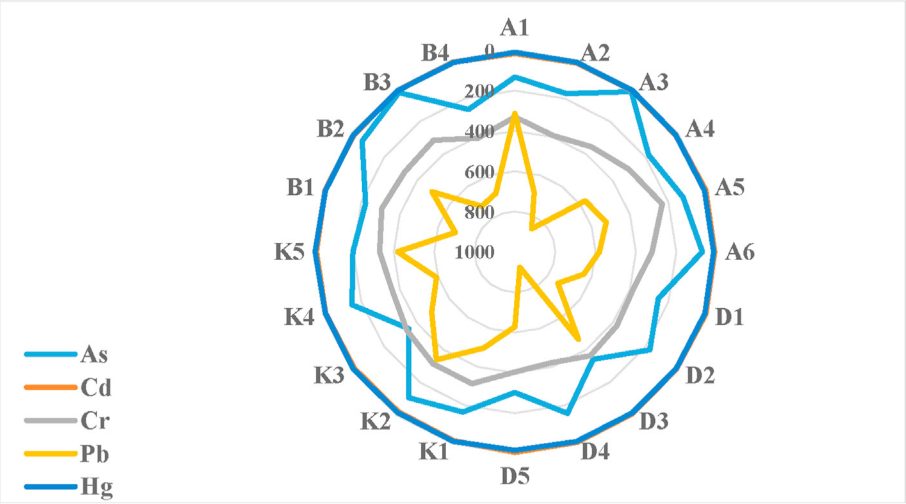

Figure 2. Spatial distribution of trace element concentrations (μg/L) in surface water samples in the Awetu watershed streams.

Table 4. ANOVA analysis for trace metal concentrations and physicochemical properties between streams in the Awetu watershed.

ANOVA		Sum of Squares	df	Mean Square	F	Sig.
As	Between Groups	51342.000	3	17114.000	2.281	.118
	Within Groups	120038.200	16	7502.388		
	Total	171380.200	19			
Cd	Between Groups	186.250	3	62.083	9.034	**.001**
	Within Groups	109.950	16	6.872		
	Total	296.200	19			
Cr	Between Groups	14384.417	3	4794.806	3.062	.058
	Within Groups	25054.383	16	1565.899		
	Total	39438.800	19			
Pb	Between Groups	127212.967	3	42404.322	1.973	.159
	Within Groups	343830.833	16	21489.427		
	Total	471043.800	19			
Hg	Between Groups	.150	3	.050	.015	.997
	Within Groups	54.800	16	3.425		
	Total	54.950	19			
DO	Between Groups	29.584	3	9.861	5.209	**.011**
	Within Groups	30.288	16	1.893		
	Total	59.873	19			
EC	Between Groups	199461.875	3	66487.292	32.755	**.000**
	Within Groups	30447.483	15	2029.832		
	Total	229909.358	18			
pH	Between Groups	1.498	3	.499	4.094	**.025**
	Within Groups	1.951	16	.122		
	Total	3.450	19			
Turbidity	Between Groups	21713.097	3	7237.699	1.034	.404
	Within Groups	112002.176	16	7000.136		
	Total	133715.272	19			

The ANOVA test result written in bold in the table 4 shows significant difference of the studied parameters between the streams in the watershed. i.e The concentration of Cd showed statistically significant differences between Dololo and Kitto streams ($p < 0.001$); DO showed statistically significant difference between Awetu and Dololo, and Awetu and Boye stream ($p < 0.05$). EC showed statistically significant difference between Awetu and Dololo, and Awetu and Boye stream ($p < 0.001$) and pH showed statistically significant difference between Awetu and Dololo, and Awetu and Boye stream ($p < 0.05$).

The mean Hg concentration was 12.1 ± 1.7 μg/L ranging from 10 to 16 μg/L, where the highest concentration was detected at D5. This is due to the elemental mercury found in dental amalgam, the emission of fossil fuels, batteries and the incineration of medical waste generated from laboratories, dental clinics and inorganic mercury from the aquatic environment (Paraquetti et al., 2004). Through plants and livestock, soil polluted by mercury or the redistribution of contaminated water may reach the food chain (Rice et al., 2014). It can bioaccumulate once Hg has entered the food chain and cause adverse effects on human health (Nagajyoti et al., 2010).

The concentration of trace elements in Awetu water streams usually shows trends correlated with source contribution and anthropogenic activities around the streams and their tributaries, primarily due to waste discharge from Jimma University, car repair garages, and car-wash. Because of the regular use of household items, such as cleaning materials, toothpaste, and cosmetics, the discharge of domestic wastewater also might increase Pb concentrations (Nagajyoti et al., 2010; Rak, 2015). The broad inter-and intra-site variations are due in part to real changes in the environment. The direct solid and liquid waste discharged at various locations from different industrial, municipal and domestic activities significantly affects the trace metal condition of the watershed streams. The numerous tributaries also contribute to trace metals' elemental concentration. Most of them received all types of waste and it was hypothesized that the downstream locations of the Awetu watershed streams would be more marked by contamination of the Awetu watershed streams with trace metals. Minimum concentrations due to percolation and dilution factors are also found in downstream Awetu watershed streams. The mobility and possible traceity effects of trace elements in a specific environment are typically governed by their existing chemical forms (Baran and Tarnawski, 2015).

Trace metal concentrations found in stream water samples were spatially varied with anthropogenic sources. The concentrations and distributions of trace elements in the water samples were potentially influenced by the physicochemical properties, such as DO, EC, pH, and turbidity (Rajeshkumar et al., 2018). High levels of these elements are observed in some specific areas, very close to garages, smelting, motor-vehicle exhaust fumes and from corrosion of lead pipework which indicates that the source of these elements could mainly from a point source pollution (Patrick, 2006; Gowd and Govil, 2008; Getaneh et al., 2014).

Tukey HSD test revealed that the concentration of Cd was significantly (p-value = 0.001) higher at Kitto while the minimum was registered at Dololo. A higher concentration of DO was recorded at Awetu which might be due to flow turbulence as oxygen will get a chance to diffuse into the water. On the contrary, the lower oxygen levels are registered at Dololo, an immediate outlet of Jimma University and Boye, where the stream passes through the wetland. The level of EC in the Dololo stream significantly differed from others, which is mainly attributed to the waste discharge from Jimma University, car maintenance garages, and car-wash. Figure 3 demonstrates the difference between streams at a 95 % confidence level.

Interelement association has also been evaluated by Pearson correlation coefficient (r) and the results are presented in Table 5 which shows that elemental pairs Pb/Cr, ($r = 0.490$, $P < 0.01$) and Pb/Cd, ($r = 0.536$, $P < 0.01$) are significantly correlated with each other, whereas the rest of elemental pairs show no significant correlation with each other. The

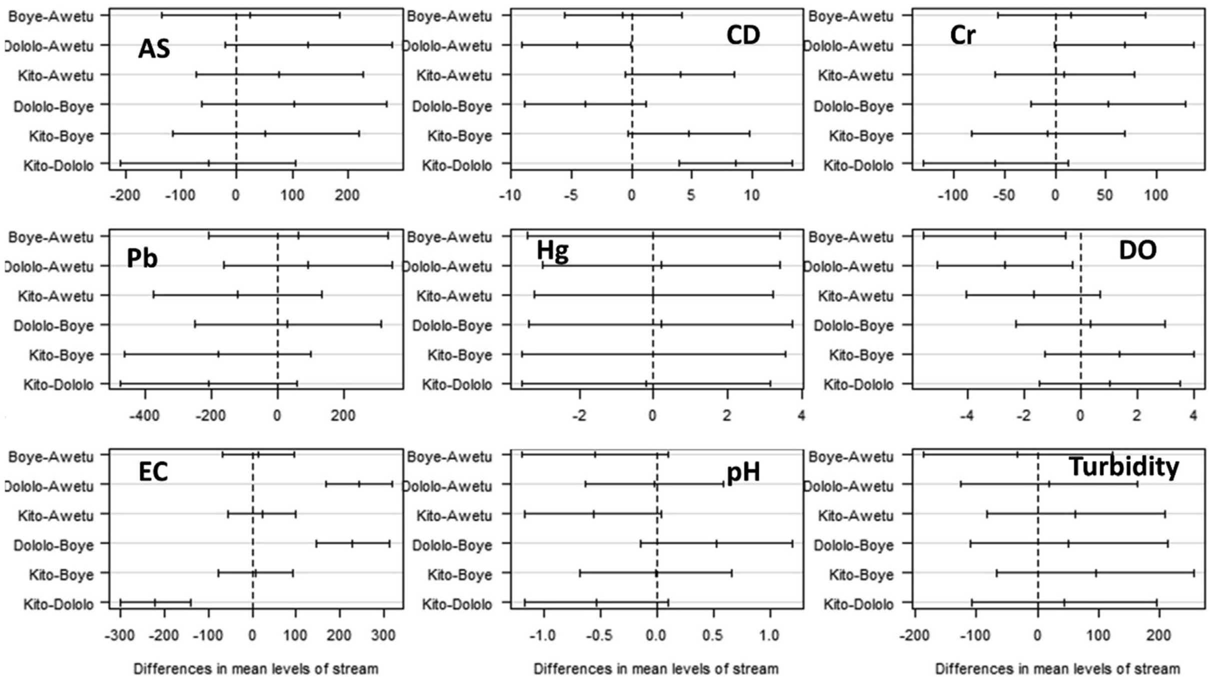

Figure 3. Tukey HSD test output showing the 95% stream-wise confidence level of the contaminants.

Table 5. Pearson correlation coefficient matrix for trace elements and physico-chemical characteristics in Awetu watershed channelized stream waters (n = 20).

	As	Cr	Pb	Cd	Hg	DO	EC	pH	Turbidity
As	1								
Cr	0.37	1							
Pb	-0.15	**0.49***	1						
Cd	-0.19	-0.28	**-0.54***	1					
Hg	0.10	-0.10	-0.10	-0.07	1				
DO	-0.09	-0.36	-0.25	0.37	-0.07	1			
EC	**0.62****	0.30	0.06	-0.14	-0.06	-0.23	1		
pH	0.01	0.32	0.18	-0.13	0.02	0.22	0.09	1	
Turbidity	0.26	-0.23	-0.39	0.24	0.07	**0.44***	0.05	-0.23	1

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

* Correlation is significant at the 0.05 level (2-tailed).

elemental association may signify that each paired element have an identical source or common sink in the streams (Sekabira et al., 2010). Metal and physicochemical associations show pairs As/EC are correlated with each other, whereas the rest are not significantly correlated.

The correlation analyses performed on the data-enabled identifying possible common characteristics of trace elements in surface water. Pb & Cr and Pb & Cd were correlated with each other, indicating that primarily anthropogenic sources such as traffic and industrial activities contribute to contamination (Ji and Jn, 2016; Yuan et al., 2018). The evaluation of the potential of DO, EC, pH, and turbidity to control metal mobility indicates similar source input. The significant positive correlations between As and EC confirm the considerable share of EC with the binding of trace elements and might be attributed to anthropogenic impacts (Alghobar and Suresha, 2017). The lack of a significant correlation between trace elements and DO might be caused by the compositional variety controlling trace elements (Das et al., 2009; Jaishankar et al., 2014).

Hierarchical multivariate CA was performed to find out the relationships between trace metal source distributions in the stream water of the Awetu watershed. From the dendrograms, two cluster groups were identified based on the various sources of trace metals. As shown in Figure 4, all the twenty sampling stations were grouped into two statistically meaningful clusters at Euclidean distance <0.5. Distance metrics are based on the Euclidean distance single linkage method (nearest neighbor). This dendrogram indicates sites (B2, D3, A1, A4, A5, A6, K1, K2, K3, K4 and K5) as cluster 1 and sites (A2, A3, B1, B3, B4, D1, D2, D4 and D5) as cluster 2 which have significant similarity of the concentrations of trace elements with each other. Their close association with each other controls the concentrations of trace elements in the clusters. This relation is due to the topography, the possible pollution source and the dilution factor of trace elements in the stream water.

Results from the principal component analysis (Figure 5) indicate that sites with high turbidity nearly have a higher concentration of cadmium which is located in the semi-urban section of Jimma city. In comparison, those sites located in the middle of the town with high electrical conductivity had a higher concentration of chromium and lead. High arsenic concentration is found at a confluence point of the two streams, Awetu stream after crossing the town and Kitto stream from a semi-urban environment. Perhaps, arsenic is released from a waste dumping located adjacent to Awetu stream before the confluence point of the two streams. The loadings of the variables and correlation between variables and the PC scores are indicated in Table 6.

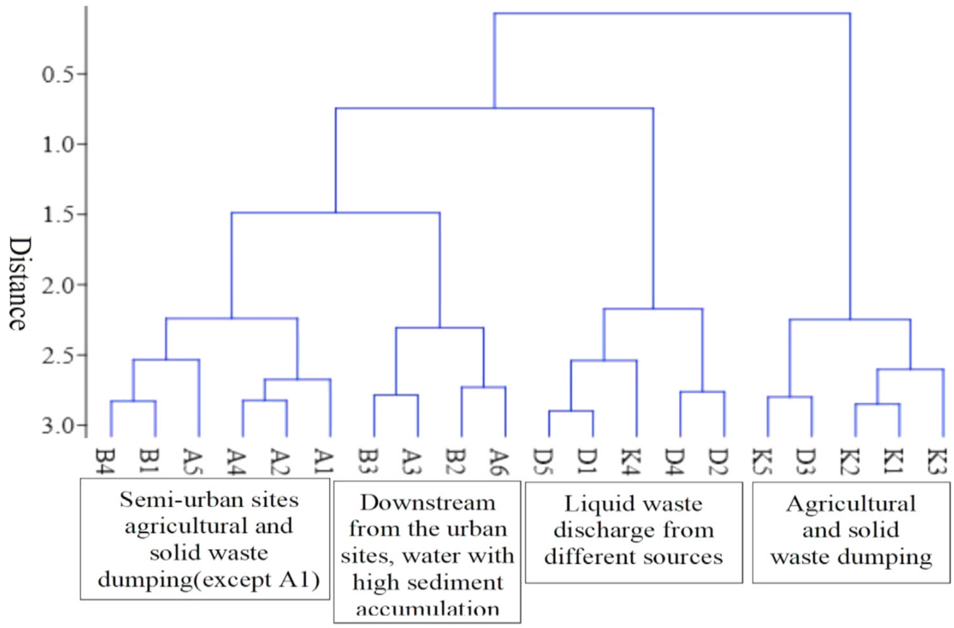

Figure 4. Dendrogram of hierarchical clustering analyses showing the relevant association among the parameters in waters of the study area.

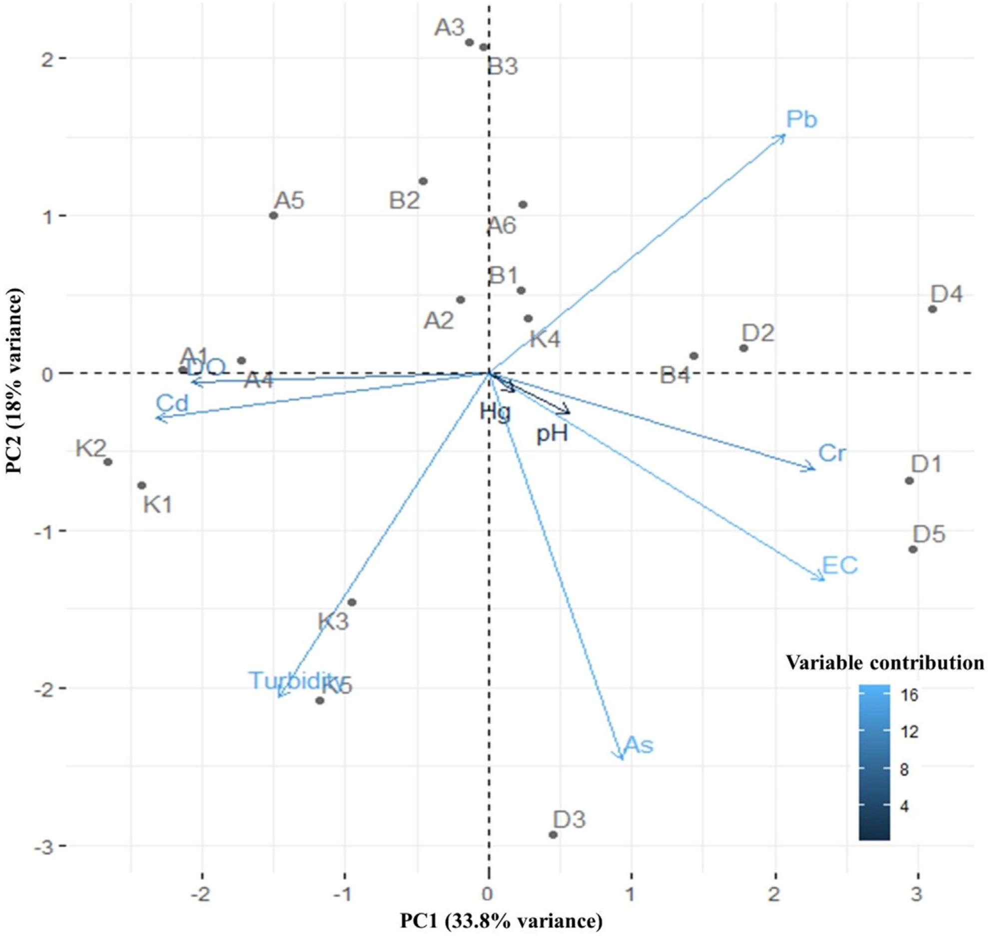

Figure 5. PCA biplot of trace metal and physicochemical characteristics of water samples from Awetu Watershed, Southwestern Ethiopia. The color bar indicates the variable contribution (degree of loading) to the plot.

Table 6. The loadings of the variables and correlation between variables and the PC scores.

	Component		
	1	2	3
DO	-0.685	0.019	0.488
EC	0.774	0.434	0.033
pH	0.187	0.084	0.760
Turbidity	-0.481	0.679	-0.004
As	0.307	0.811	-0.077
Cd	-0.766	0.096	0.165
Cr	0.751	0.201	0.325
Pb	0.682	-0.500	0.158
Hg	0.060	0.039	-0.625

Extraction Method: Principal Component Analysis.

4. Conclusion

This study provides new information on concentrations of As, Cd, Cr, Pb and Hg in surface water of Awetu watershed streams. Trace metal concentrations were relatively high beyond surface water quality standards, demonstrating a considerable potential environmental risk. From all the measured trace metals, Pb shows the highest, whereas Hg concentration remained the lowest. The highest concentration of trace elements was found at the center of the city where the maximum anthropogenic activities are practiced. The main sources are the waste discharge from Jimma University laboratories and dental clinic, car maintenance garages, car-wash, agrochemicals (phosphate fertilizers), pesticides, the emission of fossil fuels, batteries and the incineration of medical wastes.

Accordingly, a lower concentrations were detected in the downstream of the watershed due to slower water flow and sedimentation. Main sources of As and Pb were assumed to be from laboratories, smelting and carwash activities and Cd from agricultural activities as the uncontrolled effluents are disposed to the nearby water bodies even without preliminary treatment. Finally, this study justifies the need for further studies to ascertain the long-term effects of contaminants and waste dumping sites and investigations on water chemistry. The water in the area requires remediation as per environmental quality criteria and regular monitoring of trace metals. Strengthening integrated waste management systems and river quality monitoring should also be implemented in the watershed streams to minimize the health effects and deterioration of the aquatic ecosystem.

Declarations

Author contribution statement

Higemengist Astatkie: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Argaw Ambelu and Embialle Mengistie Beyene: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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