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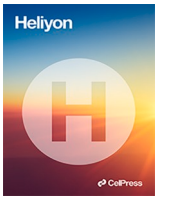

Research article

Determination of metals in water samples within the irrigation area in Telo District, Kaffa Zone, South Western Ethiopia

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ABSTRACT

Water contamination due to the accumulation of metal is not only an environmental problem, but it is also a global issue. The river flows alongside the town in its downward direction, where runoff from the uplands and municipal trash discharge during floods may contribute to the contamination of the river. Despite the fact that this river is the area's primary source of water, the water near the effluent release point is extremely corrosive. The nearby settlements depend on this untreated river water for drinking, irrigation, and other domestic uses since they have no access to a municipal water supply. The aim of the present study was to evaluate the degree of metal contamination in the Obasho river water samples collected from irrigation water sites in the Gurguba region. Three samples were collected from each of four irrigation water sites, which were 1.5 km away from each other. A total of 12 water samples were collected by following the standard water sample collection protocol. 100 mL of the irrigation water sample was digested in aquaragia, and AAS was used to determine the concentration of metals in the water samples. The concentration ranges of some metals were: Ca (1.84387–2.810824 mg/L), and its maximum limit in FAO is 20.0 mg/L; Mg (3.176942–4.543031 mg/L), and its maximum limit in FAO is 5.0 mg/L; Cr (0.039227–0.047872 mg/L), and its WHO/FAO permissible level is 0.1 mg/L; Co (0.036703–0.057218 mg/L), and its permissibility level is 0.05 mg/L WHO/FAO, Cd (0.006198–0.02856 mg/L), whose maximum limit in FAO is 0.01 mg/L, and Pb (0.065138–0.091131 mg/L) WHO/FAO permissible level is 5.0 mg/L. The mean concentrations of metals (Ca, Mg, Co, Cd, Pb, and Cr) in all study sites were below the regulatory limits except for Co and Cd; no water contamination was caused by these metals at the study sites. However, the mean concentration levels of Co in all study sites were above regulatory limits. The mean concentration of Co at Konit Kochito and Cd at Geremew Mamo, Konit Kochito, and Gereno Gebito is also greater than regulatory limits. A pair-wise comparison of some metals in study sites was carried out, thus the mean concentration of the irrigation water sites sample was significantly different from some metal concentration ($p < 0.05$) at the 95% confidence level. Generally, there was no cumulative effect of water contamination caused by Ca, Mg, Co, Cd, Pb, and Cr in Gurguba Kebele study sites, and it may not appear to pose very serious environmental problems at this moment. Thus, determining the metal content in irrigation water samples is crucial for ensuring the safety and sustainability of agricultural practices. It raises awareness regarding the contents of heavy metal contamination and sets limits for acceptable metal concentrations. It has also vital role in maintaining soil health.

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1. Introduction

Abbreviations

AAS	Atomic Absorption Spectrophotometer
EPA	Environmental Protractions Agency
LOD	Limit of Detection
MDL	Determine the Detection Limit
RML	Recommended Maximum Limit
RSD	Relative Standard Deviation
SD	Standard Deviation
SPSS	Specific Programme Social Science
SNNPR	Southern Nations Nationalities Peoples Republic

Water is one of the most essential elements of life on Earth. In its purest form, it's odorless, colorless, and tasteless, but due to human and animal activities, it is usually contaminated with solid and human waste, effluents from chemical industries, and dissolved gases [1]. Trace metal contamination of rivers and sediments remains a global threat to biodiversity and humans. In recent decades, the concentrations of essential metals in irrigation water and vegetables have been greatly increasing on farmland due to anthropogenic activities, including the absence of toilets and the expansion of urbanization [2]. In developing countries, heavy metal contamination of farmland is occurring, which is a problem due to the toxicity of heavy metals [3]. Unplanned urbanization and population growth are some of the factors that may be responsible for the pollution of water bodies [4].

The concentrations of dissolved heavy metals in water samples among the different Qalubiya drain ecosystems showed the spatial distribution in water [5]. Although heavy metals have an important and vital role in the lives of all living organisms, their presence is proven to be fatal if their levels are above the normal limits. These elements can enter the bodies of living organisms through three pathways: ingestion, skin contact, or inhalation, where the danger levels depend on the rate and duration of exposure [6].

Heavy metals are typically not removed from wastewater even after treatment, posing a risk of heavy metal contamination of wastewater-irrigated soils and, subsequently, ending up in the food chain [7]. Heavy metals can pose a health risk through the consumption of contaminated vegetables, milk, fruit, and drinking water. Vegetables are a necessary component of the human diet, providing a source of essential nutrients, antioxidants, dietary fiber, and metabolites. Vegetables are typically grown in the per-urban areas of cities because of their better growth response and high prices. Irrigation water contaminated with industrial wastewater has caused significant essential metal contamination in soils and crops. If soil is irrigated with wastewater, heavy metal concentrations will be high in the edible parts of growing plants [8]. Due to unplanned industrialization and urbanization in the country, wastewater contaminated with heavy metals is continuously released into irrigation canals; thus, soil and crops are contaminated with heavy metals, and many people consume the contaminated crops after they have been transported and sold in retail markets [9].

An increasing trend in soil metal concentrations is reported in places where wastewater has been used for irrigation. There was ample research on the risk of heavy metals to health and the environment [10]. Several authors have shown the risk of contamination by heavy metals in water [11]. Essential heavy metals are required biologically in trace amounts. Otherwise, if they exceed the level, they become toxic. Heavy metals, specifically lead, mercury, cadmium, arsenic, and chromium, are well known for causing birth defects. They can easily cross the placenta and deposit in a growing fetus [12]. In other investigations, heavy metals like Cr, Mn, Cu, and Zn in Taihu Lake sediments were found to have come from natural sources and were then somewhat disrupted by human activity through the use of source analysis. It was discovered that human activity had a significant impact on Cd, and that this impact varied widely throughout nearly all Taihu Lake strata. Furthermore, the lake bay exhibits high concentration clustering characteristics related to the anthropogenic sources of heavy metals [13].

In many developing countries, including Ethiopia, it is common practice to grow vegetables using rivers passing through urban centers. Rivers crossing urban areas have been reported to be contaminated with heavy metals because of urbanization and increasing anthropogenic activities [14]. A study in Ethiopia has shown that effluent discharge from households and solid wastes are the major sources of river pollution. Therefore, irrigation of lands with this contaminated water led to the accumulation of heavy metals in the soil and vegetables, and thus their uptake by plants, a problem that risks human health [14].

Akaki River sediments were limited to the assessment of the concentrations and distribution of some selected heavy metals [15]. Metal contaminants enter river water through anthropogenic sources such as the long-term disposal of untreated and partially treated effluent water containing toxic metals and the indiscriminate use of metal-containing fertilizers and pesticides in agricultural fields [16]. Dike et al. (2004) observed that the rapid population increase coupled with factors such as agriculture results in a huge accumulation of metal contaminants, which end up polluting water bodies such as rivers and streams. Metal contaminants are a major cause of concern for the aquatic environment because of their toxicity, abundance, persistence, and subsequent accumulation in aquatic habitats [17].

Investment in irrigation development is an important strategy for reducing the risks associated with rainfall variability and achieving food security. Ethiopia has many international rivers, high groundwater potential, and natural lakes that have high potential for irrigation. Despite the large repertoire of the river network, irrigated area only forms about 10% of the total cultivated land.

However, currently, limited land is being cultivated under irrigated agriculture. Therefore, crop production has been predominantly based on rain-fed agriculture. Irrigation agriculture is being practiced in the study area under some metals in water farming. The fact that irrigation development, particularly some metals in water irrigation systems, has significant importance to raise production, achieve food self-sufficiency, and ensure food security at the household level in particular and in the country at large. Accordingly, nearly 530,000 ha of land were irrigated, which covers 14% of the irrigated land [18].

The present study has been undertaken to assess the water quality as well as the potential source of contamination of the Obasho River by considering effluent discharged from the upland into the river at the peak of the floods and discharge from municipal waste. The Obasho River is one of the largest rivers found around Telo woreda in Gurguba Kebele. As the river runs along the side of the town, at the north-eastern part, it could be fed with contaminants brought by run-off from the upland into the river at the peak of the floods and discharge from municipal waste. At the effluent discharge site, the water is highly acidic, and the vegetation along the river appears scorched, despite the fact that water from this river is the major source in the area. Since there is no a municipal water supply for the local communities living around the river, they rely on this untreated river water for drinking, irrigation, and other household purposes. The environmental damage caused by water contamination from municipal discharge effluent in the Obasho River has not been studied yet.

These create an urgent need to assess the level of contamination of the river through consideration of the impact of effluents from municipal discharge on the water quality of the river. Tomato, onion, cabbage, potato, and carrot roaming is not equally translated to water, becoming vectors of pests and parasites that eventually spread to the surrounding vegetables, hence causing the growth of vegetable diseases in human beings. The Obasho River is mainly used to facilitate the infrastructure for the production of vegetables in Telo woreda. The biological half-lives of these heavy metals are long and have the potential to accumulate in different body organs, resulting in unwanted side effects [18].

The geology of a given place provides useable water and provides good transmission of rainfall to recharge aquifers, which produce springs and feed perennial rivers [19]. This shows that the variation in agricultural output in Ethiopia depends on rainfall. Therefore, this study aims to determine the concentration of some metals (Pb, Cd, Cr, Co, Na, and Mg) and compare the concentration of some metals with their critical level in Obasho River water used for irrigation in Gurguba Kebele irrigation water sites using AAS.

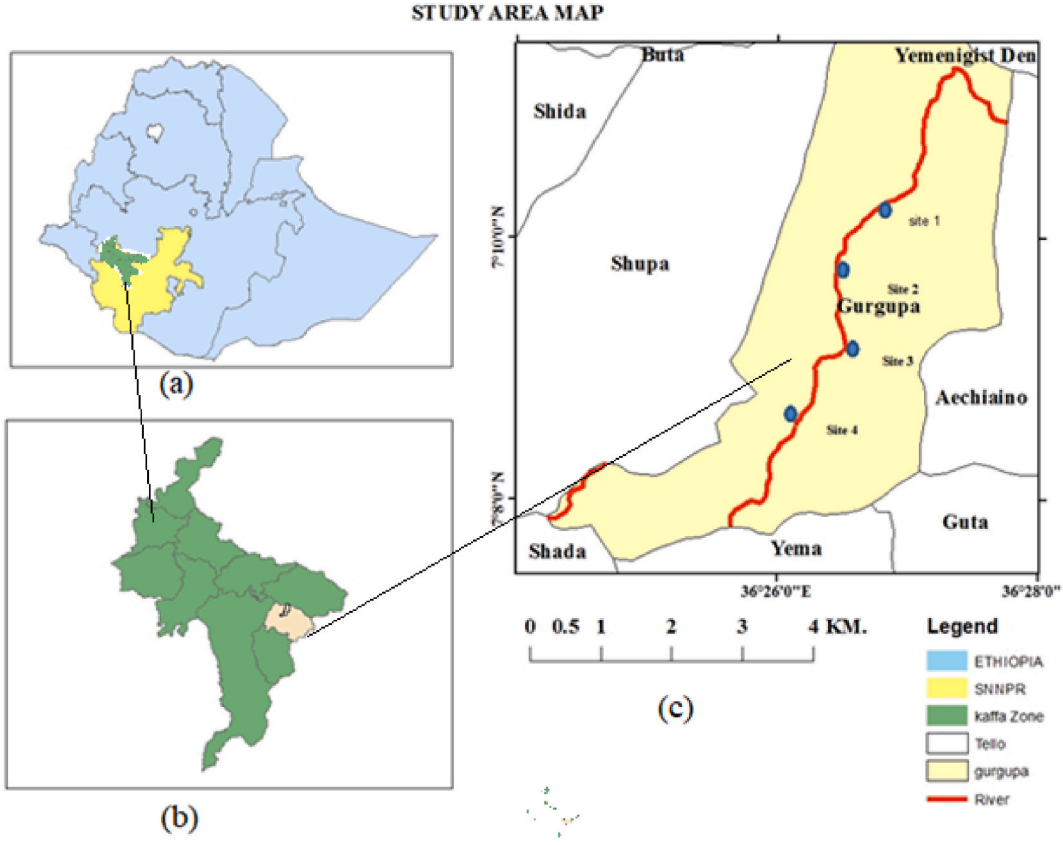

Fig. 1. Map of the study areas: (a) the map of Ethiopia; the yellow-colored shaded part is SNNPR; (b) the Kaffa Zone; and (c) the irrigation sites.

2. Materials and methods

2.1. Description of the study area

The study was conducted at Gurugba irrigation water sites, which were found in Kaffa Zone, one of the 14 administrative zones located in the SNNPR state located in the southwestern part of Ethiopia (Fig. 1a), at a distance of 468 km from Addis Ababa and 743 km from the capital of the SNNPR state, Hawassa. It is bounded by the Gojjeb River from the Oromiya region in the North and North West, Konta Special Wereda in the East, Bench-Maji Zone in the West, and the South Omo River and South Omo Zone in the South, West, and Sheka Zone in the West.

Kaffa Zone covers (Fig. 1b) a total area of about 10,446.27 km^2, or about 7.06% of the total area of the region, and lies at 6° 15′ to 8° 08' north latitude and 35° 30′ to 36° 46′ east longitude. The Kaffa zone has a mean annual rain fall ranging between 1400 and 2000 mm and an average annual temperature varying from 12 °C to 26 °C. It has three agro-ecological zones, such as the high land zone (2500–3000 m), the temperate zone (1500–2500 m), and the low land zone (500–1500 m above sea level). The Zone constitutes ten rural woredas (Gimbo, Gewata, Gesha, Sayilem, Bita, Chena, Decha, Tello, Cheta, and Addiyo) and one town administration, Bonga, which is the capital of the Zone. The total population of Kaffa Zone is 1,104,487, with a sex ratio of 545,239 (49.37%) males and 559,248 (50.63%) females. Source: Central Statistics Authority census, Ethiopia, 1999; and Kaffa zone finance and economy development statistical abstract bulletin. 2007.

Thus, a study was carried out in four different irrigation areas in the Gurugba region (Geremew Mamo, Kochto Emiro, Gereno Gebito, and Konjet Kocheto) as located in Fig. 1c. These can be seen from the map of the study area Fig. 1 the descriptions of irrigation sites outlined in Table 1 and in Fig. 2.

2.2. Apparatus and instrument

Sampling was carried out with a number of tools, depending on the purpose for which sampling was done and the nature of the sample. Equipment and the instruments used for the collection of samples, as well as those used for the preparation of samples, include: 100-mL volumetric flasks were used for filtration, as were polyethylene bottles, which were pre-washed with nitric acid (10%) and double-distilled water. 100 mL of beakers were used for each representative of water samples, a refrigerator to keep digested samples, What-Mann No. 42 filter paper ash less for filtering solution, and FAAS (Anaytika Jena., 2017) were used to analyze the concentration of studied metals.

2.3. Chemicals and reagents

Distilled water and stock standard solutions containing 1000 mg/L of Ca, Mg, Co, Cd, Pb, and Cr were used for preparing working standards (0.05, 0.10, 0.50, and 1.00 mg/L). Standard buffer solutions of H_3PO_4 (85%, India) and K_2HPO_4 (98–101%, England), Aqua regia, concentrated HCl (36%, Sigma Aldrich Darmstadt, Germany), and concentrated HNO_3 (67%, Abron Exports 133,001, India).

2.4. Sample collection and preparation

River water samples were collected in 100-mL plastic bottles from diversion points for irrigation (Fig. 2). The water from the control site was directly collected from the canals leading to the farmlands. Four composite irrigation water samples were collected in pre-rinsed 100-mL polyethylene and mixed to make representative samples of four different farmlands. The sites, farmlands used for different productions of vegetables, are about 1.5 km from each other. The samples were collected in November and April 2020, during the dry season. The total number of samples collected, with their replicated values, was four. A sample of 200 mL of water was collected from irrigation canals at three points, and each farmland (Fig. 2a–d) was selected randomly to represent the situation of contamination in each area. At the sampling site, the bottles were rinsed twice with the water to be sampled prior to filling. The water samples were acidified on-site with nitric acid. 0.5 L (500 mL) of samples from each composite irrigation water sample were taken for laboratory analysis, centrifuged to remove the suspended particles, filtrated through 0.45 μm micropore filters, and preserved with 1.0 mL of 70% HNO_3. The filtered samples were stored in a refrigerator to minimize volatilization and biodegradation between sampling and analysis periods [20].

Table 1
Irrigation sites descriptions.

Name of irrigation sites	Type of irrigation (major product)	Area of land (in hectares)	Use of river
Geremew Mamo	Tomato & Onion	1.5	Obasho
Kochto Emiro	Onion & Cabbage	0.5	Obasho
Gereno Gebito	Potato & Carrot	0.5	Obasho
Konjet Kocheto	Onion	0.875	Obash

Fig. 2. Sample irrigation water sites in the study area. (a) Partial Geremew MamoSite; (b) Partial Kochto Emiro; (c) Partial Gereno Gebito; and (d) Partial Konjet Kocheto.

2.5. Experimental procedures

All the required apparatus for this research work was cleaned with deionized water in order to prevent sample contamination. The equipment, such as plastic containers and polyethylene, was washed by using deionized water. The apparatuses were soaked in 10% (V/V) HNO_3 for 24 h, followed by rinsing with deionized water several times. Then, the apparatus was dried in the oven and kept in a dust-free place until further use.

2.5.1. Optimization of the working procedure

It is important to develop an optimum working procedure in order to get a reliable result from analytical experiments. Thus, to prepare a clear and colorless sample solution that is suitable for the analysis using AAS, different working procedures for the digestion of water samples, such as volume of the acid mixture, digestion time, and digestion temperature, were optimized. By examining the nature of the digests obtained by varying the above parameters, the optimized procedure was selected depending upon the clarity of the digests, the least digestion time, the least reagent volume consumption, and simplicity [21].

2.5.2. Method of sample digestion

A conventional aquaragia (i.e., a solution of HNO_3 and HCl with a ratio of 1:0.5)-based digestion method was used to digest the water samples. This is performed in a 250-mL glass beaker covered with watch glasses. A well-mixed water sample of 100 mL was measured and digested in 5 mL of concentrated nitric acid (HNO_3, 65%) and 3 mL of concentrated hydrochloric acid (HCl, 35%).

The samples have been gently heated on a hot plate under a fume hood to not more than 150°C. After the digestion has been completed, it then evaporated on to the lowest possible volume (about 20 mL). This step takes about 1–2 h for a 100-mL aliquot, with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. Vigorous boiling has avoided preventing the loss of the HCl–H_2O_2 azeotrope. The flasks have been covered with a watch glass to prevent sample contamination from the fume hood

environment. The flasks have allowed cooling. Then, the digested samples were filtered through glass fiber filters prior to analysis. The filtrates have been transferred to 50-mL volumetric flasks and diluted to the mark with distilled water. The digested samples have been preserved in the refrigerator for analysis. These solutions were then used for the elemental analysis. The solution was then diluted to 20 mL with distilled water and assayed for the presence of elements (Ca, Mg, Co, Cd, Pb, and Cr) using the Anaytika Jena Germany model Nova 400P FAAS (Flame Atomic Absorption Spectrometer) in an acetylene-air flame. The sample is diluted with 20 mL of 2% (V/V with water) nitric acid and transferred into a 50 mL volumetric flask after filtering through a Whatman No. 42 filter. Paper ash was mixed with distilled water and diluted to 50 mL. The volume was made up to the mark with deionized water. The samples were stored at room temperature in clearly marked containers.

2.5.3. Preparation of working solutions

The working solution was prepared from intermediate solutions of Ca, Mg, Co, Cd, Pb, and Cr. The solutions were transferred by micropipette to 50-mL flasks, and the flasks that contained HNO_3 and distilled water were identified. The concentrations of each metal were calculated [22].

2.5.4. AAS method

The measurement conditions were optimized based on the signal-to-background ratio of the least sensitive element. The measurement conditions and the selected analytical wave lengths for the metals are set for optimal conditions. The analytic emission was based on taking the difference in measured absorption at the top of the peak and the background near the peak. All detection limits given by the AAS software were based on three times the standard deviation of the background counts, including the washing time between the samples and the total time for analysis.

2.5.5. Determination of metals

The instrument was calibrated using a blank solution and five series of working standard solutions for each metal to be analyzed. The concentration of some metals (Ca, Mg, Co, Cd, Pb, and Cr) was determined using FAAS. The final concentration of some metals in the irrigation water samples was calculated using the following formula [23].

$$\text{Concentration (mg / g)} = \frac{\text{Concentration of the metal}\left(\frac{\text{mg}}{\text{L}}\right) * \text{volume(L)}}{\text{Mass of the sample(g)}}$$

2.6. Method validation

Method validation is the process of ensuring that an analytical method is accepted for the intended purpose. Because of the absence of reference material for the samples in the laboratory, the validity of the optimized digestion procedure was assured by spiking the samples with a standard of known concentration of the analyte metals. In order to validate the analytical method, the following method validation parameters were carried out: linearity, instrumental detection limit, limit of detection, limit of quantification, precision, and accuracy. After the sample is digested, percent recovery of a metal to be analyzed can be determined by using recovery formula [24].

$$\%\text{Recovery} = \frac{C_M \text{ in the spiked sample} - \text{CM in non spiked sample}}{\text{CM added for spiking}} \text{ X100\%}$$

Where, C_M = Concentration of Metal.

2.6.1. Linearity

Linearity is the range over which it is possible to obtain results of analysis directly or by a mathematical transformation proportional to the analysis concentration over the range stipulated. The equation of the calibration curve that relates the dependent (y) and independent (x) variables is $Y = ax + b$. The mathematical method known as linear regression was used to estimate the coefficients of the calibration curve from one set of experimental measurements. The value of 0.9999 was used for the coefficient of correlation (r^2) as the limit for setting the coefficients of the curve [25].

2.6.2. Instrumental detection limit

Instrumental detection limit (IDL) is the lowest signal above background noise that an instrument can detect reliably. The IDL is determined as the concentration equal to three times the standard deviation of the blank signal [26]. In this study, the IDL for each metal is determined from the analysis of three replicates of the calibration blank. Results are obtained from the manual of the instrument [27].

2.6.3. Limit of detection

The limit of detection (LOD) is the minimum concentration of analyte that can be detected but not necessarily quantified with an acceptable level of uncertainty. The LOD for each metal was determined from the analysis of six replicates of the method blanks, which were digested in the same digestion procedures as the actual samples. The LOD was calculated as [28].

$LOD = 3*SD$

where, SD is the standard deviation of the method blank.

2.6.4. Limit of quantification

The limit of quantification (LOQ) is the lowest concentration of an analyte in a sample that can be quantitatively determined with acceptable uncertainty. LOQ is the triplicate analysis of six method blanks, which will be digested in the same procedure as the actual samples. The LOQ was calculated as [24].

$LOQ = 10 * SD$

where SD is the standard deviation of the method blank.

2.7. Statistical analysis

Statistical analysis of the data was carried out using one-way analysis of variance (ANOVA) to assess the significant variation in the mean concentrations of heavy metals in irrigation water. A probability level of $P < 0.05$ was considered statistically significant. Pearson's correlation coefficient was used to determine the association between the metals in irrigation water [29]. All statistical analysis was done using SPSS version 21.

3. Results and discusions

3.1. Optimization of working procedures

To prepare a clear and colorless sample solution that is suitable for analysis using AAS, different working procedures for the digestion of irrigation water samples were carried out using mixtures of acids with varying parameters such as volume of the acid mixture, digestion time, and digestion temperature. HNO_3 and HCl 1:0.5 (v/v) ratios, 85°C and 90 min were determined as optimum conditions. By critically following the nature of the final digests obtained by varying the above parameters, the optimized procedure was selected depending on simplicity, i.e., clarity of the digests, least digestion time, and least reagent volume consumption. The optimization procedure in Table 2 was chosen for the digestion of irrigation water samples using the digestion method. The choice was made by noticing the clear and colorless appearance of the final solution, which looks free of any suspended matter.

3.2. The calibration curve and measurement of metal concentrations

The calibration curves were checked for Ca, Mg, Co, Cd, Pb, and Cr using linear regression analysis of absorbance values versus concentrations of the standard solutions. Five series of working standard solutions of metals were prepared by diluting the intermediate standard solution (10 mg/L) with deionized water. A blank and standards were run in AAS, and calibration curves were established. Each standard solution was measured three times, and the mean is plotted. The correlation coefficients of more than 0.9998 in the calibration graph show that there is a strong linear relationship between concentrations and absorbance. Each of the sample solutions was subjected to an AAS instrument, and the absorbance values of the metals were recorded. Concentrations of the metals were determined from the calibration curves.

3.3. Regression analysis and detection limits

As can be seen from Table 3, and its calibration curves for all analyzed metals show good linearity, with the coefficient of determination (r^2) ranging between 0.9959 and 0.9989, which were greater than or equal to the acceptable limit (0.9998) for the linearity of the regression line. This shows that there could be a good correlation between concentration and absorbance and a good calibration of the instrument. The instrument detection limits (IDL) ranged from 0.00012 to 0.05 mg/L, which were below the method detection limits (LOD), indicating good sensitivity of the instrument for analysis. The LOQ lied between 0.0015 and 11.145 mg/L. The result shows both LOD and LOQ values were greater than the IDL; hence, the results of the analysis could be reliable.

Table 2
Methods tested during optimization of wet digestion for water samples.

No.	Volumes of sample (ml)	Volume of reagents (mL)		Max. temp. (°C)	Time (min)	Results
		HNO_3	HCl			
1	100	1	0.5	50	30	Brown yellowish
2	100	1	0.5	60	60	Yellowish
3	100	1	0.5	70	90	Slightly yellowish
4	100	1	0.5	80	120	Clear and light yellow
5	**100**	**1**	**0.5**	**90***	**150**	**Clear and colorless**
6	100	1	0.5	140	160	Clear and colorless
7	100	1	0.5	120	170	Clear and light yellow
8	100	1	0.5	140	180	Clear and light yellow

Table 3
Linear regression equation, Correlation coefficient of determination, IDL, LOD and LOQ are written as follows.

Metal	IDL	LOD	LOQ	Correlation Coefficient (r2)	Linear regression equations
Ca	0.03	5.5316	6.4875	0.9973	$y = 0.1392x - 0.0728$
Mg	0.05	9.75	11.145	0.9964	$y = 0.1794x + 0.2214$
Co	0.0005	0.00093	0.0049	0.9989	$y = 0.1009x + 0.0035$
Cd	0.00024	0.00051	0.0047	0.999	$y = 0.4071x + 0.0043$
Pb	0.00012	0.00024	0.0015	0.9959	y = 0.0218x - 0.0011
Cr	0.00057	0.00081	0.0039	0.9988	y = 0.0509x - 0.0017

3.4. Accuracy and precision

As it can be seen from Table 4, the mean percent recovery for the studied metals in the matrix ranged between 95 and 99. All the recovery values were within the acceptable range of 80%–120% for metal analysis [30]. The relative standard deviation values obtained for the water matrix of spiked samples ranged from 0.13% to 0.73%, which was under the required control limits (i.e., $\leq$15%) [31]. These results indicate that the proposed method is precise and accurate.

3.5. The mean concentrations of metals in irrigation water samples

The mean metal concentrations (mg/L) of the irrigation water are given in Table 3 and Fig. 4, together with the concentration. Here, Mg (3.176–4.543 mg/L) had the highest and Cd (0.006–0.028 mg/L) the lowest concentration. The concentrations of potentially toxic metals in the surface water of the river are shown in Table 5. Total concentrations of metals in surface water were listed in descending order: Mg > Ca > Pb > Co > Cr > Cd in the study area. This indicates that the total concentration reaches its highest value at site 2 (Kochito Emiro), located downstream of the last farmlands. In addition, maximum values of Ca and Pb were found at site 2 (Kochito Emiro); it is speculated that the deference between deferent metals is related to the contamination input of the river. The metal contents in samples collected from Site 1 (Geremew Mamo) and Site 4 (Konit Kochito) were relatively low, which may be due to the fact that they were taken upstream of the tailings water and were less affected by the tailings water.

3.6. Concentration of some metals (Ca, Mg, Co, Cd, Pb, and Cr) in irrigation water in the study area

Calcium (Ca): The minimum calcium concentration in sampled water was 1.413 $\pm$ 0.016 mg/L (Fig. 4b), which was recorded in the water of site 3 (Gereno Gebito). The maximum concentration of calcium was 2.810 $\pm$ 0.003 mg/L, which was recorded in the hand-dug well of site 2 in Kochito Emiro. The average concentration was 2.594 mg/L. The threshold value permitted for the calcium concentration in water is within the range of 20.0 mg/L [32]. According to this value, all water samples had a calcium concentration below the stated value and were fine for utility. According to Ref. [33], the accepted limits of Ca concentration usually used for irrigation are that, considering these limits, using this water for irrigation would have no impact on water properties or crop growth. But all the water samples in the study area had a calcium concentration below 20.0 mg/L and were safe for irrigation.

Magnesium (Mg): To an extent exceeding the amount of calcium (Fig. 4a), the presence of magnesium in water resulted in the hardness of the water. It is usually expressed as the equivalent quantity of calcium carbonate. Water can be a contributor to calcium and magnesium intake and could be important for those who are marginal for calcium and magnesium. Although there is evidence from epidemiological studies for a protective effect of magnesium or hardness on cardiovascular mortality, the evidence is being debated and does not prove causality. Further studies are being conducted [33].

The result obtained from water samples shows that the minimum concentration is 3.176 $\pm$ 0.081 mg/L recorded in the (Geremew Mamo) hand-dug well in Site 1, and the maximum value is 4.543 $\pm$ 0.0130 recorded in the hand-dug well water sample taken. The mean value of magnesium measured among all samples is 3.20 mg/L. Still, the measured values are not exceeding the stated guideline, and hence all water is recommended for irrigation water (Fig. 3). According to the FAO (1994), the accepted limits of Mg are 5.0 mg/L used for irrigation. Considering these limits, using this water for irrigation would have an impact on water properties and crop growth. And also, it recommends that vegetables affect magnesium in portable water.

Magnesium deficiency in healthy individuals who are consuming a balanced diet is quite rare because magnesium is abundant in both plant and animal foods and because the kidneys are able to limit urinary excretion of magnesium when intake is low [34].

Table 4
Recovery and precision test results of metals for water matrix spike sample.

Metal	Un spiked Sample (mg/L)	Spiked sample (mg/L)	Known analyte added (mg/L)	%RSD of spiked sample	% of recovery
Ca	1.158	2.311	1.200	0.460	96.000
Mg	0.464	1.938	1.550	0.130	95.000
Co	2.872	3.070	0.200	0.730	99.000
Cd	0.035	0.960	0.501	0.480	99.000
Pb	1.882	2.080	0.200	0.72	99.000
Cr	0.035	0.950	0.601	0.160	99.000

Table 5
Mean concentrations of some metals (Mean +SD mg/l) in irrigation water sample.

Metal	Mean concentration (mg/l)				RML
	Site 1 (Geremew Mamo)	Site 2 (Kochito Emiro)	Site 3 (Gereno Gebito)	Site 4 (Konit Kochito)	FAO (WHO)
Ca	2.593 ± 0.003	2.810 ± 0.003	1.413 ± 0.016	1.843 ± 0.002	20.0
Mg	3.176 ± 0.081	4.543 ± 0.0130	3.368 ± 0.036	3.257 ± 0.0043	5.0
Co	0.036 ± 0.001	0.046 ± 0.001	0.046 ± 0.002	0.057 ± 0.005	0.05
Cd	0.015 ± 0.0002	0.006 ± 0.001	0.012 ± 0.0001	0.028 ± 0.0008	0.01
Pb	0.065 ± 0.010	0.091 ± 0.011	0.087 ± 0.007	0.072 ± 0.014	5.0
Cr	0.047 ± 0.002	0.039 ± 0.002	0.043 ± 0.007	0.039 ± 0.001	0.1

RML = recommended maximum limit, source [32].

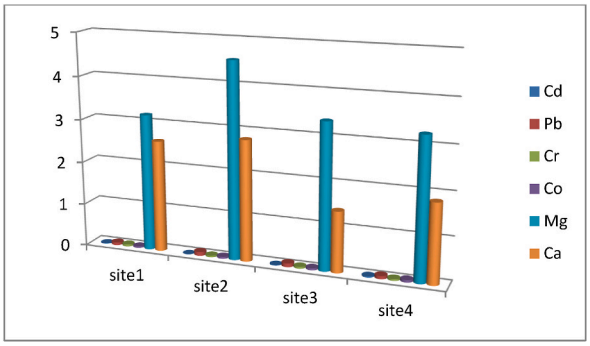

Fig. 3. Mean concentration variation of some metals in water sample.

Therefore, the water samples in the study area had a magnesium concentration below 5.0 mg/L and were not safe for the growth of vegetables and effects of plant health.

Lead (Pb): The concentration of Pb in samples varied between them (Table 5). The values of lead range from a minimum of 0.065 ± 0.010 mg/L at Site 1 (Geremew Mamo) to a maximum of 0.091 ± 0.011 mg/L at Site 2 (Kochito Emiro). In all the entire selected sites of the river (Fig. 4f), the values recorded were above the minimum permissible limit of WHO (5.0 mg/L). These values were far below the maximum permissible value (5.00 mg/L; [33]), and, therefore, the amount of Pb in the water does not have harmful effects for irrigation use. It shows that, among the sampling sites, the mean concentration of Pb was significantly different ($P < 0.05$). Most of the lead we take is removed from our bodies in urine; however, as exposure to lead is cumulative over time, there is still a risk of buildup, particularly in plants. In the studied river, domestic waste and deteriorating household paints, which have discharged through small tributaries that pass through the center of the town, have probably contributed to the increase in Pb concentration. The agricultural activities practiced around the river may also have contributed to the observed high levels of lead, since this metal can occur as impurities in fertilizers, metal-based pesticides, compost, and manure. A high concentration of Pb is known to impair the proper functioning of the reproductive are consequences of Pb poisoning [35].

As Abdel-Rahman et al. [36] indicated, some metals, such as Pb, Cd and Ni were above the maximum residue limits (MRLs) in Sewi dates. This means that even at very low concentrations, Pb is a threat to agricultural activities because it usually builds up in the plant. It is essentially harmful to children under the age of the cause's physical growth [37]. Therefore, the water samples in the study area had a lead concentration below 5.0 mg/L and were not safe for the growth of vegetables and plant health.

Chromium (Cr): The mean chromium level (Fig. 4c) is at Site 1 (Geremew Mamo), with a maximum of 0.047 ± 0.002 and a minimum level of 0.039 ± 0.001 mg/L at Site 4 (Konit Kochito) water source. When compared to 0.1 mg/L (WHO., 2001) and (FAO., 1994), in order for irrigation water to have a chromium concentration of 0.10 mg/L, the FAO and WHO both have the same guideline value of 0.10 mg/L for Cr in domestic water. The Cr concentrations in the river water (Table 5) failed to comply with the set guidelines for all of the sampling. All water samples in the study area have a chromium concentration below 0.1 mg/L, and the analyzed sources of the town are within the acceptable limit and are safe for portable water.

Cadmium (Cd): The concentration of Cd (Fig. 4d) in water samples varied from 0.006 ± 0.001 to 0.028 ± 0.0008 mg/L. The mean concentration and Cd content were considered safe; the maximum acceptable value was 0.01 mg/L (WHO., 2001; FAO., 1994). Table 5. Cd is reported to be a component of pesticides and fertilizers. The volatilization of Cd from fertilized agricultural lands introduces significant amounts of Cd into the atmosphere, which, through runoff, gets into the aquatic ecosystem [38].

The maximum permissible limit for Cd in water is 0.01 mg/L [30]. The concentration of cadmium in the water is shown in Fig. 3. In almost all the water, the concentration of cadmium was recorded above the permissible limit except at Site 2 (Kochito Emiro), and others are not safe for the irrigation water in the study area.

Cobalt (Co): The results obtained in the present study showed that the concentrations of Co (Fig. 4e) in the water were between 0.036 ± 0.001 mg/L and 0.057 ± 0.005 mg/L (Table 5); the lowest concentration was found in site 1 (Geremew Mamo) and the highest

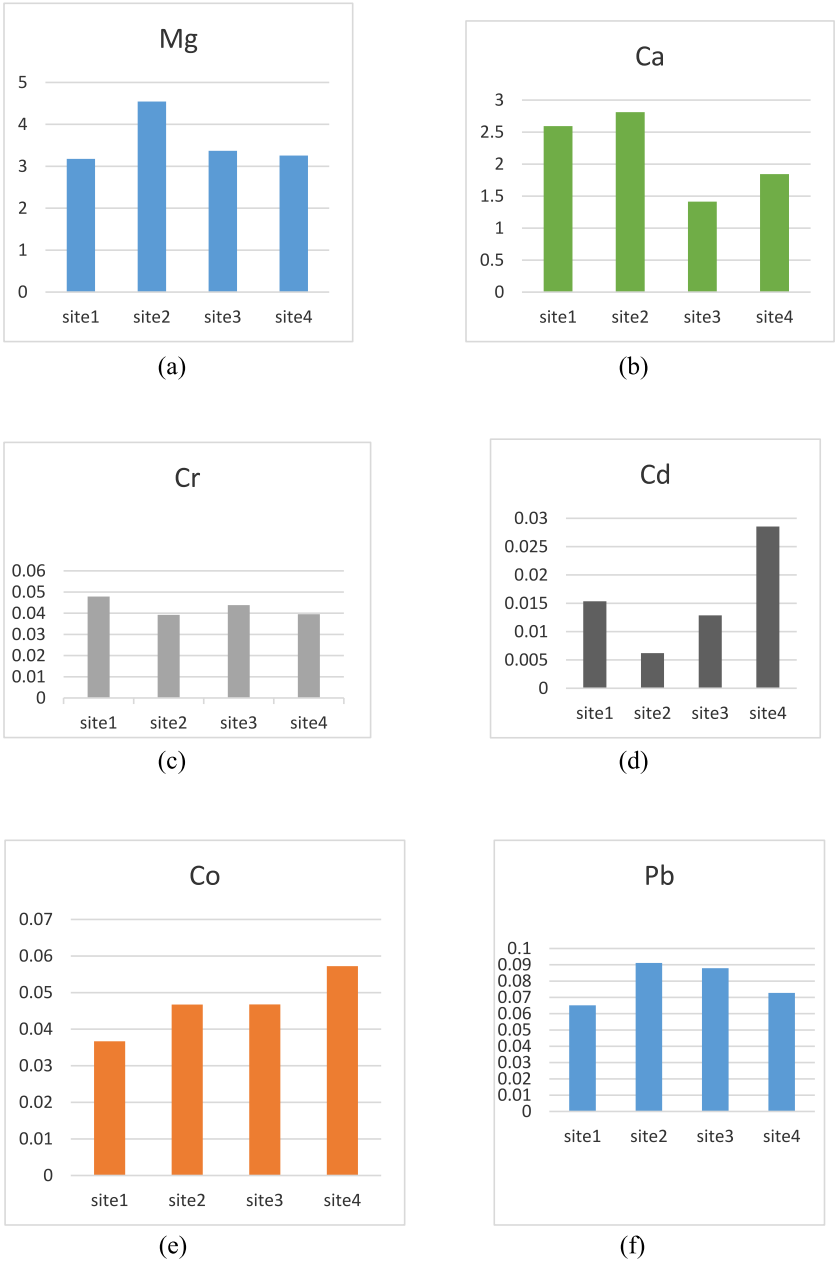

Fig. 4. Mean concentration of metals: (a), (b), (c), (d), (e) and (f) are the mean concentration of Mg, Ca, Cr, Cd, Co and Pb respectively in four study sites.

in site 4 (Konit Kochito). The concentrations were substantially above Konit Kochito land; the value permitted for the Co concentration in water is within the range of 0.05 mg/L [24,32]. Yet, there were significant differences in Co concentrations in the analyzed water ($p < 0.05$). Explain the degree of variation in contamination from the sources of cobalt in all farmland locations. Among the metals under consideration in the present study, all the water samples in the study area had a Co concentration below 0.05 mg/L, except Konit Kochito Land, which is safe for irrigation.

3.7. Comparison of concentrations of some metals (Ca, mg, Co, Cd, Pb and Cr) in irrigation water with literature values and guidelines with their critical levels

There are reports from different countries on the determination of some metals in irrigation water sites. Comparison of results obtained in this study with the values determined in other literature is important. The comparative study of some metals determined in

this work and reported values in other literature are given in Table 6 below.

Table 6 presents comparison of metal concentrations in irrigation water sites of some area in different countries with data obtained from Guruguba Kebele sites in Ethiopia. For example in Akaki River water it is observed that metals like Mg, the highest concentration is recorded as compared with the results recorded at Guruguba Kebele sites while the least concentration of Mg was recorded at Lusaka irrigation water sites in Zambia. As indicated from Table 6 the concentration values of metals recorded in different countries were different depending on the feeding style, culture and development of the country. Higher concentrations of metals are reported in developed countries than developing countries. This might be attributed to the existence of different sources of metals, such as the graphic industry, the food industry, large household waste, and municipal solid waste residues, which are considered as the major sources of metals [39]. The lower concentrations of metals are recorded in developing countries like the Akaki River, Lusaka, and Ethiopia. This indicates that the concentration of metals in irrigation water sites increases with the development of the country.

As indicated from Table 6, most of the metals determined from irrigation water sites were below the standards recommended by the WHO except Co and Cd Konit Kochito, whose concentrations were found to be greater than regulatory limits. At this moment in time, there is no toxicity risk to the environment or vegetables caused by the existence of metals like Ca, Mg, Cr and Pb due to their lower concentrations as compared with standards. But the higher concentration of Co and Cd at the indicated sites may cause health of effect plant and environment [40].

3.8. Contamination factor (CF)

In this study, water contamination was determined by comparing the concentration values, as indicated in Table 7, of heavy metals in study area sites with some regulatory limits for heavy metals. As indicated in Table 5, the mean concentrations of Co and Cd were above the regulatory limits in all study sites, and this shows that contamination in the study area was caused by these metals. The mean concentration of Ca, Mg, Cr, and Pb in all sites is lower than the regulatory limits; this shows that no water contamination is caused by the concentration of metals in the study area. There were no baseline threshold values given by researchers, as there was no study conducted regarding a similar issue. Therefore, WHO standards are used as a baseline to calculate contamination factors. Many researchers have utilized the standard baseline concentration values to measure the contamination factors of irrigation water samples. Irrigation water contamination in irrigation water sites in Gurguba was measured by using maximum permissible limits for each metal according to the WHO.

The contamination factor formula, according to Ref. [41], is written as: $CF = CT/BV$. Where CT refers to the concentrations of trace or toxic heavy metals in the irrigation water samples, BV refers to the baseline or background value. $CF < 1$ refers to a low contamination factor. $1 \leq CF < 3$ indicates a moderate contamination factor. $3 \leq CF \leq 6$ shows a high contamination factor, and $CF = 6$ implies a very high contamination factor. As a result, water samples in the study area had magnesium concentrations above 7.92 mg/L, which had an effect on vegetable growth and health.

3.9. Statistical analysis

A pair-wise analysis of metals was carried out to determine statistical significance in the mean concentration values of metals in the irrigation water sample sites. The analysis of variance was calculated using SPSS software version 21. Site1 Cd compared with Site1 Cr, and their resulted probability level was ($P = 0.015$), which is smaller than 5% (0.05), and thus the mean concentration of Cd in two sites was significant, which means concentration variation was observed between the two sites. The result of SPSS indicated that the concentration variation of Cr was observed in other sites: Geremew Mamo with Gereno Gebito at baseline, Gereno Gebito with Kochito Emiro, and Konit Kochito with baseline at the probability level of $P \leq 0.05$. This could be attributed to the existence of different sources of irrigation water for this metal. Similarly, the mean concentration of Geremew Mamo Cr was compared with Kochito emiro, Gereno Gebito chromium with Konit Kochito, Konit Kochito chromium with Geremew Mamo, and Kochito emiro Co with Geremew Mamo Co, and the mean concentrations were not significant ($P \leq 0.05$) at the 95% confidence level. Generally, the mean concentrations of metals in irrigation water sample sites were compared with metals in all sites, and the mean concentrations were significant at $P \leq 0.05$. This concluded that discarded irrigation water is the main source of metals in dumpsites.

Table 6
Comparison of some metal concentrations in irrigation water sites of Guruguba Kebele with other findings.

Area (Country)	metals concentration (mg/l)					
	Ca	Mg	Co	Cd	Pb	Cr
Bangladesh (Taufique Arefin.,2016)	5.44	2.53	–	–	0.36	0.32
Akaki River water (Mohamed., 2002)	53	16	–	0.1	0.1	0.1
Lusaka (John and Olusegun.,2016)	11.9	1.15	4.33	–	0.06	0.05
Ethiopia (Chem. Soc. Ethiop. ,2012)	23	30	<0.01	<0.007	<0.1	0.44
Maximum limit (FAO., 1994 and WHO., 2001)	20.0	5.0	0.05	0.01	5.0	0.1
Guruguba (present study)	2.16	3.58	0.046	0.015	0.079	0.042

Table 7
Contamination factor (CF) of metals in each of the study sites.

Sites	Metals					
	Ca	Mg	Co	Cd	Pb	Cr
Site 1 (Geremew Mamo)	2.59	7.92	0.72	1.5	0.013	0.47
Site 2 (Kochto Emiro)	2.81	11.35	0.92	0.62	0.018	0.39
Site 3 (Gereno Gebito)	1.41	8.4	0.92	1.2	0.017	0.43
Site 4 (Konjet Kocheto)	1.84	8.12	1.14	2.8	0.014	0.39

3.10. Correlation analysis

The Pearson correlation coefficient matrix among the selected heavy metals is presented in Table 8. There is a significant correlation between the metals between Cr with Co ($r = 0.827$), Cd with Mg ($r = 0.695$), Pb with Mg ($r = 0.730$), and Cd with Pb ($r = 0.621$). This strong positive correlation indicated that the elements. Ca and Cr ($r = 0.018$) and Pb and Ca ($r = 0.117$, weakly) could indicate the same or similar source input. The other metals have a weak positive correlation, indicating that the source of water for these metals was not the same and that the presence or absence of one metal affected it to a lesser extent than the other [42]. There were no negative correlation values observed between metals at all study sites.

4. Conclusion

In this study, all the sites where samples were taken possessed most of these metals. It was also observed that irrigation water sample sites showed a higher concentration of metals (Co and Cd) than using the maximum permissible limits for each metal according to WHO/FAO. This is attributed to the presence of waste carrying higher amounts of these metals. The concentration of Co (Konit Kochito) was higher than the other site, and Cd was except Kochito Emiro, above the regulatory limits of metals, and Cr and Pb below the regulatory limits of metals. This implies Co and Cd are the most abundant on the earth's crust to efficiently distribute vegetable root. The mean concentrations of Cr and Pb in all sites were below the regulatory limits, while the mean concentrations of Pb at Site 1 (Geremew Mamo) and Site 4 (Konit Kochito) and Cr in all irrigation water sample sites were below the regulatory limits. Thus, the study could most probably be due to irrigation water wastes, which contain small amounts of those metals and have no significant effect on vegetable growth. From the results, it can be concluded that the cumulative effect of these metal concentrations in irrigation water waste dumpsites in Guorguba Kebele may not appear to pose very serious environmental problems at this moment due to the low contamination factor except for magnesium. However, the accumulation of these metals may later pose a threat to human health and the environment. The general higher concentration values observed in the waste sites against the WHO could be due to considerable proportions of animals' movement, canals across land, biodegradations, the absence of toilets, and metal rubbish, which are known to be real sources of metals. Generally, using SPSS version 21, the mean concentrations of metals in irrigation water sites were compared with metals in FAO/WHO, and the mean concentrations were significant ($P \leq 0.05$) at a 95% confidence interval. This concluded that discarded irrigation water wastes are the main sources of metals in dumpsites. It is essential to ascertain the metal content of irrigation water samples in order to guarantee the sustainability and safety of agricultural methods. It raises awareness of the contents of contaminated areas with heavy metals and establishes acceptable metal concentration limits. Therefore, this research study may be important to provide information on different samples of irrigation water so that the community can take action to ensure the productivity of vegetables with regards to the status of the concentration of some metals in the water. It provides insight to policymakers, NGOs, community-based organizations, and other stakeholders who are concerned with small productivity.

Additional information

No additional information is available for this paper.

Data availability

The data generated and analyzed during this study are available within the study.

CRediT authorship contribution statement

Teferi Tademe Dadebo: Writing – review & editing, Validation, Supervision, Software, Methodology, Conceptualization. **Gezahagn Tilahun Gelaw:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used Free Grammar checker-QuillBot AI in order to check the grammar problems. After using this service, the authors reviewed and edited the content as needed and take full responsibility for the content of the

Table 8
Pearson correlation coefficients of metals in irrigation water samples sites.

	Cd	Pb	Cr	Co	Mg	Ca
Cd	1					
Pb	0.621[a]	1				
Cr	0.108	0.558[b]	1			
Co	0.586[b]	0.239	0.827[a]	1		
Mg	0.695[a]	0.730[a]	0.591	0.041	1	
Ca	0.453	0.117	0.018	0.470	0.568[b]	1

[a] Correlation is significant at the 0.01 level (2-tailed).
[b] Correlation is significant at the 0.05 level (2-tailed).

publication.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Teferi Tademe Dadebo reports financial support was provided by Wolaita Sodo University. If there are other authors, they 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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