

Full Length Research Paper

Heavy metals concentration in tannery effluents, associated surface water and soil at Ejersa Area of East Shoa, Ethiopia

Aklilu Asfaw

Abstract

Department of Natural Resource Management, School of Agriculture, Adama Science and Technology University, Adama, Ethiopia, P. O. Box 1888

E-mail: aklilplanet49@gmail.com or akhir@ethionet.et

Discharges from tanneries are the major causes of environmental contamination in Ethiopia. A field experiment was carried out during 2012/2013 to assess the contamination of surface water (effluent) and soil by heavy metals. Surface water and soil samples collected from tannery industry located near Ejersa area of East shoa, Ethiopia from six different sample areas in triplicates from the tannery outlet up to Koka lake by dividing in S₀ (control, out of effluent point), S₁ (near the out let, upstream), S₂ (0.75 km), S₃ (1.50 km), S₄ (2.25 km) and S₅ (3.0km at Koka lake, downstream). The control soil samples were collected from the farm land at the vicinity placed out of the effluent points. The water samples were collected in plastic containers from five different points in 0.75 km distances. Soil samples also collected from the proximate of the effluent samples collected at the depth of 0-10 cm and 10-20 cm. The physico-chemical analysis for metallic parameters was determined using Graphite furnace atomic absorption spectrometer and atomic absorption spectrophotometer. The determined parameters were like: pH, Electrical conductivity (EC), Biological Chemical Demand (BOD), Chemical Oxygen Demand (COD) and Total Dissolve Solids (TDS) and for heavy metals namely: Cd, Cr, Cu, Fe, Pb, and Zn. The concentrations of analyzed parameters shows decreasing from S₁-S₅ except TDS, Cu, Fe and Zn, that was recorded less than the maximum allowable limits. Fe and Zn recorded more than the maximum allowable limit in all sampling sites. The concentrations of Cr in sample S₁, S₂ and S₃ in both depths recorded more than the maximum allowable limit. In the analysis result the concentration of Fe in all samples also recorded higher than the maximum allowable limit (50,000 mg kg⁻¹). The concentration of Cd, Cu, Pb and Zn in all samples recorded under the maximum the guideline for total soil. Generally the concentrations all metals observed decreasing from sample S₁(near the effluent out let,) S₅ (near the Koka lake) in both depths of 0-10 cm and 10-20 cm. The control soil sample in both depths was recorded less than the maximum allowable limit. The pH of soil samples in both depths was relatively constant throughout the sampling sites.

keywords: Contamination, Ejersa, Ethiopia, Heavy metals, Soil, Surface water and Tannery.

INTRODUCTION

Ethiopia is located in the horn of Africa, and lies between 8°00N and 38°00E geographical coordinates. It has a total area of 1.14 million square kilometers (444,000 square miles). Out of the total area,

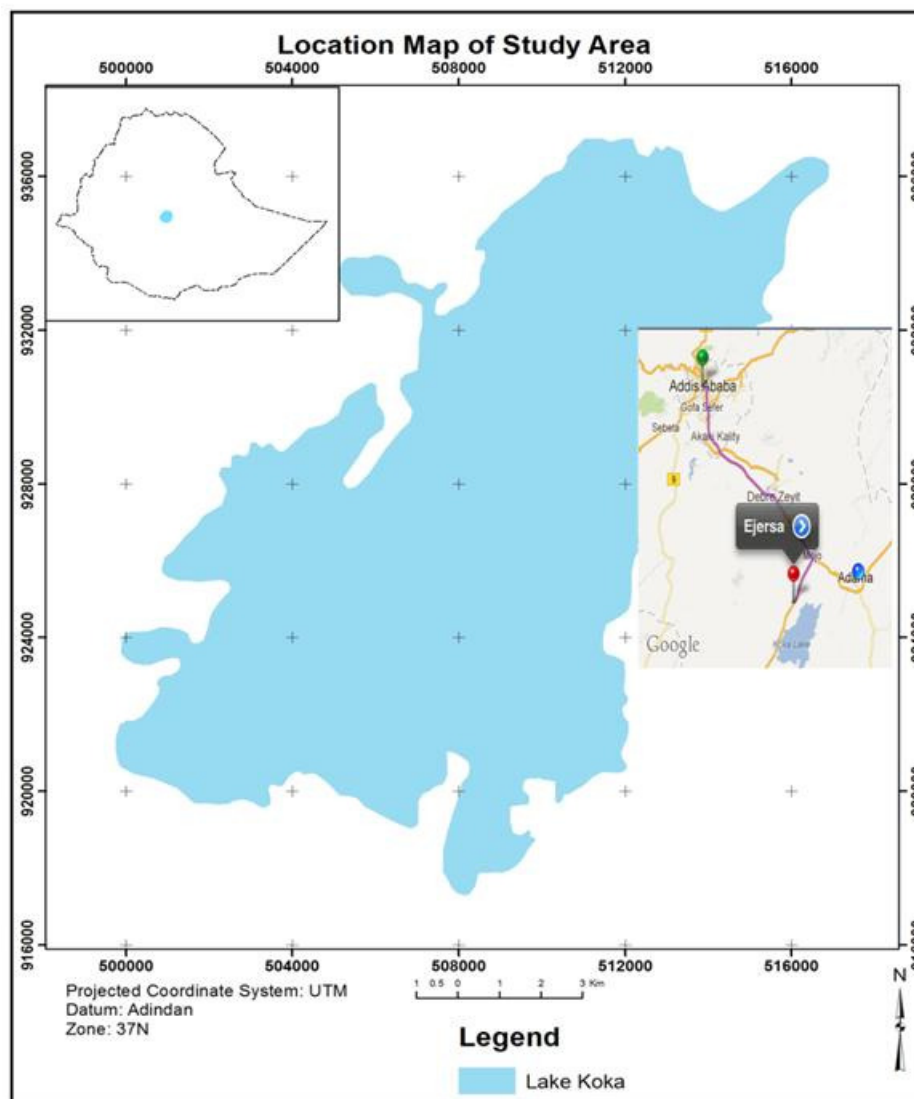


Figure 1. Location map of the study area.

about 65% of the land is arable, with 15% presently cultivated (http1). The population of Ethiopia is about 84,320,987, with a growth rate of 2.9% and a birth rate of 38.5/1000 population (2012 estimate) (http 2). Food processing, beverages, textiles, chemicals, metal processing, and tanneries are among the industries functioning in Ethiopia. Water shortage along with deforestation, overgrazing, soil erosion and desertification are the current environmental issues (Samuel Melaku, 2005).

The tannery industry in Ethiopia is among the country's largest external income earners. Consequently, during the past 20 years the industry has had significant government support and has multiplied throughout the country. With the ever increasing demand on irrigation water supply, farmlands are frequently faced with utilization of poor quality water. In many parts of Ethiopia,

wastewater (effluent), which is disposed to wells, ponds, streams and treatment plants, is used as a source of irrigation water as well as for drinking. Though, the continued application of poor quality irrigation water can reduce the yield of farmlands (Eskindir Zinabu, 2002).

Heavy metals are important for proper functioning of biological systems but their deficiency or excess could lead to a number of disorders (Ward, 1995). Industrial effluents which discharged from the textile and tannery contains a higher amount of metals especially chromium, copper and cadmium. These effluents released on the land as well as dumped in to the surface water which ultimately leaches to ground water and lead to contamination due to accumulation of toxic metallic components and resulted in a series of well documented problems in living beings because they cannot be completely degraded (Malarkodi et. al. 2007). All these

Table 1. Sampling areas for surface water (effluent) and soil collection

Sampling site	Latitude /Longitude	Coordinates		Elevation (m)	Location
		X	Y		
S ₀	N8°27.257' E39°04.331'	507945.64	934435.76	1687	Out of the effluent point
S ₁	N8°27.052' E39°04.126'	507569.62	934058.00	1630	At the effluent outlet (upstream)
S ₂	N8°26.79' E39°04.039'	507410.09	933575.27	1576	0.75 km from the outlet
S ₃	N8°26.475' E39°03.907'	507168.01	932994.87	1464	1.5 km from the outlet
S ₄	N8°26.164' E39°04.245'	507788.23	932421.99	1387	2.25 km from the outlet
S ₅	N8°26.016' E39°03.655'	508540.51	932149.45	1352	3.0 km from the outlet at Koka lake (downstream)

metals in effluents cause serious health hazards due to unsafe disposal on soil and into water. Hence, industrial effluents offer a wide scope of environmental problems and health hazards are becoming more complex and critical not only in developing countries but also in developed countries. In the present context of study, particular emphasis is placed on the status of metals in effluents of textile and tannery industries.

Surface waters, soils and vegetation, volcanic activity, forest fires and land run-off are among the most important natural sources of metals (Friberg et al., 1986). Natural weathering of rocks and leaching processes can be the source of trace elements through dissolving and reacting with materials, mobilization and distribution to the various environmental compartments (Fifield and Haines, 1995).

Most of the hazards coming to human and ecosystem are due to water pollution (Khurana and Pritpal, 2012). The untreated sewage, industrial effluents and agriculture wastes are often discharged into the water bodies. This contaminated water spread wide range of water borne diseases. The agricultural field around these water bodies is affected. Indiscriminate discharge of effluents (either from industrial, municipal and agricultural activities) containing toxic substances into aquatic environment, create problems of water pollution rendering water no longer fit for drinking, agriculture and aquatic life. Heavy metal accumulation in soils is of concern in agricultural production due to the adverse effects on food quality (safety and marketability), crop growth (due to phytotoxicity) (Msaky and Calvert, 1990; Fergusson, 1990). Metals such as lead, mercury, cadmium and copper are cumulative poisons. These

metals cause environmental hazards and are reported to be exceptionally toxic (Yargholi and Azimi, 2008).

MATERIALS AND METHODS

Location and climatic condition

The research was conducted and repeated over years during 2010/11, 2011/12 and 2012/13 at Ethiopia Tannery Share Company (ETSC), in Ejersa area which is located 85 km Southeast of Addis Ababa with a grid reference of 8°27.154' latitude and 39°03.894' longitude (Figure 1). This area is characterized by a semi-arid climate having an altitude of 1630 m a.s.l, an average annual rainfall of 800 mm and the minimum and maximum temperature of 17.5°C and 26°C, respectively. The area is part of the Southern Rift Valley of the country.

The target area selected for collection of effluent and soil samples is within three kilometer radius of effluent discharge site. As the koka lake is 3 kms far away from the outlet of tannery effluent, the effluent and soil sampling areas were selected following the effluent drainage canal.

Locations of sampling points were recorded using GPS (eTrex™), (Table 1).

Metals in surface water (effluent) samples

The study was conducted during 2012/13. Surface water (effluent) samples were collected plastic containers from five representative sampling points in 0.75 km interval

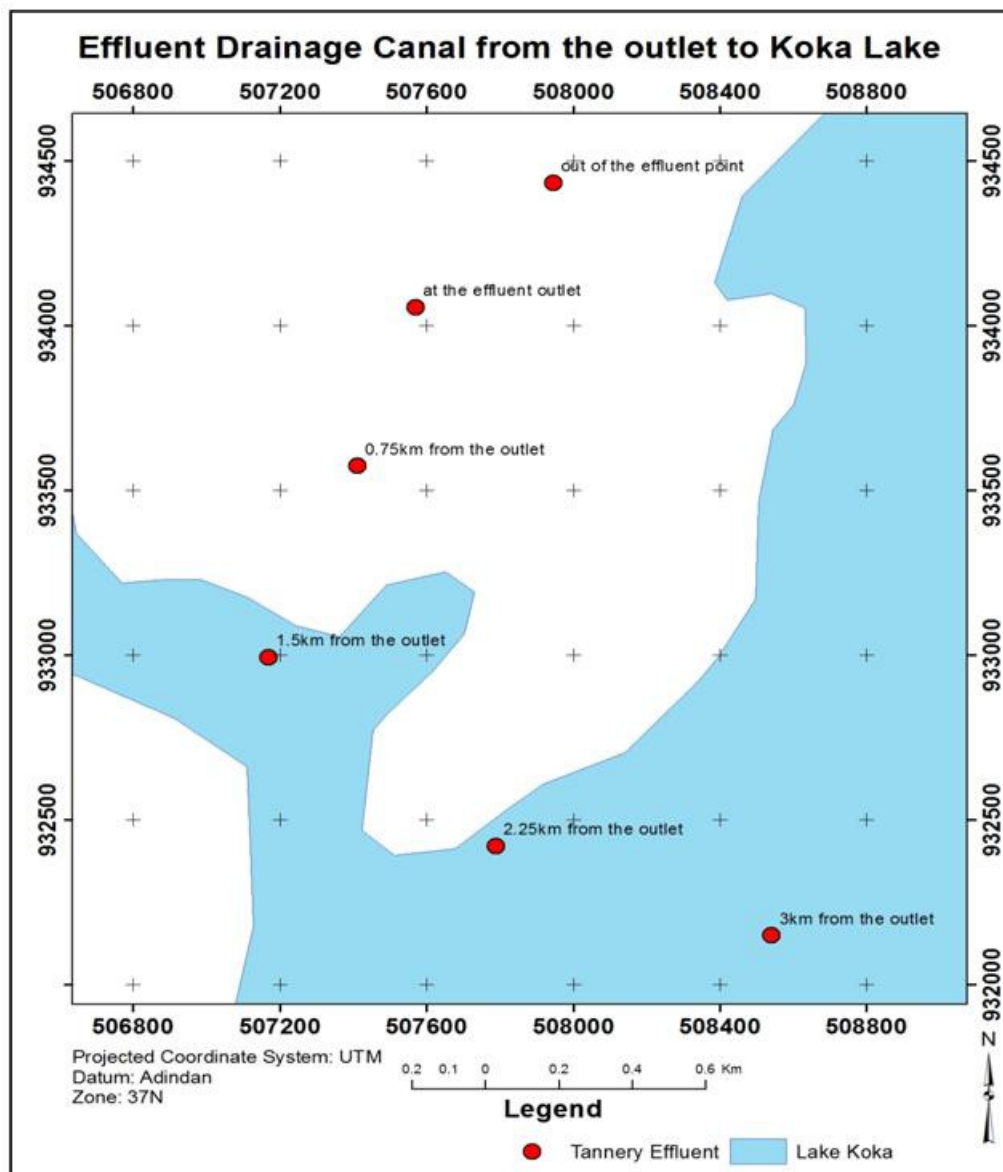


Figure 2. Map of sampling points

from the effluent outlet (up stream) to the lake (down stream), (Figure 2). The collected samples were transported to the laboratory for analysis.

Effluent samples (500 ml) were filtered using Whatman No 41[(0.45) μm pore size] filter paper for estimation of dissolved metal content samples (500 ml each) and were preserved with 2 ml nitric acid to prevent the precipitation of metals (Prabu, 2009). The samples were boiled slowly and then evaporated on a hot plate to the lowest possible volume (about 20 ml). The beakers were allowed to cool and another 5ml of concentrated HNO_3 was added. Heating was continued with the addition of concentrated HNO_3 as necessary until digestion was complete. The samples were evaporated again to dryness (but not baked) and the beakers were cooled, followed by the

addition of 5ml of HCl solution (1:1 v/v). The solutions were then warmed and 5ml of 5M NaOH was added, then filtered. The filtrates were transferred to 100 ml volumetric flasks and diluted to the mark with distilled water. These solutions were then used for the elemental analysis.

Samples were analyzed for physico-chemical properties and heavy metals concentrations, the physico-chemical parameters were analyzed by Graphite Furnas Atomic Absorption Spectrometer model AAnalyst 600 Perkin Elmer. Heavy metals were determined using Atomic Absorption Spectrophotometer as described by Gregg (1989). The determined parameters were Temperature, pH, EC, BOD, COD, TDS, Cd, Cr, Fe, Pb and Zn (APHA, 1998; Babushakila, 2009; Clesceri et al., 1998).

Table 2. Mean concentrations of heavy metals and other parameters in surface water (effluent) sample collected from the tannery outlet (upstream) up to the koka lake (downstream)

Sampling sites	parameters (mg/l)										
	P ^H	EC (μ s/cm)	COD	BOD	TDS	Cd	Cr	Cu	Fe	Pb	Zn
S ₀ (control)	6.2 ^{cb}	313.4 ^f	102.9 ^f	43.7 ^f	88.6 ^f	0.005 ^b	0.006 ^f	nd	0.003 ^f	0.008 ^f	nd
S ₁	6.4 ^{ab}	942.0 ^a	930.6 ^a	147.3 ^c	319.0 ^e	0.006 ^a	3.91 ^a	0.001 ^b	1.70 ^e	0.98 ^a	0.21 ^d
S ₂	6.2 ^{cb}	917.0 ^b	864.3 ^c	154.2 ^b	308.7 ^e	0.006 ^a	1.84 ^c	0.001 ^b	2.11 ^d	0.73 ^b	0.27 ^c
S ₃	6.5 ^a	903.0 ^c	821.2	148.6 ^c	316.4 ^d	0.005 ^{ab}	1.99 ^b	0.001 ^b	2.68 ^c	0.58 ^c	0.31 ^b
S ₄	6.23 ^{cb}	897.4 ^d	894.1 ^b	155.3 ^a	321.3 ^b	0.005 ^{ab}	1.39 ^d	0.013 ^a	2.82 ^b	0.34 ^d	0.35 ^a
S ₅	6.15 ^c	887.2 ^e	832.4 ^d	148.1 ^d	334.1 ^a	0.004 ^b	1.26 ^e	0.017 ^a	3.28 ^a	0.21 ^e	0.36 ^a
CV(%)	1.50	0.01	0.01	0.08	0.03	12.2	0.38	0.33	3.66	0.99	2.14
Guideline for irrigation water (mg/l) b* (total mg/kg)*c	6.0-8.5	500	120	60	100	0.01	0.55	0.5	0.017	0.065	0.2

S₀ (control) = Tap water, S₁ = near the outlet, S₂ = 0.75 km, S₃ = 1.5 km, S₄ = 2.25 km, S₅ = 3.0 km from the outlet (near the Koka lake)

nd = not detected

Means followed by different letters within the same column are significantly different at 5% probability level.

Means followed by same letters within the same column are not significantly different at 5% probability level.

b* Source Ayres and Westcott, (1994).

Metals in surface soil samples

The study was conducted during 2012/ 2013. Before sample collection, site characterization and soil profile description were done by close observation and examination of dug pits on the study area. Before taking soil samples from the fields irrigated with the effluent from the Ethiopia Tannery, the 3 km distance between the tannery and Koka lake was divided in to five equal intervals (750.0 m or 0.75 km) (Figure 2).

From six sampling points a total of thirty six soil samples were collected from (0-10 and 0-20 cm depths) for sampling location at different distance of 0, 0.75, 1.50, 2.25 and 3.0 Km on a line to the east and south of the tannery effluent drainage canal in January 2013. The composite soil samples

were collected from each sampling point, and each sampling positions had a dimension of 20 cm by 20 cm.

The collected samples were put in plastic bags and transported to the laboratory. The soil samples were air dried on a clean plastic sheet placed on a flat surface in the green house until its dryness and then weighed the dry sample for the moisture content air-dried and ground in a stainless steel grinder and sieve with 2 mm mesh size and made ready for analysis of pH, Ec, Cd, Cu, Cr, Fe, Pb and Zn.

Heavy metal analysis of soil samples was done as described by Alef and Nannipieri (1985). The soil samples were dried using an oven drier at 107°C for 24

hrs. The dried samples were grinded using a grinding disc mill and then sieved with 75 micron size and used for metal analysis. One gram of soil was then burnt into ashes in a crucible. These ashes were taken and moistened with a little double distilled water. Concentrated HNO₃ and HCl were added successively in a ratio of 3:1. Concentrated HNO₃ and HCl were added successively in a ratio of 3:1. Soil samples in the beaker were then heated gently on a heating plate until the samples were digested, which was indicated by the formation of a clear solution above the soil residue. The mixture was reduced to a volume of 1 ml and diluted with double distilled water and then filtered through Whatman filter no. 42. Double distilled water was added to make the volume up to 100 ml. Digested soil samples were analyzed for metal concentration by Graphite Furnace Atomic Absorption Spectrophotometer (AAnalyst 600 Perkin Elmer) following APHA (2005) method, pH analyzed by Digital pH meter.

RESULTS AND DISCUSSIONS

Concentration of heavy metals in surface water

The analysis result of heavy metals and other parameters in surface water (effluent) sample collected from the tannery effluent outlet (upstream) up to the Koka Lake

Table 3. Total concentrations of heavy metal in surface soil samples collected from the tannery (upstream) up to the Koka lake (downstream)

Sampling sites	Depth (cm)	Parameters (mg/kg)						
		P ^H	Cd	Cr	Cu	Fe	Pb	Zn
S ₀ (control)	0-10	6.2 ^b	0.34 ^c	10.34 ^c	0.30 ^f	32345 ^f	1.40 ^f	0.63 ^f
	10-20	6.2 ^b	0.35 ^c	15.13 ^c	0.26 ^f	32987 ^f	0.67 ^f	0.79 ^f
S ₁	0-10	6.2 ^b	0.74 ^a	122.68 ^a	17.64 ^a	59437 ^b	10.72 ^a	107.04 ^a
	10-20	6.1 ^b	0.65 ^a	125.20 ^a	17.66 ^a	59578 ^b	10.69 ^a	107.21 ^a
S ₂	0-10	6.3 ^b	0.47 ^b	126.17 ^a	17.42 ^b	59612 ^a	10.84 ^b	105.19 ^b
	10-20	6.2 ^b	0.40 ^b	121.04 ^b	17.34 ^b	59784 ^a	9.98 ^b	104.07 ^b
S ₃	0-10	6.2 ^b	0.28 ^d	116.50 ^b	15.62 ^c	56432 ^c	9.64 ^c	97.02 ^c
	10-20	6.1 ^b	0.19 ^d	116.89 ^b	15.12 ^c	56917 ^c	9.01 ^c	98.02 ^c
S ₄	0-10	6.1 ^b	nd	95.72 ^c	12.36 ^d	53832 ^d	8.64 ^d	95.79 ^d
	10-20	6.3 ^b	nd	96.01 ^c	11.71 ^d	54765 ^d	7.96 ^d	95.74 ^d
S ₅	0-10	6.4 ^a	nd	92.86 ^d	10.12 ^e	50744 ^e	7.42 ^e	92.78 ^e
	10-20	6.4 ^a	nd	95.34 ^d	10.65 ^e	50963 ^e	6.98 ^e	92.42 ^e
CV(%)		0.53	8.59	1.79	1.74	0.31	1.91	0.42
Guideline for Soil (total mg/kg)*c		6-9	3	100	100	50000d	100	300

S₀ = Out of the effluent point, S₁ = near the outlet, S₂ = 0.75 km, S₃ = 1.5 km, S₄ = 2.25 km, S₅ = 3.0 km from the outlet (near the Koka lake)

nd = not detected

Means followed by different letters within the same column are significantly different at 5% probability level.

Means followed by same letters within the same column are not significantly different at 5% probability level.

*C Source: Ewers, (1991)

d Source: Pendias and Pendias, (1992).

(downstream) depicted on table 16. The value of pH of collected samples were relatively constant throughout the sampling sites (S₁- S₅), which ranged from 6.1- 6.5 which is in the normal range for irrigation water, (Table 2). The distance from tannery to the lake did not influence the pH value. The EC value decreased with increasing distance from tannery to the lake.

Similarly the mean concentrations of EC, COD, Cd, Cr and Pb decreased with increasing distance from tannery to the lake (S₁- S₅), but their values were more than the maximum allowable limit for irrigation water. Whereas, the mean concentration of TDS, Cu, Fe and Zn increased with increasing distance from tannery to the lake where the values were more than the maximum allowable limit for irrigation water.

Fe and Zn recorded more than the maximum allowable limit in all sampling sites. In this study the concentrations of Cr, Fe and Pb in samples S₁ (near the effluent out let) recorded 3.91, 1.70 and 0.98 mg/lit in S₂

(0.75 km from the outlet) = 1.84, 2.11 and 0.73 mg/lit in S₃ (1.5 km from the outlet) = 1.99, 2.68 and 0.58 mg/lit, in S₄ (2.25 km from the outlet) = 1.39, 2.82 and 0.34 mg/lit, in S₅ (3.0 km from the outlet, near the Koka Lake) = 1.26, 3.28 and 0.21 mg/lit which were more than the maximum allowable limits (Table 2).

The mean concentration of Cr, Fe, Pb and Zn were highest in all analyzed effluent samples tested. The mean concentration of Cd and Cu (mg/lit) was recorded under the guideline for irrigation water. Cr concentrations (mg/lit) in S₁, S₂, S₃, S₄ and S₅ were 3.91, 1.84, 1.99, 1.39 and 1.26 mg/lit which was more than the guideline for irrigation water. The concentrations of Pb (mg/kg) were 0.98, 0.73, 0.58, 0.34 and 0.21, and of Zn were 0.21, 0.27, 0.31, 0.35 and 0.36 mg/lit respectively, which was higher than the maximum allowable limit (guideline for irrigation water). The mean concentration of all analyzed parameters was significantly difference between sampling sites.

Concentration of heavy metals in soil

The concentrations of heavy metals in soil at different depths are indicated in tables 3. Cr sample S₁, S₂ and S₃ in both depths (0-10 cm and 10-20 cm) recorded more than the maximum allowable limit for soil, but in sample S₄ and S₅ of both depths it was less than the maximum allowable limit for soil. The concentration of Fe in all samples ranged from 59,437 to 50963 mg/kg, which were recorded higher than the maximum allowable limit (50,000 mg/kg), (Table 3).

The concentration of Cd, Cu, Pb and Zn in all samples recorded under the maximum the guideline for total soil. Generally the concentrations of all metals decreased from sample S₁(near the effluent out let) to S₅ (near the Koka lake) at both depths of 0-10 cm and 10-20 cm. The control soil samples in both depths were recorded less than the maximum allowable limit. The pH of soil samples in both depths were relatively constant throughout the sampling sites.

In regard to the depth through the soil layers, the highest concentrations of Fe were recorded in the 10-20 cm layer more than while the least were recorded in the 0-10 cm of the soil in most cases and this shows a linear correlation of reduction with depth through the soil layers.

Temmerman et al., (1984), also recorded the same results for the concentrations of heavy metals (mg/kg) in agricultural soil collected from different crop production sites ranged from a minimum of 9.8 to a maximum of 19.3 for Cu, 83-133 for Zn, 0.6-2.3 for Cd and 2.9-10.3 for Pb. The upper limits of Cu, Zn and Cd in the soil during the present study were higher than the values reported for uncontaminated soil (Cu; 15, Zn; 100 and Cd; mg/kg), but were lower for Pb (50 mg/kg).

Tamiru Alemayehu (2010). also stated that the highest concentrations of metals in soil samples for Zn, Cr, Pb, and Cd are 113, 47.8, 17.7 and 0.250 mg/kg respectively.

In Curtis and Smith, (2002) findings, the limits of heavy metals concentrations in soils in some other countries. Only Luxembourg and the United Kingdom set the maximum permissible limits for Pb in soil as 300 mg/kg. The limits are lower in the other countries namely Austria and France, 100 mg/kg of soil; Germany, 70 mg/kg of soil; Netherlands and Sweden, 40 mg/kg of soil (Adelekan and Abegunde, 2011). This situation points at a far reaching recognition of excessive levels of Pb in soil as potentially dangerous and the need to regulate it to yet lower levels. Reasons for elevated Pb levels in soil are basically anthropogenic. Due to past uses of lead in industrial processes and consumer products (for example paint, gasoline, diesel, other petrochemicals, accumulators), urban soils often contain high lead concentrations, up to 1840 mg/kg or more

CONCLUSION

The pH values ranged between 6.1- 6.5 which is in the normal range for irrigation water (Table 2). The distance from tannery to the lake did not influence the pH value. The EC value decreases with increasing distance from tannery to the lake. Similarly Cd, Cr and Pb concentrations were decreased in increasing of distance from the tannery which leads the regression correlation values on distance should stay negative relationships.

In the surface water (effluent) sample Fe and Zn recorded more than the maximum allowable limit in all sampling sites. In this study the concentrations of Cr, Fe and Pb in samples S₁ (near the effluent out let), S₂ (0.75 km from the outlet), S₃ (1.5 km from the outlet), S₄ (2.25 km from the outlet) and S₅ (3.0 km from the outlet, near the koka lake) were more than the maximum allowable limits.

The mean concentration of Cr, Fe, Pb and Zn were highest in all the effluent samples tested. The mean concentration of Cd and Cu (mg/kg) was recorded under the guideline for irrigation water.

Elevated values of Cd, Cr, Cu, Fe, Pb and Zn were found in soils from different sampling areas from tannery to the lake when compared to control samples, it was found that Cd, Cr, Cu, Pb and Zn generally has the highest concentrations in both soil layers while Fe generally has the least and the order observed for this study is Pb > Cu > Cr > Cd > Zn which were above the maximum allowable limit.

The accumulation of heavy metals in the soil, sediment and water may lead to an increase of their concentration in crops. Furthermore, ageing and weathering processes may increase the irreversibility of the association of heavy metals-soils (particularly with clay and organic matter fractions), making soil clean-up more difficult in future remediation programs.

REFERENCES

- Adelekan, B.A. and Abegunde K.D. (2011). Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan, Nig. Int. J. Physical Sci. Vol. 6 No.5, 1045-1058 .
- Alef K, Nannipieri P (1985). Methods in Applied Soil Microbiology and Biochemistry" *Academic Press Ltd., London*.
- APHA (1998). 'Standard Methods for the examination of water and wastewater' 18th Ed. American Public Health Association, Washington D., 12.
- APHA (2005). American Water Works Association, and Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater, 20th Ed.*, 18.
- Ayers RS, Westcot DW (1994). Water quality for agriculture. *FAO Irrigation and Drainage Papers*, Vol. 29, No.1, 1-120.
- Babushakila P (2009). Effect of Diluted Effluent on Soil Properties and Plant Growth, *Advanced Studies in Biology*. Vol.1, No.8, 391-398.
- Clesceri LS et.al. (1998). Standard Methods for the Examination of Water and Wastewater. Method 2540B (total solids), Method 2540C (Total Dissolved solids) and Method 2540D (Total Suspended Solids) 20th Edn., Am. Pub. Health Asso. USA.

- Curtis LR, Smith BW (2002). Heavy Metal in Fertilizers: Considerations in Setting Regulations in Oregon. *Oregon Department of Agriculture, Salem, Oregon*, 10.
- Eskindir Z (2002). Assessment of the Impact of Industrial Effluents on the Quality of Irrigation Water and Changes on Soil Characteristic (a Case of Kombolcha Town).
- Ewers U (1991). Standards, guidelines and legislative regulations concerning metals and their compounds. In: Merian E, ed. *Metals and Their Compounds in the Environment: Occurrence, Analysis and Biological Relevance*. Weinheim: VCH, 458-468 pp.
- Fergusson JE (1990). The heavy elements: chemistry, environmental impact and health Effects. *Pergamin Press, Oxford*. 382-399.
- Fifield FW, Haines PJ (1995). *Environmental Analytical Chemistry*, Blackie Academic and Professional, Chapman and Hall, UK .
- Friberg L, et al. (1986). *Handbook on the Toxicology of Metals, 2nd edition, Elsevier Science Publishers B.V., Amsterdam*.
- Gregg LW (1989). *Water analysis Handbook*. H.A.C.H Company', USA. 33- 39.
- http 1 (2012). http://www.indexmundi.com/ethiopia/birth_rate.html.
- http1 (2013). www.mapsofworld.com; [en.wikipedia.org/wiki/Demographics of Ethiopia](http://en.wikipedia.org/wiki/Demographics_of_Ethiopia).
- Khurana MP, Pritpal S (2012). Waste water Use in Crop Production Resources and Environment Vol. 2(4), 163-618.
- Malarkodi M, et al., (2007). Characterization of heavy metal contaminated soils of Coimbatore district in Tamil Nadu. *J. Agron*, Vol. 6, No.1, 147-51.
- Msaky JJ, Calvert R (1990). Adsorption behavior of copper and zinc in soils: influence of pH on adsorption characteristics. *Soil Science* 150(2): 513-522.
- Pendias AK, Pendias H (1992). Elements of Group VIII. In: *Trace Elements in Soils and Plants*. Boca Raton: *CRC Press*, 271-276.
- Prabu PC (2009). Impact of Heavy Metal Contaminations of Akaki River of Ethiopia of Soil and Metal Toxicity on Cultivated Vegetable Crops, *Electronic J. Environ. Agric. Food Chem.* 819-820.
- Samuel M (2005). Investigation of input and distribution of polluting elements in Tinishu Akaki River, Ethiopia, based on the determination by ICP-MS, PhD thesis.
- Tamiru A (2010). Metal Concentration in Vegetables Grown in the Hydrothermally Affected Area in Ethiopia', 86-93.
- Temmerman LO, et al., (1984). Determination of normal levels and upper limit values of trace elements in soils. Vol.147, 687-694.
- Ward NI, et al., (1995). *Environmental Analytical Chemistry in Trace Elements*. *Nackie Academic and Professional*, UK., 320-328.
- Yargholi B, AA Azimi (2008). Investigation of Cadmium absorption and accumulation indifferent parts of some vegetables. *American American-Eurasian J. Agric. Environ. Sci.* 3(3), 357-364.