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Potentially Toxic Trace Element Contamination of the Little Akaki River of Addis Ababa, Ethiopia

Minbale Aschale[1*] Yilma Sileshi[2] Mary Kelly-Quinn[3] Dereje Hailu[1,2]
1.Ethiopian Institute of Water Resources, Addis Ababa University, Ethiopia
2.School of Civil and Environmental Engineering, Institute of Technology, Addis Ababa University
3.School of Biology and Environmental Science, University College Dublin, Belfield, Dublin 4, Ireland
E-mail: minsinas@yahoo.com

Abstract

In this study, river water samples taken from 26 different locations along the course of the Little Akaka River in Addis Ababa were analyzed to determine potentially toxic trace element concentrations. The mean concentrations in µg L^{-1} for Mn 1540.04, Fe 1075.92, B 383.04, Sr 336.75, Ba 132.17, Cr 67.04, Sb 42.80, Zn 25.50, Ni 6.66, Cu 5.61, V 4.87, Pb 3.13, Co 2.62, As 1.46, Cd 0.06 and Hg <0.05. Overall metal concentration were in the order Mn > Fe > B > Sr > Ba > Cr > Sb > Zn > Ni > Cu > V > Pb > Co > As > Cd > Hg. A strong positive correlation was observed between several of the trace elements indicating common sources. The concentrations of Cr, Mn, Sb, B and Pb exceeded the permissible limits of the Ethiopian, European Community and WHO for drinking water quality guidelines. Fe and Sr exceeded the permissible limits of the Ethiopian drinking water guideline and Sr exceeded the WHO thresholds. The concentration of Cr, Zn, Cu and Pb exceeded the annual average thresholds for surface waters set in SI 272 of 2009. The concentration of Cr, Mn and Sr were also higher than the international guidelines value for irrigation water. The pollution of the river water is increasing alarmingly and poses serious threat to human health. Many of the concentrations were higher than previously reported. It is, thus, necessary to take serious and essential measures from the concerned bodies. Adoption of adequate measures to remove the heavy metal load from the industrial waste water and upgrading of sewage treatment plants are suggested to avoid further deterioration of the river water quality.

Keywords: River water, Potential toxic elements, Heavy metal contamination, Drinking water standards

1. Introduction

Among the wide range of pollutants affecting water resources heavy metals contamination is one of the major quality issues in many fast growing cities of developing countries. Provision of sanitation and wastewater infrastructure has not kept pace with population and urbanization growth. Heavy metals are among the most common environmental pollutants, and elevated occurrences in waters and biota usually indicate the presence of anthropogenic sources. The main natural sources of metals in waters are chemical weathering of minerals and soil leaching, while anthropogenic sources are associated mainly with industrial and domestic effluents, surface runoff, landfill leachate, mining of coal and ore, atmospheric sources and inputs from agricultural activities in rural areas (Zarazua *et al*., 2006). Rivers in urban areas in many developing countries have water quality problems because of domestic and industrial wastes are often discharged untreated into water bodies which leads to the increase in the level of potentially toxic element concentrations *(*Sekabira *et al.,* 2010*)*. Trace metal contamination is of concern due to their potential toxicity to the environment and human beings (Kar *et al*., 2008; Aktar *et al*., 2010*)*. The contamination of surface water by heavy metals is a serious ecological problem as many heavy metals such as Hg, As, Pb, Sb, Ni, Sr and Cd are toxic even at low concentrations. They are non-degradable and can accumulate in the human body and causing damage to nervous system and internal organs (Lee *et al*., 2007; Lohani *et al*., 2008). Though some metals such as Cu, Fe, Mn and Zn are essential as micronutrients for living organisms, they can be detrimental to their physiology at higher concentrations (Kar *et al.,* 2008; Nair *et al.,* 2010).

Addis Ababa city with approximately 5 million population hosts large numbers of industries whose wastewaters are discharged into small river network, most often untreated. Accordingly, old as well as new factories, commercial, public and domestic utilities in Addis Ababa release untreated wastes into any receiving environment found nearby. To date there have been limited studies and knowledge dealing with the concentrations of potentially toxic elements in the Little Akaki River, of two major rivers flowing through the city. Kebede *et al* (2012) in their studies of some fresh water bodies in Ethiopia found out that the concentration of Cr, Mn, Co, Ni, Ag, Hg and Pb were generally elevated because of the disposal of domestic and factory wastes. Melaku *et al* (2004) in their studies on the Little Akaki river related the elevated levels of Cr, Cd, Co, Cu, Ni, Pb, Zn and Mn to mainly industrial activities and disposal of domestic and municipal wastes. Studies on trace elements in vegetables and farmlands of Addis Ababa by Itanna (1998, 2002) to assess their toxicological implications reported higher concentrations of trace metals in the more industrial sites of the river catchment and gradual increases in soils over time. Later Weldegebriel *et al* (2012) determined the concentrations of metals in vegetables grown in soils irrigated with Little Akaki river water in Addis Ababa and the result indicated that Cd, Co, Cu, Mn, and Ni in most water samples used for irrigation surpassed irrigation water guideline limits. The present study aimed to assess the present water quality status of Little Akaki River with respect to potential toxic trace elements namely Sb, B, Ba, Sr, As, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg and to evaluate how these trace elements are distributed in different areas of Little Akaki river. For this purpose, water samples collected from 26 different sites were analyzed for trace elements using ICP-MS. The findings of this study will provide baseline information about water quality for stakeholders and the concerned authorities for further work and intervention.

2. Study Area

Addis Ababa, Ethiopia, the nation's capital and largest city lies high in the foothills of Mount Entoto in central Ethiopia. It is geographically located at 9°N and 38°E between 2200 and 2500 meters above sea level. It is the country's commercial, manufacturing and cultural center. The two major rivers in the city are the Little Akaki River, locally known as Tinishu Akaki River, which flows through the western part of the city and Big Akaki River, locally known as Tiliku Akaki River, which flows through the eastern part of the city (Figure 1). Most of the industries are established along the course of the Little Akaki river and its major tributaries. These include tanneries, breweries, wineries, distilleries, pharmaceutical and national alcohol liquor factories. At the same time the river is used for irrigation, washing, livestock watering and other domestic needs for the rural people living outside Addis Ababa and Akaki. The water is also used to irrigate vegetables in some of the farms within the city. The same vegetables are consumed by the residents of the city.

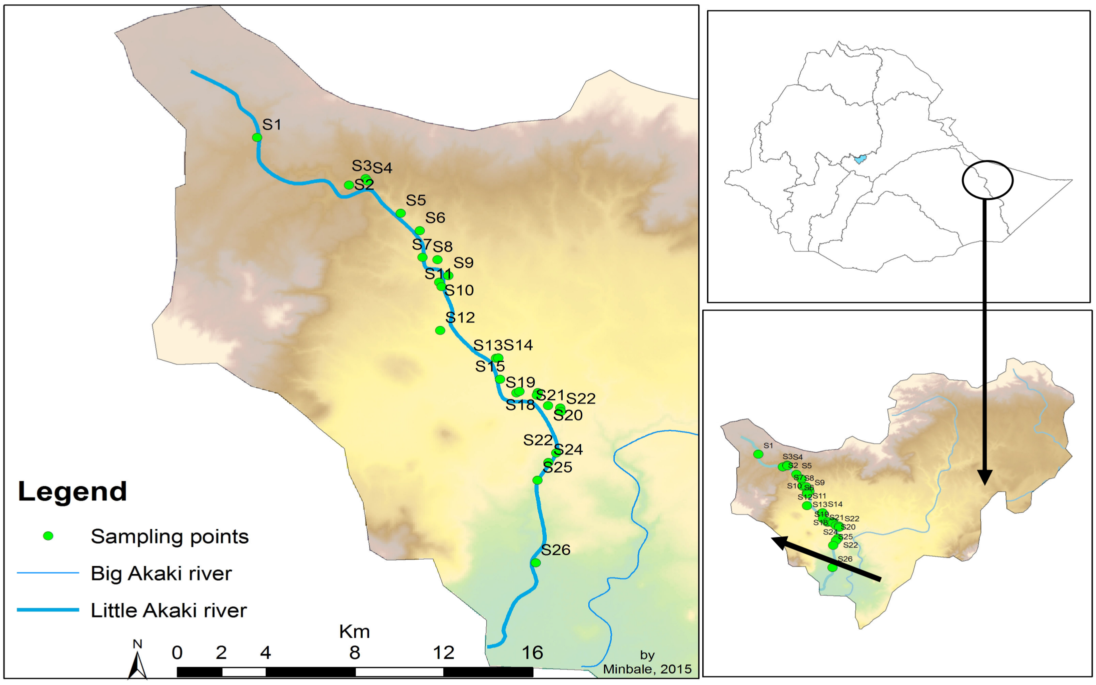

Figure 1: Location of sampling sites on the Little Akaki River and its tributaries.

3. Materials and Methods

3.1. Reagents and standard solutions

The reagents of the highest purity grade were used. All prepared stock solutions used were of analytical grade. High-purity water (18.2 MΩ cm^{-1}) from a Milli-Q water purification system (Millipore, France), concentrated nitric acid (BDH, England) and argon of 99.999% purity were used. Analytical multi-element standard solutions were prepared by appropriate dilution of single and multi-element standard solutions containing the metal ions of interest supplied commercially for ICP-MS. For preparation of the calibration standards, stock solutions of 1000 mg L^{-1} single element metal standard solutions of Ba, B, As, Cr, Pb, Sb, Mn, Fe, Co, Hg, Sr, Ni, Cu, Zn, Cd and V were used. Quality control multi-element standard solutions were used as certified material to evaluate the accuracy and precision for the quantification of elemental concentration of water samples.

The nonspectral matrix effects associated to the ICP-MS measurements were resolved by the addition of internal standards and matrix matching. The internal standard solution was prepared by diluting single elemental stock solutions with Milli-Q water containing 0.5% HNO_3 up to get 1000 mg L^{-1} of germanium, rhodium, rhenium and iridium. The purpose of the internal standards is to correct the analyte signal for any changes observed in the associated internal standard accomplished by using intensity ratio's. The matrix of all samples, standards, wash solutions and quality control standards was made in a 0.5% HNO_3.

All polyethylene bottles were washed with detergent, followed by repeated rinsing with distilled water and soaked overnight in 10% HNO_3 for 24 hr and finally rinsing three times with doubly deionized water. Until collection dried sample containers were kept in sealed polyethylene bags. Supra pure grade nitric acid was used to acidify the samples.

3.2. Water sampling and preparation

Samples which are representatives of the river water were collected from a total of 26 sampling sites shown in Figure 1. The sites were chosen on the basis of possible sources of potential toxic metals pollution, based on industry locations, agricultural activities, population density, and other possible sources of pollutants (Table 1). The sites included diversion points for irrigation and some of the tributaries that enter the river. At each sampling station 500 mL of water sample was collected by lowering pre cleaned polyethylene bottles into the upper surface of the river, 30-50 cm deep, and allowing them to over flow before withdrawing. Before taking the final water samples, the bottles were rinsed three times with the river water to be collected. Sampling took place between February-June, 2014. The collected river water samples were brought to the laboratory and filtered using Whatman 42 pore size filter paper and preserved with 1 ml of 69% HNO_3 in 200 ml polyethylene bottles. The filtered samples were stored in a refrigerator to minimize volatilization and biodegradation between sampling and analysis periods. Finally, the preserved samples were transported to the Laboratory of Environmental Protection Agency in Dublin, Ireland for trace element analysis.

Table 1: Description of sampling sites of the study area in Addis Ababa

Site	Elevation(m)	Location		Description
S1	2597	09° 4.643'N	038° 38.161'E	Gefersa River before entering water treatment plant
S2	2516	09° 3.314'N	038° 40.393'E	Gefersa River after water treatment plant
S3	2507	09° 3.497'N	038° 40.802'E	Burayu River
S4	2502	09° 3.430'N	038° 40.842'E	LAR after mixing with Gefersa and Burayu River
S5	2426	09° 2.525'N	038° 41.651'E	LAR after mixing with Addis Ababa Tannery and glass factory
S6	2401	09^{o} 2.035’N	038^{o}42.118’E	LAR at the bridge of Kolfea
S7	2351	09° 01.293'N	38° 42.183'E	LAR after mixing with Gerbeja River
S8	2352	09^{o}01.232’N	038^{o}42.540’E	Worenchiti River
S9	2348	09°00.780’N	038^{o}42.811’E	LAR after mixing with Worenchiti River
S10	2325	09° 00.597’N	038^{o}42.587’E	Melkaqurani River
S11	2322	09°00.475’N	038^{o}42.644’E	LAR after mixing with Melkaqurani River
S12	2254	08°59.252’N	038^{o}42.608’E	LAR at Zenebe work: receives Alert hospital and domestic
S13	2224	08°58.478’N	038^{o}43.969’E	LAR at Mekanisa after mixing with National Alcohol Wastes
S14	2215	08°58.487’N	038^{o}44.025’E	Kera River: It receives Abattoir and slaughter house wastes
S15	2212	08°57.890’N	038^{o}44.064’E	LAR at Gofa after mixing with Kera River
S16	2215	8°57.511'N	038° 44.458'E	Lafto River
S17	2214	8° 57.555'N	038° 44.537'E	LAR after mixing with Lafto River
S18	2206	08°57.522’N	038^{o}44.978’E	Jaja stream
S19	2203	08°57.445’N	038^{o}44.953’E	LAR after mixing with Jaja River
S20	2213	08°57.152’N	038^{o}45.230’E	LAR at Biheretsige
S21	2197	08°57.090’N	038^{o}45.527’E	Kaba River: receives industrial, domestic and public wastes
S22	2202	08°56.988’N	038^{o}45.541’E	LAR after mixing with Kaba River
S23	2145	08^{0}55.836’N	038^{o}45.424’E	LAR before the Kaliti bridge and after mixing with Batu Tannery
S24	2147	08° 55.571'N	38° 45.237'E	LAR after mixing the effluent of leather and DESCO factory
S25	2126	08^{0}55.073’N	038^{o}44.976’E	LAR at Kaliti after mixing with Wastewater Treatment Plant
S26	2062	08° 52.771'N	38° 44.932'E	LAR before entering to Aba Samuel reservoir: Yetu Kebele

3.3. Sample analysis

Inductively coupled plasma mass spectrometry/ICP-MS (ELAN DRC-e ICP Mass Spectrometer Axial Field Technology, PerkinElmer SCIEX, Concord, Ontario, Canada) in the Environmental Protection Agency laboratory in Dublin, Ireland was used. The instrument was conditioned for a minimum of 30 minutes and optimized by running the daily performance check solution. The daily performance was checked based on the recommended optimization values of Mg > 50,000 counts per second (cps), In > 250,000 cps, U > 200,000 cps, CeO/Ce < 3%, Ba^{++}/Ba < 3% and autolens 0.5% < slope < 2%. On verifying configuration of the various operating parameters such as the nebulizer flow rate, the position of the torch and RF power and the interference corrections, analysis of samples was preceded. The analysis of sequence was: blank, working standard solution, blank, certified calibration blank, samples of the interest and at the end of the sequence the standard. The selected trace elements in river water samples were quantified using a calibration curve. Three independent replicates of each sample were measured and the concentrations were determined as average of replicates. For ICP-MS measurements, 5 mL of sample was pipetted into a 10 mL polyethylene tube. Then the volume was adjusted to 10 mL with 0.5% HNO_3. Where sample dilutions were necessary, they were performed by pipetting the required volume of sample into a sample tube and pipetting the required volume of 0.5% HNO_3 i.e. a 5x dilution is made by combining 1 ml sample and 4 ml 0.5% HNO_3 in a 10 ml sample tube, capping and inverting several times in order to avoid signals that were too high for the detector to measure adequately.

3.4. Analytical performances

Sensitivity, limit of quantification, precision, linear dynamic range and interference corrections were established for each individual target analyte. Hence, the certified reference material has been used to observe accuracy. Analytical performance as accuracy was considerable high since the concentrations of all the element analyzed fell within in the range of given certified value. The careful choice of internal standard in ICP-MS is used to compensate for signal drift, to correct for instrumental instability and non-spectral interferences. Since the analyte elements are spread over a wide range of atomic masses, to obtain optimal accuracy and precision results, the internal standard should closely match the analyte in terms of mass number and ionization potential of the analyte element. For this reason, in this study, multi-element internal standard, containing Ge for As, B, Cr, Co, Cu, Fe, Mn, Ni, V and Zn; Rh for Sb, Cd and Sr, Re for Ba and Pb and Ir for Hg were used. When the element of interest had more than one isotope, careful selection of the isotopes of the given element is critical. The masses of at least two were monitored and the isotope with less interference and higher abundance was selected. And thus, ^{10}B, ^{51}V, ^{52}Cr, ^{54}Fe, ^{55}Mn, ^{58}Ni, ^{59}Co, ^{65}Cu, ^{66}Zn, ^{75}As, ^{87}Sr, ^{114}Cd, ^{121}Sb, ^{137}Ba, ^{202}Hg and ^{208}Pb isotopes were used for this analysis. Before conducting sample analysis, different concentrations of standards were analyzed and a linear curve was prepared. The linear calibration curve was acceptable for all reported elements correlation coefficient $R^2 > 0.999$ and where blank results were < limit of quantification in each case. For metals whose calibration extend above 2 million cps, the linearity between the pulse and analog measurements should be verified visually that is data from the highest pulse measurement should lie on the same calibration line as the point from the highest analog measurement. The lower limits of quantification/LOQ were established for all isotope masses utilized for each type of matrix analyzed, and values were given in Table 2.

Table 2: Lower limits of quantification ($\mu g\ L^{-1}$) of the procedure

Element	Sb	As	Ba	B	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Sr	V	Zn	Hg
LOQ	1	1	1	10	0.02	1	1	1	10	1	0.25	1	10	1	1	0.05

4. Results and Discussion

4.1. Trace element concentrations in water samples of the river

The mean concentrations of As, Pb, Hg, Sb, Cr, Zn, Co, Ni, Cu, Mn, Ba, B, Fe, V, Cd and Sr in the river water samples along with permissible limits are given in Table 3. Some descriptive statistics are given in Table 4. The element concentrations in descending order were Mn > Fe > B > Sr > Ba > Cr > Sb > Zn > Ni > Cu > V > Pb > Co > As > Cd > Hg. Wide variations in the concentration of potential toxic elements were obtained spatially along the course of the river. The variability from upstream to downstream of the river could be due to the direct solid and liquid waste discharge from industrial, municipal and domestic activities, natural geologic deposits and wastes from agricultural practices which contribute significantly to the potential toxic elements load of the river. Most of elemental concentrations were decreased in the downstream sampling sites. These could be due to the river water being diverted for irrigation purposes at different locations and inputs of cleaner water from some of the tributaries are relatively unpolluted; and thus play a dilution role. Similar trends of results have been observed in this river previously studied by Melaku *et al* (2004). Figure 2, 3, 4 and 5 show elevated concentrations of metals at some particular sampling points due to the potential sources.

Table 3: Dissolved trace element average concentrations, µg L^{-1}, in the Little Akaki River and its tributaries

	Concentration of element (µg L^{-1})															
Site	**Sb**	**As**	**Ba**	**B**	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Sr**	**V**	**Zn**
S1	**45**	<1.0	58	<10	0.04	4.2	1.8	7.1	**3050**	1.7	**73**	<0.05	14	**92**	8.8	48.5
S2	**66.5**	<1.0	55.5	11	0.06	2.4	<1.0	5.75	**974**	1.6	38	<0.05	3.1	**98.5**	3.2	13
S3	**35.5**	1.9	115	25	0.08	3.2	3.25	6.65	**2900**	5.25	**1850**	<0.05	9	**150**	8.95	40.5
S4	**42.5**	1.1	98.5	18	0.07	3.1	1.4	4.55	**1375**	1.8	**1150**	<0.05	4.35	**135**	6.1	34
S5	**50**	3.05	215	**6135**	0.06	**360**	2.75	7.7	**1300**	**8.6**	**3950**	<0.05	12.3	**565**	10.9	48.5
S6	**28.5**	1.3	125	**1000**	0.06	**255**	2.05	3.3	**905**	1.4	**2000**	<0.05	4.9	**315**	5.95	21
S7	**34.5**	<1.0	130	**402**	0.03	**117**	2.8	3.65	**665**	1.7	**1800**	<0.05	3.95	**290**	2.45	10.2
S8	**40**	1.85	135	62	0.12	26.2	8.85	11.55	**4800**	**11.35**	**2450**	<0.05	13.35	**390**	6.45	77.5
S9	**47.5**	1.8	120	196	0.10	**70.5**	5.4	8.55	**2500**	7.3	**2600**	<0.05	9.6	**335**	4.6	34.5
S10	**49.5**	1.05	165	22.5	0.03	1.5	1.8	3.9	**580**	1.3	**2300**	<0.05	3.6	**265**	1.5	12
S11	**65**	1.15	155	**415**	0.06	**57.5**	2	5.15	**525**	1.65	**1850**	<0.05	4.6	**330**	3.15	14
S12	**66**	1.15	175	275	0.05	**66.5**	3.7	5.15	**470**	1.55	**2550**	<0.05	5.15	**345**	3.25	9.75
S13	**53.5**	1.15	150	225	0.04	11.4	2.75	4.2	**530**	1.15	**1150**	<0.05	4.15	**350**	3.9	8.35
S14	**45**	1.1	102.5	53.5	0.06	2.35	2.65	5.55	**945**	5.05	**1150**	<0.05	5.15	**395**	3.4	21.5
S15	**31**	1.2	130	148	0.04	3.85	2.1	6.55	**565**	4.1	**1300**	<0.05	3.9	**350**	3	10.9
S16	**9.45**	2.85	280	66.5	0.03	29.5	3.8	2.1	**465**	1.15	**2350**	<0.05	12	**400**	7.15	12
S17	**24.5**	1.35	170	145	0.04	5.25	1.2`	3.5	**510**	1.35	**1650**	<0.05	2.85	**465**	2.9	8.7
S18	**45.5**	1.5	61.5	39.5	0.05	1.25	<1.0	4.2	175	1.5	**520**	<0.05	3.15	**300**	8.75	12.5
S19	**49**	1.4	110	76	0.08	5.45	1.95	5.65	**475**	2.05	**995**	<0.05	6.3	**345**	4.95	19.5
S20	**41**	2.85	115	55	0.05	2.25	1.7	6.7	290	2.15	**1085**	<0.05	9.05	**515**	3.85	22.5
S21	**27.5**	1.55	115.5	85	0.05	6.55	1.7	5.65	**840**	5.05	**1080**	<0.05	5.85	**430**	5	27
S22	**34.8**	1.3	135	95.5	0.05	10.05	2.6	5.15	**880**	2.55	**1300**	<0.05	7.2	**340**	4.35	30
S23	**48.5**	1.35	130	90	0.04	**83.5**	2.4	5.7	**580**	1.65	**1350**	<0.05	7.5	**385**	3.65	46.5
S24	**55**	1.1	125	104	0.05	**485**	2.55	5.45	**625**	2.25	**1150**	<0.05	5.3	**425**	3.25	32
S25	**47.5**	1.4	120	94.5	0.06	**83.5**	2.4	6.05	**495**	1.85	**950**	<0.05	6.25	**380**	3.25	25.5
S26	**30**	1.9	145	115	0.06	46	2.15	6.35	**555**	4.3	**1400**	<0.05	6.5	**365**	3.9	22.5
ES[a]	**5**	**10**	**700**	**300**	**3**	**50**	**-**	**2000**	**300**	**10**	**500**	**1**	**-**	**-**	**-**	**5000**
EU[b]	**5**	**10**	**-**	**1000**	**5**	**50**	**-**	**2000**	**-**	**10**	**50**	**0.1**	**20**	**-**	**-**	**-**
WHO[c]	**5**	**10**	**700**	**300**	**3**	**50[fg]**	**-**	**2000**	**-**	**10**	**400[h]**	**0.6[i]**	**70**	**10**	**-**	**-**
AA-EQS[d]	**-**	**25**	**-**	**-**	**≤0.08-0.25[j]**	***3.4[k]***	**-**	***5 or 30[l]***	**-**	**7.2**	**-**	**0.05**	**20**	**-**	**-**	***8, 50 or 100[m]***
FAO[e]	**-**	**100**	**-**	**-**	**10**	**100**	**50**	**200**	**5000**	**5000**	**200**	**-**	**200**	**20**	**100**	**2000**

Notes: Exceedances values are in bold

[a] Ethiopian Standards (ES) for drinking water (2001)

[b] European Union Directives for drinking water guidelines (1998)

[c] World Health Organization (WHO) for drinking water guidelines (2011)

[d] Annual Average (AA) thresholds for surface waters set in SI 272 of 2009 Environmental Quality Standards(EQS) (2009)

[e] Food and Agricultural Organization (FAO) for irrigation water (Ayers and Westcot, 1994)

[f] Provisional guideline value, as there is evidence of hazard, but the available information on health effect is limited.

[g] Total Cr.

[h] Concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odor of the water, leading to consumer complaints

[i] Inorganic Hg.

[j] EQS values vary dependent upon the hardness of the water as specified in five class categories –(Class 1 - ≤0.08 µg/L: < 40 mg CaCO3/1, Class 2 – 0.08 µg/L: 40 to < 50 mg CaCO3/1, Class 3 – 0.09 µg/L: 50 to <100 mg CaCO3/1, Class 4 – 0.15 µg/L: 100 to <200 mg CaCO3/1 and Class 5 - 0.25 µg/L: 200 mg CaCO3/1).

[k] Standard is for chromium V1 Where the result for total chromium is less than the EQS for Cr VI, no further investigation is deemed necessary. Where the total Chromium level is above the EQS, an assessment should be made of the potential discharges of Cr VI into the water body.

[l] The value 5 applies where the water hardness measured in mg/l CaCO3 is less than or equal to 100; the value 30 applies where the water hardness exceeds 100 mg/l CaCO3.

[m] In the case of Zinc, the standard shall be 8 µg/l for water hardness with annual average values less than or equal to 10 mg/l CaCO3, 50 µg/l for water hardness greater than 10 mg/l CaCO3 and less than or equal to 100 mg/l CaCO3 and 100 µg/l elsewhere.

Table 4: Summary statistics for the analyzed elements across all sites (µg L^{-1}).

Metal/metalloid	Mean	Median	Standard deviation	Skewness	Kurtosis	Minimum	Maximum	Range
Sb	42.80	45.00	13.37	-0.25	0.41	9.45	66.50	57.05
As	1.46	1.325	0.66	1.04	1.15	0.50	3.05	2.55
Ba	132.17	127.50	46.58	1.15	3.35	55.5	280	224.50
B	383.04	92.25	1190.78	4.87	24.31	0.50	6135	6134.5
Cd	0.06	0.05	0.02	1.50	2.81	0.03	0.12	0.09
Cr	67.04	10.73	119.57	2.57	6.40	1.25	485	483.75
Co	2.62	2.28	1.69	2.20	7.54	0.50	8.85	8.85
Cu	5.61	5.6	1.89	1.08	2.94	2.10	11.55	9.45
Fe	1075.92	602.5	1069.54	2.30	5.35	175	4800	4625
Pb	3.13	1.83	2.60	1.86	3.20	1.15	11.35	10.20
Mn	1540.04	1325	843.53	0.70	1.50	38.00	3950	3912
Ni	6.66	5.58	3.29	1.0	-0.03	2.85	14.00	11.15
Sr	336.75	347.5	115.58	-0.60	0.56	92.00	565	473
V	4.87	3.9	2.36	1.09	0.45	1.50	10.90	9.40
Zn	25.50	22.0	16.53	1.42	2.46	8.35	77.50	69.15

Chromium (Cr) in water occurs in the trivalent and/or hexavalent state and is potentially quite toxic to aquatic animals and plants in the dissolved form (Water UK, 2001). The 'hexavalent' form is generally more toxic than the metallic or 'trivalent' form because of its high rate of adsorption through intestinal tracts. Epidemiological studies have shown that prolonged contact with some Cr components results in dermatitis, swallowing problems and carcinogenic effects. Very large amounts of Cr can cause vomiting, diarrhoea and kidney failure (Abdul *et al.,* 2012, Water UK, 2001). Cr is used by stainless, electroplating, paints and inks, wood preservatives, textiles, refractories, metal plating and leather tanning industries. Total Cr concentrations in the analyzed water samples ranged from 1.25-485 µg L^{-1}, with a mean of 67.04 µg L^{-1} (Table 3). The Cr concentrations at sites S5, S6, S7, S9, S11, S12, S23, S24 and S25 do not fulfill drinking water quality criteria set by WHO (2011), EU (1998) and Ethiopian Standard (2001). Water samples from S5, S6, S7 and S24 were also not appropriate for use as irrigation water (FOA, 1994). If the SI 272 of 2009 annual average value for Cr were applied all but one site would be considered impacted. The reason for the elevated concentrations at S1, outside of the city, is not obvious. The other exceedances relate to industrial discharges such as Addis Ababa Tannery and Batu Tannery (Figure 3). The average concentration of Cr in this study was higher when compare with the previously reported average value of 22.14 µg L^{-1} by Melaku *et al* (2004).

Lead (Pb) is the most significant toxin of the heavy metals. The main sources of lead contamination of the aquatic environment are the industrial discharges from smelters, paints and ceramics, through vehicular emissions, runoff from contaminated land areas, atmospheric fallout and sewage effluents. In some cases, lead is used to stabilize land pipes/plastic pipes and results in lead contamination of river water (WHO, 1995). The concentration of lead in the study area varied from 1.15-11.35 µg L^{-1}, with a mean of 3.13 µg L^{-1} (Table 3). The acceptable limit of lead reported by WHO, EU and Ethiopian standard in drinking water is 10 µg L^{-1}. The values obtained in all the analyzed samples were below this limit except at site S8. Concentrations at site S5, S8 and S9 exceeded the average thresholds for surface waters set in SI 272 2009. This could be due to poor environmental control, increasing industrialization and population of the city. However, the obtained values were less than the international guideline values for irrigation water of 5000 µg L^{-1} (FAO, 1994). The mean Pb concentrations obtained in this work was also much higher than previously reported of 0.96 µg L^{-1} by Melaku *et al* (2004).

Mercury (Hg) is present in the inorganic form in surface and groundwater (WHO, 2011). The recommended guideline values for Hg are 0.1, 0. 6 and 1 µg L^{-1} for drinking water as given by the EU, WHO and Ethiopian standards, respectively. Hg concentrations in all the river water samples were below the detection limit and thus not of concern. Copper (Cu) is an essential nutrient and is present in water in ionic form or in complex organomineral. At low concentrations Cu ions cause headache, nausea, vomiting and diarrhea and at high concentrations it causes coronary heart diseases, chronic anemia, gastrointestinal disorder and also leads to liver, high blood pressures and kidney malfunctioning (USEPA, 1999). The concentration of Cu in the analyzed water samples ranged from 2.1-11.55 µg L^{-1} and the mean value was 5.61 µg L^{-1}. The desirable limit of Cu in drinking water is 2000 µg L^{-1} by EU, WHO and Ethiopian Standards. As shown in the Table 3 all the samples had lower Cu levels compared to the safe limit for drinking and irrigation water. However, when compared of the thresholds given in SI in 272 of 2009 all sampling points except S4, S6, S7, S10, S13 and S16 exceeded the permissible value of 5 µg L^{-1} which applies where the water hardness measured in mg L^{-1} $CaCO_3$ is less than or equal to 100. High level of copper may be due to presence of industrial, municipal and domestic wastes.

Cobalt (Co) enters water bodies from effluents discharged from industries dealing with corrosion and wear-resistant alloys. The other sources of Co contamination are pigments used to color glass and ceramic objects, lithium-cobalt batteries and permanent magnets. In the analyzed water samples it was found in the range of 0.5- 8.85 μg L^{-1} with a mean value of 2.62 μg L^{-1}. No guideline value for Co in drinking water is given in the WHO, EU and Ethiopian standards. This is probably because Co is not a health concern at concentrations normally observed in drinking water. The mean concentration of Co in this study was higher when compared with the previously reported mean value of 1.82 μg L^{-1} by Melaku *et al* (2004). Despite this the concentrations were less than the international guideline values for irrigation water of 50 μg L^{-1} (FAO, 1994). Zinc (Zn) is an essential trace element found in aquatic environments in the form of salts or organic complexes. There are several sources of elevated Zn found the water bodies including industrial discharges, sewage effluents, domestic wastes, municipal wastes, mining, as well as natural chemical weathering of geological materials (Boxall *et al*., 2000). The values of zinc obtained in this study were in the range of 8.35-77.5 μg L^{-1} with a mean of 25.50 μg L^{-1} (Table 3). No health-based guideline values have been proposed for Zn in drinking water by the WHO but Ethiopian Standards have a value of 5000 μg L^{-1} for drinking water. All the values obtained were below this limit. The values were also less than the international guideline values for irrigation water of 2000 μg L^{-1} (FOA, 1994). However, all were exceeded the 8 μg L^{-1} annual average threshold in SI 272 of 2009 for water with hardness values less than or equal to 10 mg L^{-1} $CaCO_3$. Site S8 exceeded 50 μg L^{-1}. Acute and long-term exposure of Zn may lead many health disorders such as fever, vomiting, stomach cramps, diarrhoea and carcinogenic (WHO, 2003).

Nickel (Ni) contamination can arise from various industrial activities, domestic wastes, municipal sewage, multicolored paints, electroplating, coal and oil combustion, household appliances, pigments and batteries. In the present case, the concentration of Ni in water samples lay between 2.85-14 μg L^{-1}, with an average of 6.66 μg L^{-1} (Table 3), all of the samples falling below the permissible limit of drinking water stipulated by EU and WHO guidelines. There are no limits set in Ethiopia. The obtained values were also much less than the international guideline values for irrigation water, 200 μg L^{-1} (FOA, 1994). The mean concentration of Ni in this study was higher than previously reported mean value of 4.63 μg L^{-1} by Melaku *et al* (2004). Boron (B) does not exist in elemental form but is combined with oxygen as borate minerals and various boron compounds such as boric acid, borax and boron oxide. Boron compounds have been used in mild antiseptics, glass manufacture, cosmetics, pharmaceuticals, boron neutron capture therapy, pesticides and agricultural fertilizers (WHO, 1998). In the water samples the concentration of boron was in the range of 0.5-6135 μg L^{-1} with a mean of 383.04 μg L^{-1}. The permissible limit is specified as 300 ppb by WHO and the Ethiopian standard for drinking water, whereas in the analyzed samples S5, S6, S7 and S11 showed much higher concentration than these guideline values. Concentrations in water from sites S5 and S6 exceeded the standard set by EU directives (1998). This could be due to the discharge of industrial, domestic and municipal wastes in these sampling areas. The toxicity of boron is manifested by generalized or alternating focal seizure disorders, irritability and gastrointestinal disturbances. The most frequently occurring symptoms are vomiting, headache, fever abdominal pain, diarrhoea, nausea, lethargy and muscle cramps. Boron can also infect the stomach, liver, kidneys and brains, and can eventually lead to death (WHO, 1998). The levels of arsenic (As) in the analyzed water samples were in the range 0.5–3.05 μg $L^{-1}$with a mean of 1.46 μg L^{-1}; all were within the acceptable limit specified of 10 μg L^{-1} for drinking water, 25 μg L^{-1} for surface water and 100 μg L^{-1} for irrigation water.

The samples analyzed contained Iron (Fe) in the range of 175-4800 μg L^{-1} with the mean of 1075.92 μg L^{-1}. Fe content in all the water samples (except site S18) exceeded the permissible limit stipulated by the Ethiopian Standards for drinking water. The high Fe concentrations in this river water may be due to iron ore tailing from the metal workshops and discharge of iron loaded industrial wastes. However, the river water is appropriate for irrigating crops as all values were below the 5000 μg L^{-1} threshold (FOA, 1994). High level of Fe results in heamochromatosis, brain haemorrhage, anxiety, tension, cardiac arrest, abdominal pain, fatique, joint pains, loss of body hair and metabolic disorder (Bacon, 2007). The concentration of manganese (Mn) in the analyzed samples ranged from 38 to 3950 μg L^{-1} with the mean of 1540 μg L^{-1}. Manganese content in all the water samples except from sites S1 and S2 exceeded the permissible limit stipulated by WHO, EU and the Ethiopian standards for drinking water and the annual average thresholds for surface waters set in SI 272 of 2009. The lower concentrations at S1 and S2 are probably due to its location outside of the city where it is free from any anthropogenic discharges. Water samples from sites within the city are unfit for irrigation purposes (FOA, 1994). Furthermore, the average results obtained in this study are higher than the previously reported average value of 902.85 μg L^{-1} by Melaku *et al* (2004) in Little Akaki River. This observation may be linked to industrial activity including distilleries, a battery factory, municipal and domestic waste, hospitals, and which discharge treated and untreated waste water into the various drains feeding into the river (Melaku *et al*., 2004). Health effects of high uptake of Mn include liver and pancreatic malfunctioning, muscle weakness, kidney failure, sensory problems and inadequate testesteron levels (Lakshmi *et al*., 2012). The concentrations of vanadium (V) in the analyzed water samples were in the range of 1.5-10.9 μg L^{-1} with the mean of 4.87 μg L^{-1}. The obtained values are less than the international guidelines value for irrigation water of 100 μg L^{-1} (FOA, 1994). In low levels, V causes irritation the upper respiratory tract, however, high concentrations can result in bronchitis, lung cancer and pneumonitis.

Antimony (Sb) and its compounds can be used in fire-retardant formulations for plastics, rubbers, textiles, paper and paints, explosives, pigments, antimony salts, ruby glass, lead storage batteries, solder, sheet and pipe metal, bearings, castings and pewter (Sundar and Chakrayaty, 2010). The concentration of antimony in the analyzed water samples ranged from 9.45 to 66.5 µg L^{-1} with the mean of 42.80 µg L^{-1}, all exceeded the WHO, EU and Ethiopian Standards thresholds of 5 µg L^{-1}, the maximum permissible limits for Sb in drinking water. No international guideline values are set for Sb in irrigation water; this is probably due to the assumption that the concentrations in irrigation water are generally negligible. The health effects from exposure to antimony and it compounds in humans include alterations in pulmonary function, chronic bronchitis, cardiovascular, gastrointestinal, dermal, reproductive, carcinogenicity and genotoxicity (Sundar and Chakrayaty, 2010, WHO, 2003). Effluents from industries such as battery production, dye and manufacture of pigments and alloys making are the major sources of elevated cadmium (Cd) in the water bodies (Rao and Yoshida, 2004). In this study Cd concentration varied between 0.03 and 0.12 µg L^{-1} and mean value was 0.06 µg L^{-1}, which is much less than the recommended upper limit for Cd in drinking water of 3 µg L^{-1} set by the WHO and the Ethiopian Standards. Furthermore, the values for Cd did also not exceed the international guideline for irrigation water of 10 µg L^{-1} (FAO, 1994) but the values were higher when compare with previously reported average value of 0.048 µg L^{-1} by Melaku *et al* (2004). Cd is a poisonous metal and can cause serious health problems even if ingested in small amounts. It has the tendency to accumulate in body tissues causing lung problems, kidney lesions, neurological disorders and skeletal damage (Abdul et al. 2012; Makino, 2012; Jarup, 2003).

Naturally-occurring strontium (Sr) is released into fresh water from geologic weathering associated with sedimentary rocks. Sr compounds are used in making ceramics and glass products, pyrotechnics, paint pigments, fluorescent lights, medicines and a range of other products (Alfredo *et al.,* 2014). The concentration of Sr in the analyzed water samples ranged from 92 to 565 µg L^{-1} with the mean of 336.75 µg L^{-1}. The permissible limit is specified as 10 µg L^{-1} for drinking water by WHO (2011) and 20 µg L^{-1} for surface water. The values obtained in all cases were much higher than these guideline values. Concentrations increased from upstream to downstream stations (Figure 3). The elevated Sr in this river could be industrial activities and domestic waste water. Barium (Ba) levels in analyzed samples were in the range of 55.5-280 µg L^{-1} and the mean was 132.17 µg L^{-1} which lower than the WHO and Ethiopian Standards limit of 700 µg L^{-1}. There are no guideline values for Ba in drinking and irrigation water set by EU (1998) and FOA (1994).

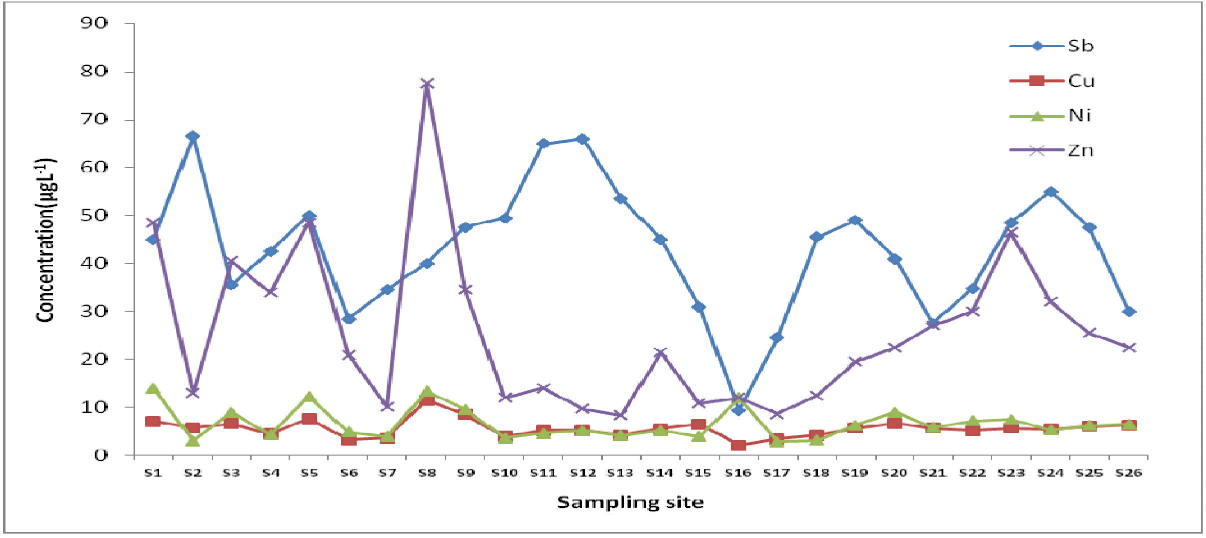

Figure 2: Sb, Cu, Ni and Zn concentration at different locations along the river

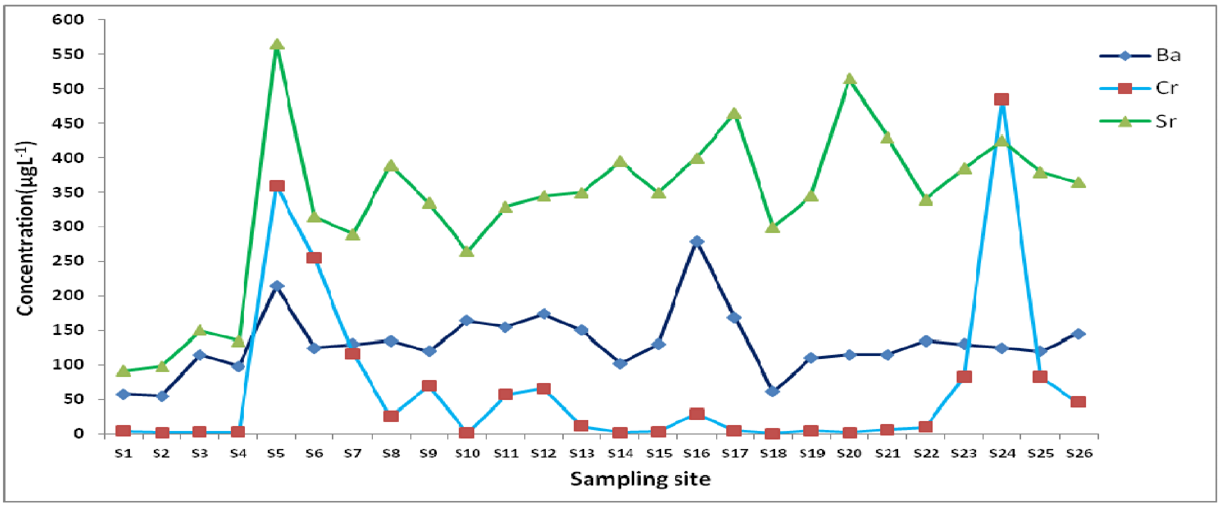

Figure 3: Ba, Cr and Sr concentration at different locations along the river

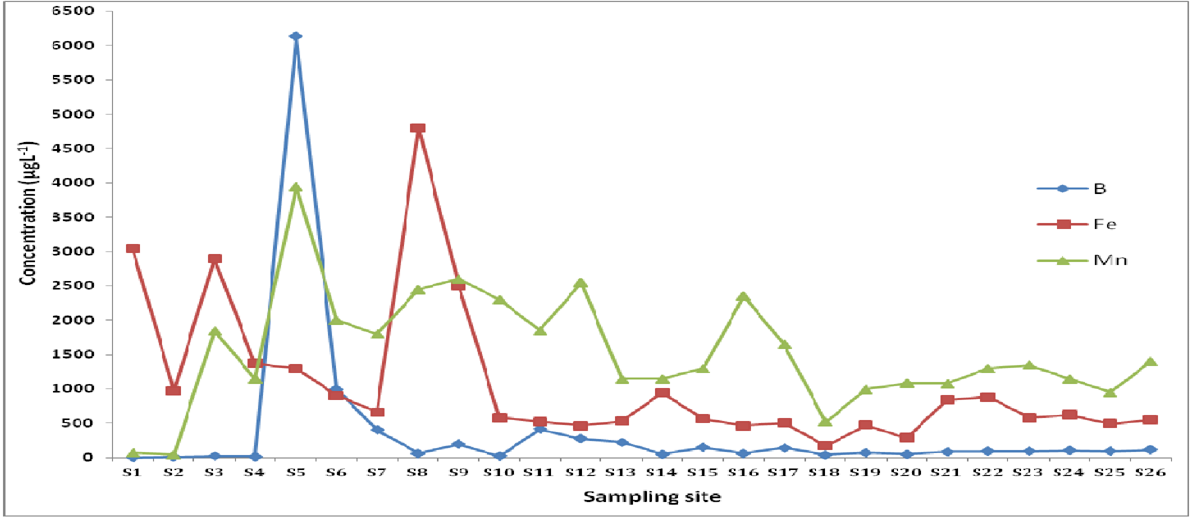

Figure 4: B, Fe and Mn concentration at different locations along the river

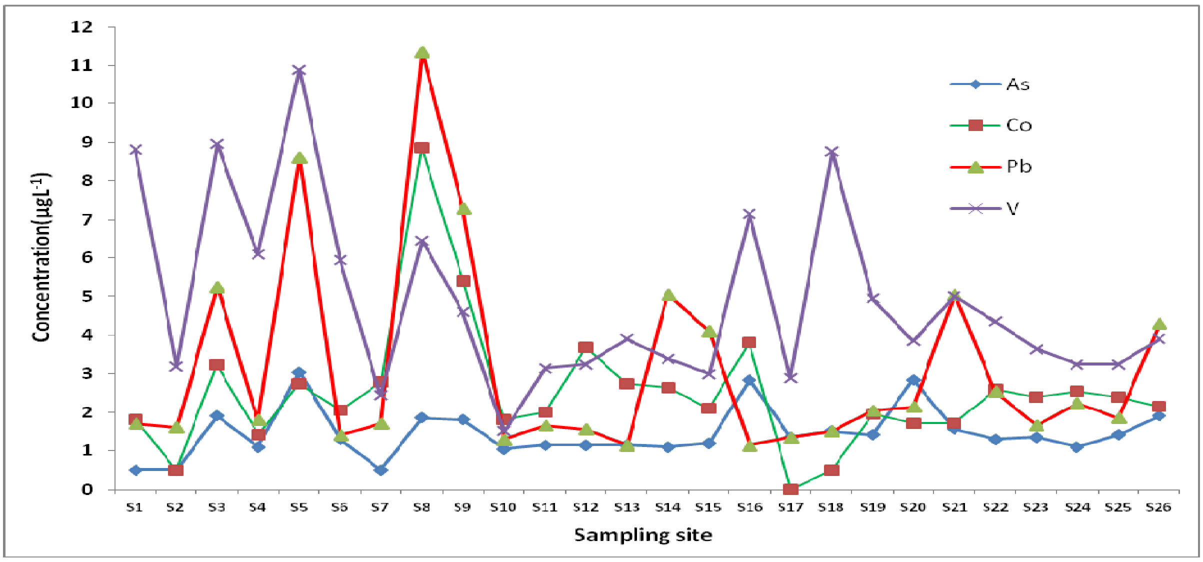

Figure 5: As, Co, Pb and V concentration at different locations along the river

4.2. Correlation analysis

Sb and Sr showed moderately negative skewness values indicating bulk of the values on the higher right side of the frequency distribution curve. Mn, As, Ba, Cu, Ni and V showed positive moderately skewed values as depicted in the Table 5. This points to a common relationship between these elements as they approach normal distribution with their lower skewness. Higher positive skewness values were observed for B, Cd, Cr, Co, Fe, Pb and Zn which indicated bulk of the value on the lower left side of the distribution curve. Thus, Mn-As-Sb-Sr-Ba-Cu-Ni-V and Pb-Cd-Cr-Co-B-Fe-Zn formed two groups based on their frequency distribution curves. Similar trends can be observed in the Kurtosis values. To further explore possible common sources of the trace metals in river water, Pearson correlation coefficients were calculated and summarized in the Table 6. A correlation coefficient (r) value of more than 0.7 indicates high level of significance at p=0.05; between 0.5 and 0.7 is moderately significant at P=0.05 level and less than 0.5 is insignificant. Correlation analysis showed strong correlation between Cu-Pb (r=0.83), Cu-Zn (r= 0.77), Zn-Fe (r=0.81), Cu-Cd (r=0.72), Cd-Fe (r=0.72), Cd-Pb (r=0.72), Pb-Zn (r=70), Cu-Fe (r=0.74), Co-Fe (r=0.70), Co-Pb (r=0.70), Ni-Zn (r=0.74) and Fe-Pb (r=0.70) at significant level P<0.05 forming a group of Cu-Pb-Zn-Fe-Cd-Co-Ni. This suggests that these metals have common contamination sources as oxides and hydroxides (Mrazovac and Mirjana, 2011). Also significant but relatively moderate correlations, significant at P<0.05 were found between Cd-Co (r=0.64), Co-Zn (r=0.60), Cd-Zn (r=0.60), Co–Ni (r=0.60), Co-Cu (r=0.63), Fe-Ni (r=0.66), Pb-Ni (r=0.55), Pb-Mn (r=0.50), Ni-V (r=0.63), B-Mn (r=0.62), As-Mn (r=0.55), As-Ni (r=0.54), Cu-Ni (r=0.58), As-Sr (r= 0.62), Ba-Sr (r=0.54), As-Ba (r=0.57), Co-Ni (r=0.60) and Co-Mn (r=0.52), suggesting that the sources of these metals is to some extent linked. Ba was significantly positively correlated with Mn (r= 0.74) at p<0.05. A considerable number of significant correlations, significant at P<0.05 are also observed between As-Ba (r=0.57), As-Mn (r=0.55), As-Ni (r=0.54), V-Zn (r=0.51) and Mn-Sr (r=0.47), B-Cr (r=0.56) and B-V (r=0.50). Also significant but relatively weak correlations, were found between B-Sr (r=0.41), Ar-B (r=0.47), As-B (r=0.47), As-V (r=0.46), As-Pb (r=0.42), Fe-V (r=0.45) and B-Pb (r=0.40). These findings may be related to the adsorption of the heavy metals by metal oxides or hydroxides (Mrazovac and Mirjana, 2011)

Table 5: Pearson's correlation coefficient between trace metal levels in Little Akaki river (n=26)

Metal	Sb	As	Ba	B	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Sr	V	Zn
Sb	1.00														
As	-0.37	1.00													
Ba	-0.34	0.57^{**}	1.00												
B	0.10	0.47^{*}	0.38	1.00											
Cd	0.16	0.18	-0.22	0.05	1.00										
Cr	0.15	0.14	0.22	0.56^{**}	-0.04	1.00									
Co	-0.04	0.28	0.27	0.03	0.64^{**}	0.08	1.00								
Cu	0.23	0.21	-0.25	0.17	0.72^{**}	0.02	0.63^{**}	1.00							
Fe	-0.03	0.04	-0.19	0.02	0.72^{**}	-0.08	0.70^{**}	0.74^{**}	1.00						
Pb	-0.08	0.42^{*}	0.07	0.40^{*}	0.72^{**}	0.13	0.70^{**}	0.83^{**}	0.70^{**}	1.00					
Mn	-0.10	0.55^{**}	0.74^{**}	0.62^{**}	0.24	0.37	0.52^{**}	0.16	0.18	0.50^{**}	1.00				
Ni	-0.21	0.54^{**}	0.24	0.31	0.35	0.09	0.60^{**}	0.58^{**}	0.66^{**}	0.55^{**}	0.33	1.00			
Sr	-0.21	0.62^{**}	0.54^{**}	0.41^{*}	-0.10	0.36	0.16	0.08	-0.30	0.28	0.47^{*}	0.12	1.00		
V	-0.20	0.46^{*}	0.02	0.50^{**}	0.29	0.14	0.15	0.25	0.45^{*}	0.37	0.20	0.63^{**}	-0.01	1.00	
Zn	0.01	0.24	-0.13	0.24	0.60^{**}	0.20	0.60^{**}	0.77^{**}	0.81^{**}	0.70^{**}	0.21	0.74^{**}	0.01	0.51^{**}	1.00

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

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

5. Conclusions

The water samples collected from 26 sampling sites in the Little Akaki River were analyzed for Cr, Sb, Zn, Ni , Mn, Fe, B, Sr, Ba, Cu, V, Pb, Co, As, Cd and Hg using ICP-MS. The order of the mean concentrations of potentially toxic elements were Mn > Fe > B > Sr > Ba > Cr > Sb > Zn > Ni > Cu > V > Pb > Co > As > Cd > Hg. The analyses was limited to two sets of samples because of financial constraints. The correlation analysis showed good to strong positive correlations among Pb, Cu, Zn, Fe, Cd, Co, Ni, V, B, Mn, Sr, As and Ba, suggesting that these metals have common sources. It was not possible with this set of analyses to attribute the contaminants to specific sources.

Guidelines were applied for assessment of contamination. The elemental concentrations of Cr, Sb, B, Pb, Sr, Fe and Mn were found to exceed the permissible limits of WHO, European Community and the Ethiopian Standards of drinking water at some sites. The concentrations of Cr, Mn and Sr were higher than the irrigation guideline at some sampling points. The river is further degraded in quality compared with the previous studies. This could be due to recent rapid urbanization and industrialization, poor waste management system in the city, the direct discharge of industrial, domestic and hospital wastes in to the river. The river is simply used as a receptacle of all kinds of wastes released in the city. Based on the above mentioned points, it is clear that the river water of some of the study area is contaminated by potential toxic elements and, therefore, using this water for drinking purpose, irrigation, water animals, recreational and washing is detrimental to human health and the environment. It is, thus, necessary to take serious and essential measures from the concerned bodies to control industrial effluents, the entry of the sewage, treat it before entering the river, manage the quality of the river water to enable it to be utilized for various purposes. Adoption of new and environmental-friendly technologies, such phytoremediation to remove or lower harmful metals load from the industrial waste water and upgrading of sewage treatment plants are suggested to avoid further deterioration of the river water quality. Further analysis of water samples is required to track the sources of the various contaminants. Finally, a biological monitoring programme should be initiated to provide a more integrated measure of the prevailing water quality.

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