Temporal and Spatial Variations on Heavy Metals Concentration in River Mojo, Oromia State, East Ethiopia

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Abstract: ***This study was aimed to reveal the temporal and spatial concentration variations of trace heavy metals in extreme wet rainy season, semi – wet and semi - dry period (autumn), and extreme dry season (winter). The experimental results of this study unveiled that the level of As increases from the wet to dry periods of the year showing the dilution effects. Except for a single result, all analyzed results of As are above WHO Drinking Water Guidelines (DWG) (0.01mg/l). Cd pollution load is observed to be low in all study locations and sampling periods (mean value = 0.12 ±0.075mg/l). All the experimental results of Hg are significantly ($p = 0.043$, $p < 0.05$) greater than the WHO/FAO set standards for fresh water (0.05mg/l) and maximum acceptable DW for livestock (0.003mg/l).The analytical results of Pb, pointed out that more than half the analyzed results are above the maximum permissible limit of WHO for DWG (0.01mg/l). The mean registered value for Cr was 2.51±5.94mg/l and half of the results lie below FAO set standard for surface water for irrigation (0.1mg/l) and WHO DWG (0.05mg/l) but all results fall above the FAO set standard for fresh water set standard (0.005mg/l). The findings warns that much care and precaution has to be taken especially on the use of water from River Mojofor vegetable irrigation, livestock watering and for different domestic uses by the local dwellers. Investigation on the implication of these high concentrations of heavy metals in water uptake by irrigated vegetables is decidedly recommended.***

Keywords: Spatio – temporal, trace metals, guideline, livestock, pollution load

1. Introduction

The natural processes and human economic activities sum – up with agricultural land use, climate change, sewage and industrial discharges, precipitation and hydrological features contribute much to deterioration of surface water qualities [1 -4]. Crosa et al, Sarkar et al. and Zhou et al [5 – 7] independently reported that the gathering of sufficient scientific information on water quality status and pollution level and sources are important for the implementation of sustainable water-use management strategies. Because of seasons and location of river waters, assessing spatio-temporal variations of river water quality at a watershed level has become an important aspect for the physical and chemical characterization of aquatic environments [8, 9].

The river water is one of the surface water bodies which human societies consume for economic activities in times past up until the present. Its pollution by the emission of anthropologic activities is the current issues of public concern [10, 11]. Khaki, C, et al [12], describes that these various economic activities and processes have led to discharge of municipal wastewater treatment plant, accelerated industrial activities, as well as the uses of chemicals inputs for the rapid agricultural development which causes non-point source runoff containing pesticides, herbicides and which fertilizers were the main challenges of heavy metal pollution in rivers. Excessive inputs of trace metals, especially cadmium, chromium, mercury, lead, arsenic, copper and zinc due to poor management practices from agricultural activities accelerated the leaching of metals to ground and surface waters, thus deteriorating its water quality and affecting aquatic organisms [15]. Heavy metals could cause poisoning in aquatic organisms, even when the exposure is low [15 – 17]. Due to their persistence and through bioaccumulation and food chain, human beings are potentially affected. Amongst trace metals, chromium, arsenic, cadmium, lead and mercury are of great concern due to their acute and chronic poisoning effects [15].

Ravichandran [18] and different researchers [19] clearly described that worldwide deterioration of surface water quality has been attributed to both natural processes and anthropogenic activities, including hydrological features, climate change, precipitation, agricultural land use and sewage discharges. Other studies [20 – 22] indexed that the information on water quality and pollution sources is important for the implementation of sustainable water-use management strategies.

Ouyang et al [23] and Sundaray et al [24] reasoned out that the regional and seasonal assessing spatio - temporal variations of the river water quality at a watershed level has become an important aspect for the physical and chemical characterization of aquatic environments. Studies investigating the spatial and seasonal variability of water quality report that water quality issues, such as eutrophication, are highly dependent on land use patterns and influence from watershed [25]. Anthropogenic activities such as mining, agriculture, residential and industrial wastes systematically discharge dissolved compounds and suspended matter into the rivers, decreasing water quality significantly [26]. Polluted inflows of rivers can have severe impact on human health as well as on terrestrial and aquatic ecosystems [15]. Zinabu and Elias [27] stated that in Ethiopia, human activities such as land use and modification, urbanization, human settlement and other practices associated with rapid population growth are the major water quality degrading factors.

The water quality and the overall health of water systems can be affected by changes in a River/Lake's chemical and/or physical conditions [28]. Species living in the aquatic environments are sensitive in varying degrees to: pH, biological oxygen demand (BOD), dissolved oxygen (DO), sedimentation, temperatures, nutrient enrichment, chemicals and organic pollutions [29].

2. Materials and Methods

2.1 Description of the Study Area

The study area is located in Oromia State, in eastern Showa zone, about 60 – 105km away from the capital city of Ethiopia, Addis Ababa, to the east (Figure 1). This study was conducted along the River Mojo from 7km up Mojo town to the junction of Lake Koka, within about 50km length. The river receives effluent discharges from several industries in the area, viz, car battery refilling and recharging small household industries, textile factories, meat processing plants, and tanneries. On both sides, along the banks, starting from its middle up to nearer to its junction with Lake Koka, it is surrounded by intensive and extensive agricultural irrigation and rain season activities. The river water serves the communities as water source for domestic consumption to the inhabitants dowelling near by the river and wild animals of the area.

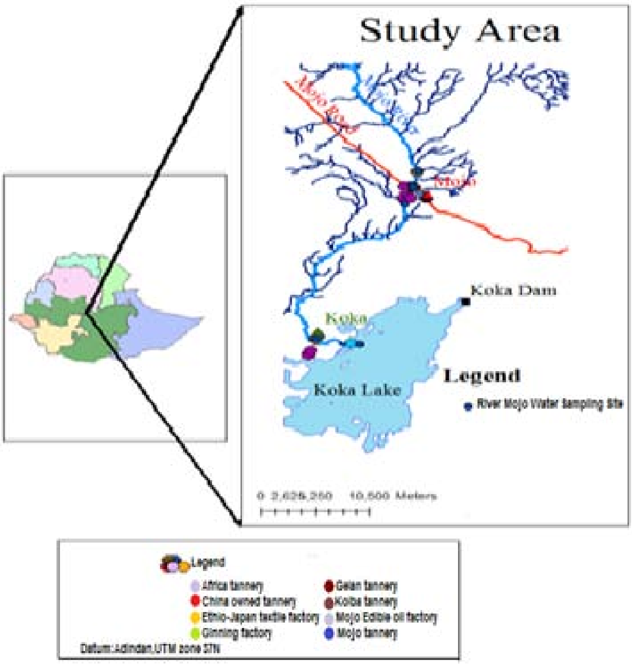

Figure 1: Geographical description of the study site

2.2 Sampling and sample treatment

Samplings were carried out temporally and spatially during the extreme wet rainy season (summer) (June, 2013), semi – wet and semi - dry period (autumn), (October, 2013) and extreme dry season (winter), (February, 2014). Sample collection and chain – of – custody was based on the method 1060B and sample preservation follows method 1060C of APHA, AWW, WEF, 2012. Sampling was based on temporal and spatial variations viz sampling of water was conducted at four different geographic locations and three times annually. The sample collection methods were rooted on APHA 1998 procedures. Four composite samples (n = 4) were collected from each site in acid pre-washed high density polyethylene plastic bottles of each a liter volume. Each composite sample was made by mixing of 8 – 10 grab samples. The dissolved oxygen (DO), temperature and pH measurements were taken on site at the point of sampling. Samples for the analysis of electrical conductivity (EC), biochemical oxygen demand (BOD), nitrate (NO_3 – N), sulphate (SO_4^{-2}), phosphate (PO_4^{-3} - P), As, Hg and sulfide (S^{-2}) were not acidified in the field while the samples for the analysis of Cd, Cr and Pb were acidified with 65% concentrated nitric acid to pH < 2 and the sample for chemical oxygen demand (COD) was acidified by H_2SO_4 to pH < 2 at the field. All the samples were transported to Addis Ababa Environmental Protection Authority (AAEPA) laboratory being kept in ice box. At the laboratory, the samples were preserved in refrigerator at approximately 4°C until analysis, APHA 1998.

3. Experimental

The experimental analyses of this study were carried out for various water quality physicochemical parameters: pH, Electrical conductivity (EC), Total Dissolved Solids (TDS), reactive phosphorus (RP), nitrate (NO_3^- - N), ammonia (NH_3 – N), sulfate $(SO_4^{2})^{-}$, sulfide (S^{2-}), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), arsenic (As), cadmium (Cd),chromium (Cr),mercury (Hg) and lead (Pb).

The analyzing processes were started by *in situ* measurements which were carried out at the sampling points on the pH, temperature and DO using pH – meter (CP – 105, Elmeiron), and DO - meter (AD 630, Adwa) respectively. The other parameters such as EC was analyzed using conductometry, TDS by spectrophotometer (HACH DR/2010), COD by reactor digestive (LANGE LCK 514, Titrimetry), $BOD_{5,}$ incubation at 20^{o}C, by Titrimetry, RP by Vanadomolybdophosphoric Acid Colorimetric, NH_3 – N, PO_4^{3-}, S^{2-}, SO_4^{2-} by Spectrophotometer, reactor SulfaVer 4 methods. Trace heavy metals like Cd, Cr, and Pb was analyzed by FAAS, novAA 400, analikjena), direct air-acetylene method. Hg and As were analyzed by HG – AAS, novAA 400, analikjena) methods at laboratory of AAEPA) based on FAO 1997 methods. The results of the 1st, 2nd and 3rdanalyses are summarized in Table 2, 3 and 4. All the chemicals and reagents used in the experiments were of analytical grade. All the results were statistically significant at P< 0.05.

Table 2: Details of the result of the water samples collected during extreme wet season (summer), June 2013 (n = 4).

Parameters	Result of Analysis at each Sample Sites							
	S_o	S_1	S_2	S_3	Min.	Max.	Mean	StD
pH	8.30	7.83	7.76	7.66	7.66	8.3	7.89	0.28
Temperature (˚C)	14.6	15.3	16.2	18.8	14.6	18.8	16.22	1.83
DO (%)	128.1	87.5	77.72	66.5	66.5	128.5	89.95	26.84
EC, µs/cm	127.4	222	525.2	547.7	127.4	547.7	355.58	212.6
TDS, mg/l	263.9	361.0	362.7	472.9	263.9	472.9	365.13	85.41
RP PO_4^{3-}, mg/l	1.0	18.2	10.0	9.6	1.00	18.2	9.7	7.02
NO_3^- - N, mg/l	24.2	17.2	20.5	19.2	17.2	24.2	20.28	2.95
SO_4^{2-}, mg/l	12.01	13.5	65.2	97.6	12.01	97.6	47.08	41.79
T - NH_3 , mg/l	0.06	0.51	28.7	15.9	0.06	28.7	11.23	13.74
COD, mg/l	812	867	906	884	867	1110	861.67	108.3
BOD, mg/l	50	150	25	50	25	150	68.75	55.43
S^{2-}, mg/l	0.27	0.342	0.28	0.29	0.27	0.34	0.296	0.032
As, µg/l	0.10	0.19	0.12	0.268	0.1	0.27	0.17	0.078
Cd, mg/l	0.03	0.1	0.4	0.3	0.03	0.4	0.21	0.17
Cr, mg/l	0.01	0.2	0.15	3.148	0.01	3.15	0.89	1.52
Pb, mg/l	0.01	0.03	0.02	0.04	0.01	0.04	0.025	0.013
Hg, µg/l	0.32	0.68	0.59	1.00	0.32	1.00	0.65	0.280

Table 3: Description of the result of the water samples collected during semiwet - semi dry season (autumn), October 2013 (n = 4).

Parameters	Sample Sites							
	S_o	S_1	S_2	S_3	Min.	Max.	Mean	StD
pH	7.86	7.56	7.30	7.27	7.27	7.86	7.49	0.27
Temperature (˚C)	20.5	21.6	21..8	24.52	20.5	24.52	22.1	1.71
DO (%)	83.4	84.5	20.8	7.7	7.7	84.5	49.1	40.59
EC, µs/cm	416	510	1137	824	416	1137	721.7	3272
TDS, mg/l	208	205	569	413	205	569	348.7	176.2
RP PO_4^{3-}, mg/l	3.8	2.5	3.5	32	2.5	32	10.4	14.4
NO_3^- - N, mg/l	0.5	0.3	6.0	1.4	0.3	6	2.05	2.67
SO_4^{2-}, mg/l	16	18	85	100	16	100	54.8	44.02
T - NH_3 , mg/l	0.05	0.41	29.5	13.5	0.05	29.5	10.9	13.91
COD, mg/l	1129.6	1220.3	1455	1231.4	1129.6	1455.1	1259.1	138.4
BOD, mg/l	43	46	424	369	43	424	220.5	204.5
S^{2-}, mg/l	0.04	0.03	0.23	0.327	0.03	0.33	0.16	0.15
As, µg/l	0.993	1.15	0.98	1.074	0.98	1.15	1.044	0.079
Cd, mg/l	0.001	0.01	0.13	0.133	0.00	0.13	0.066	0.075
Cr, mg/l	0.51	0.57	11.9	9.499	0.52	11.9	5.62	5.94
Pb, mg/l	0.001	0.001	0.002	0.004	0.00	0.00	0.002	0.001
Hg, µg/l	1.060	1.65	1.06	1.479	1.06	1.65	1.31	0.3

Table 4: Explanation of the result of the water samples collected during extremely dry season (winter), February 2014 (n = 4).

Parameters	Sample Sites							
	S_o	S_1	S_2	S_3	Min.	Max.	Mean	StD
pH	8.25	8.01	7.85	7.47	7.47	8.25	7.895	0.327
Temperature (˚C)	20.0	21.9	21.2	25.40	20.0	23.4	22.38	1.42
DO (%)	5.10	4.2	2.9	3.10	2.9	5.10	3.82	1.02
EC, µs/cm	427.0	404	1415	796.0	404	1415	761.0	471.9
TDS, mg/l	214.0	200	714	396.0	200	714	381.0	239.27
RP PO_4^{3-}, mg/l	6.40	3.2	14.30	2.50	2.50	14.3	6.60	5.41
NO_3^- - N, mg/l	22.40	15	24.10	41.8	15	41.0	25.82	11.36
SO_4^{2-}, mg/l	16.0	18	475.0	87.5	16	475.	149.13	219.78
T - NH_3 , mg/l	0.50	1.0	14.50	2.5.0	0.50	14.5	4.63	6.64
COD, mg/l	1229.6	1320.3	1455	1331.4	1229.6	1455	1334.08	92.61
BOD, mg/l	45.0	256	421.5	389.0	45	424	273.5	167.6
S^{2-}, mg/l	0.05	0.016	0.90	0.275	0.02	0.9	0.311	0.41
As, µg/l	1.217	0.798	1.08	1.28	0.8	1.28	1.09	0.21
Cd, mg/l	0.0001	0.02	0.046	0.32	.00	0.32	0.14	0.15
Cr, mg/l	ND	0.03	2.058	1.982	.00	2.06	1.02	1.16
Pb, mg/l	2.399	1.05	0.764	2.143	0.76	2.40	1.59	0.80
Hg, µg/l	0.9967	1.454	1.861	1.371	1.00	1.86	1.42	0.35

Table 5: Descriptions of the average results of all the three seasons

Parameters	X_w	X_{SWD}	X_D	XX_M	StD
pH	7.89	7.49	7.895	7.77	0.23
Temperature (˚C)	16.22	22.10	21.62	20.23	3.27
DO (%)	89.95	49.1	3.82	47.62	43.08
EC, µs/cm	355.58	721.70	761	612.76	223.59
TDS, mg/l	365.13	348.70	381	364.94	16.15
RP PO_4^{3-}, mg/l	9.70	10.40	6.6	8.90	2.02
NO_3^- - N, mg/l	20.28	2.05	25.82	16.05	12.44
SO_4^{2-}, mg/l	47.08	54.8	149.13	83.67	56.82
T – NH_3, mg/l	11.23	10.90	4.63	8.92	3.71
COD, mg/l	941.75	1259.10	1334.05	1151.62	253.89
BOD_5, mg/l	68.75	220.5	273.5	187.58	106.26
S^{2-}, mg/l	0.296	0.16	0.311	0.256	0.83
As, µg/l	0.17	1.044	1.09	0.768	0.58
Cd, mg/l	0.21	0.066	0.14	0.138	.0.07
Cr, mg/l	0.89	5.62	1.02	2.51	2.69
Pb, mg/l	0.025	0.002	1.59	0.539	0.91
Hg, µg/l	0.65	1.31	1.42	1.127	0.41

X_w =Mean of wet season, X_{SWD} = Mean of semi-wet-dry season, X_D = Mean of Dry season, XX_M = Mean of the means, StD = standard deviation

Table 6: comparison of the recorded results with WHO and FAO Guidelines

Parameters	WHO Health Based DWG	FAO Guideline for surface water for irrigation	$\bar{x}$ ± StD
As, µg/l	0.01mg/l	0.1mg/l	0.768 ±0.58
Cd, mg/l	0.003mg/l	0.01mg/l	0.138 ±0.07
Cr, mg/l	0.05mg/l	0.1mg/l	2.51 ±2.69
Pb, mg/l	0.01mg/l	0.5mg/l	0.539 ±0.91
Hg, µg/l	0.001mg/l	0.001mg/l	1.127 ±0.41

$\bar{x}$: The Spatial and Temporal Analyzed Mean of Means of the Results of River Mojo Water samples.

4. Results and Discussions

The seasonally analyzed different physicochemical parameters: pH, Temperature, DO, EC, TDS, COD, BOD, RP, NO_3^- - N, aNH_3 – N, $SO42^-$, $S2^-$ and trace heavy metals concentrations, minimum, maximum standard deviation in the River Mojo water samples were illustrated in Table 2, 3 and 4 while the overall means of wet, semi wet – semi dry and dry seasons and mean of means is indicated in table 5.

In this study, the onsite measured pH values ranged from 7.28 to 8.3 which lies in the range prescribed by WHO/APHA1 (6.5 – 8.5). The result of the analysis indexed that in all the sites and seasons, the water is alkaline in nature. The pH mean values for the four sites and three seasons are respectively: 7.89, 7.49 and 7.895. The maximum pH value, 8.3, was recorded in the month of June (summer season) at site S_o and minimum, 7.27 at site S_3, in the season of autumn (month of October). The result showed the slight variations in location in decreasing manner from the upper to the lower part of river during all the seasons. In all the sites, the minimum values were registered during autumn season (Table 3).

The measured temperature of the River Mojo water falls below the set standard by WHO for irrigation uses (Maximum 30°C).The registered temperature of the River Mojo water ranges from 14.6 - 25.4 ^{0}C which lies in the range of atmospheric temperature of the study area [30]. The temperature of the water body during sampling periods increases from the wet to dry seasons respectively (14.6 to 25.4 ^{o}C). During the summer period, water temperature was high due to low water level, high sun overhead radiation and clear atmosphere. The mean of means temperature of all sites of the three seasons was measured to be 19.98^{o}C while the mean temperature values for the four sites and three seasons (wet, semi wet – semi dry) are respectively: 16.22, 22.1 and 21.62^{0}C. Temporally, the least temperature values were registered during the summer season and there were no significant temporal and spatial variations in all sites during autumn and summer (Table 3 and 4).

EC values in the River Mojo water samples ranged from 127.4 to 1415µs/cm the minimum and maximum being during wet and dry seasons at sites S_o and S_2 respectively (Table 2 and 3). The EC values registered are within the maximum permissible limit of FAO guidelines for irrigation water quality, 2000 µS/cm. The results indicated that the distribution of EC in the water in the study area is not uniform. The results of the summer season increases from the upper to the lower part of the river showing the spatial variation. Comparatively, the larger values were registered during autumn and winter seasons and there were significant differences ($p = 0.043$, $p < 0.05$, Table 7) between the two seasons in all sites. The recorded high EC values at S_2 site indicates the converging of different industrial effluents in to the River Mojo water as this site is located near different populated industrial plants. During the dry season, there is no additional water and on the other hand, the rate of evaporation increases and hence the salts content increases which leads to increase of conductivity [30]. Low conductivity values during the rainy season may be due to dilution from the enormous amount of rainfall and much flood entering in to water body.

The results of the analysis DO range from 3.1% to 128.1% saturation. The maximum was registered during summer period at site S_o and the minimum result was recorded at site S_3 during winter time (Wet season). At all sites (S_o to S_3), the values decrease from the wet season (summer), autumn to dry season (winter). This result shows temporal and spatial variation and except for at site S_o and S_1 during June and October and S_2 and S_3 during June months, all results showed poor quality (< 60% saturation). All the results of winter season (summer) are ≤ 5.5% saturation (Table 2, 3 and 4). The higher result recorded during wet season at all sites is attributed to the high flow rate of the water that assists the mixing up of atmospheric air. On the other hand, the low record of the result during winter time is due to slow flow rate, less turbulence and the increase of concentration of pollution loads from industries to the water body. The percentage saturation of all the three seasons at site S_o is higher than all the sites. This is the result expected because site S_o is geographically at higher altitude and the rate of elevation change is greater than the rest of the sites that can cause the water to move faster and increase the mixing of air. Additionally, S_o is up the River where there is no industrial activities except the agricultural inputs polluting factors.

The study showed the analyzed results of minimum and maximum records of TDS at sites S_1 and S_2 during winter and autumn respectively (i.e., 200mg/l and 1137mg/l). The WHO standard for TDS test specifies maximum value at 150 mg/l for drinking water, accordingly, none of the results observed does meet the drinking water standard. All the results are within FAO recommended result for irrigation uses (maximum limit is 2000mg/l, FAO Irrigation Water Quality Guidelines, 1985). All the results, at all sites of autumn are greater than the wet and dry seasons showing the temporal and spatial variations. The recorded results of site S_3 is comparatively greater than that of the others for the three seasons. This is the expected result because site S_3 is lower down the river where the effluents from all tanneries and meat processing plants meet the river water.

The experimental results of this study showed that the minimum and maximum values of reactive phosphorus (RP) at sites S_0 and S_1 during wet seasons ranges from 1.0 – 18.2mg/l respectively (WHO permissible limit is 45mg/L). At the period of autumn, the concentration of RP was registered to be low (3.8, 2.5, 3.5 and 3.2mg/l). The means of wet, semi wet – semi dry and dry seasons were respectively: 9.7, 10.4 and 6.6mg/l which showed the least mean recorded was during dry season. But these results are above USEPA set standard (0.1 mg/l max.) and accordingly, the water is susceptible to eutrophication.

In this study, the analytical results for all seasons and sites revealed the spatial and temporal variations. The maximum and minimum values were recorded at site S_3 and S_2 during dry and semi- wet semi - dry periods respectively (41.8 and 0.3mg/l). The least result was recorded during autumn period (0.5, 0.3, 6.0 and 1.4mg/l). (Table: 2, 3 and 4). The ranges of the results are 0.3 - 41.8mg/l. During the dry season, the variations increase from the upper to down the river while at wet time the results decrease from the upper to down river. The highest mean result recorded was during dry period (25.82mg/l) (Table 5). The presence of nitrate in water indicates the presence of fully oxidized organic matter. There is no substantial difference between NO_3^- concentrations between sites $S_o$to S_3 in the wet season. The higher values recorded during wet season may be due to the uses of nitrogen fertilizers by the farmers along the left and right sides of the river. The higher concentration of NO_3–N at dry period also may indicate that effluent releases to the reduced volume of the river from the proximity industries that are rich in nitrogen. The level of nitrate in the river is in the FAO standard limit for irrigation uses (15mg/l and except for two results all are above the WHO maximum permissible level (2.27mg/l of NO_3-N) for drinking purposes.

The experimental results showed the minimum and maximum values of sulfate to be 12.01 and 475.0 mg/l respectively. The least record of result was at site S_o during wet time and the maximum value was observed at site S_2 during dry season. In all the sites and seasons, the results increase from the upper to downstream indicating the spatial differences. Except for one result, all results are within recommended WHO Drinking Water Quality Criteria (200mg/l) but one result (475.0mg/l) is beyond the WHO guideline for surface water for irrigation (250.0mg/l). The increase of the result may be attributed to the excessive uses of chromium sulphate in tanneries or metallic or ammonium sulfate fertilizers.

The analyzed values for total ammonia in all the sites showed spatial and seasonal differences. At site S_o, during the three time periods, all the registered values are low and higher results were recorded at all seasons at S_2 followed by site S_3. The maximum result observed at sampling point, S_2, was 28.7mg/l and the minimum values registered during the period of semi wet – semi dry at sampling point was 0.05mg/l. The range of the values lies between 0.05 and 28.7mg/l. The mean value of wet season (11.23mg/l) is greater than the values registered during semi wet – semidry (10.9mg/l) and dry time periods (4.63mg/l). Except for four results, all analyzed experimental values are beyond EU Drinking Water Standard (1998) set for ammonium ion (0.50mg/l) and hence based on EU standard the water is polluted and cannot be used for drinking purposes.

The tested results of COD show temporal changes which range from 812 to 1455mg/l, the minimum record at location point, S_o, and the maximum at sampling point, S_2, during the periods of rainy and dry seasons respectively. The WHO's tolerable limit is 10 mg/l, standard specifying maximum value is 50 mg/land standard limit for river/stream is 1000mg/l. According to the analyzed sample results, except for the results of rainy season, all values are by far above the set WHO standard. The results registered (812 – 906mg/l) during summer are less than those of autumn and winter. There is no significant differences ($p = 0.01$, $p < 0.05$, Table 7) between the results of autumn and winter both showing higher loads of COD (1129.6 – 1455mg/l). The higher results recorded at autumn and winter periods may be attributed to the decrease of rainfall causing less dilution of the effluents discharged to the river water. Site S_2 has higher records of results in all seasons than the other three sites because it is the immediate recipient junction of most industries.

The experimental analysis of this study showed the values are discontinuously increased and decreased along the sites and seasons. The range of the results falls between 25 to 424mg/l. During autumn, the level of BOD increased from point S_o to S_2. The results also indicate temporal and location variability. The experimentally obtained values show that six results were below WHO standard limit for stream/river (50mg/l) and the rest values were above this set limit.

In this present study, the result under sulphide test shows values ranging from 0.016 to 0.90mg/l, during dry season at sites S_1 and S_2. The results showed time and location variations. Compared to the others, the rainy season has registered higher values at all sites and the least mean value was recorded during autumn. It was stated that the water is alkaline in nature. This leads to the increase of the concentration of S^{-2} in the water body. In this study, only three observed results (0.327, 0.342 and 0.9mg/l) are greater than the safe limit of S^{-2} in WHO DWG (0.3mg/l) value. The sources of the results can be correlated to the tannery effluents.

Trace Heavy Metals (As, Cd, Cr, Hg and Pb)

Different factors can affect the mobility and transport of metals to and within surface water systems. The study conducted by Landre et al. [31] on the effects of dissolved organic carbon, acidity and seasonality on metal geochemistry within a forested catchment on the Precambrian Shield, detailed that the pH, organic matter mineralization and chemical processes, e.g. sulphate concentration changes and ionic strength, can influence metal solubility and mobility. Metal ions can also be adsorbed to oxides or clays and precipitate or they may occur in suspended forms as colloids and particles [32].

This experimental results exhibited the mean concentration of the heavy metals analyzed for all sites and seasons for the trace metals: As, Cd, Cr, Pb and Hg were respectively: 0.768 ± 0.58, 0.12 ± 0.07, 2.51 ± 2.69, 0.539 ± 0.91 and 1.127 ± 0.41mg/l. During all seasons at all sites, the minimum and maximum results for trace metals, As, Cd, Cr, Hg and Pb were respectively: 0.099 – 1.28, 0.00 – 0.32, 0.00 – 11.9, 1.324 – 1.86 and 0.001 – 2.143mg/l. For all metals at the four sites and the three seasons, the least values registered were 0.00mg/l and the maximum result was 11.9mg/l. The recorded values showed time and location changes. The metals can be arranged in ascending order of their mean concentrations of the three seasons follows: Cd <Pb< As < Hg < Cr. The maximum acceptable level set for drinking water for livestock is: As = 0.025mg/l, Cd = 0.08mg/l, Cr = 0.05mg/l, Hg = 0.003mg/l and Pb = 0.1mg/l. According to this standard, considering As and Hg load, the use of River Mojo water for watering of livestock at all sites and all seasons is not advisable. Furthermore, in the dry season, River Mojo water is loaded by Pb above the set standard. At site S_2 and S_3, the water is also polluted by As, Cd, Cr and Hg and the water is not safe for watering of livestock (cattle, sheep, goat, pigs, horses, donkeys, etc).

Arsenic is distributed throughout the sites in all seasons. This may be attributed to the use of As compounds for the agricultural inputs and the loading from the nearby tanneries and textile factory. The upper and lower values of levels of the analyzed arsenic (As) in River Mojo water samples were respectively 0.099 and 1.28mg/l. The higher value was registered at site S_3 during dry season whereas the lower result was recorded at the control site, S_o, at the period of rainy season. In all sites and seasons, there were observation of changes of concentration due to season and location. Least results were tested at the time of rainy season and relatively higher results were recorded at site S_3, down the river and all the seasons. The mean values of the summer, autumn and winter times were respectively: 0.17, 1.044 and 1.09mg/l. This confirms that the increase of the level of As from the wet to dry periods of the year showing the dilution effects. Except for a single result, all analyzed results are above WHO Guidelines for Drinking Water Quality GDWQ) (0.01mg/l). Cd, Cr, Hg and Pb pollution loads were minimal during the rainy seasons showing the effect of dilution.

The tested Cd and Cr levels were low compared to the other metals under consideration uniquely at the control site, S_o. The concentrations of all metals along the sites, during the three seasons, increase from upriver to downriver indicating the lower course of the river suffering from the pollution load which the sources may be the industrial effluents. Cd pollution load is observed to be low in all study locations and sampling periods (mean value = 0.12 ±0.075mg/l). Except the two tested results, all values are above FAO surface water standard for irrigation (0.01mg/l) and health based WHO DWG, 1993, (0.003mg/l) (Table 6).

At site S_2, where the effluents of all industries immediately confluence, the level of Cr was observed to be highest (11.9mg/l) during autumn. The mean registered value was 2.51± 5.94mg/l and half of the results lie below FAO set standard for surface water for irrigation (0.1mg/l) and WHO DWG (0.05mg/l)Table 6) but all results fall above the FAO set standard for fresh water set standard (0.005mg/l). Interpretation of the mean value leads to the conclusion that the River Mojo water is inconvenience for watering of livestock and domestic purposes (max. acceptable DW for livestock =0.05mg/l) regarding Cr loads. Since the analyzed pH of the River Mojo water is above the neutral condition, the form of Cr expected to exist in the water body is Cr^{6+} because it is highly water- soluble at all pH values whereas the other forms of Chromium, Cr^{+2} and Cr^{+3} are not normally found in water at near-neutral pH, because the hydroxides of these two oxidation species are insoluble in alkaline environment [33].

Hg is a metal of rare geological occurrence. Concentrations in the environment are normally very low. The occurrence of Hg contaminants in water is predominantly site-specific and related to identifiable site-specific discharges. Hg is unlikely to occur naturally in surface waters at concentrations which are of concern but it may occur at high concentrations in water bodies subject to industrial pollution.

Alarmingly, the results of this study revealed that at all sites and seasons, the level of Hg recorded were significantly high ($p = 0.043$, $p < 0.05$) showing spread distribution. Even at the control site, S_0, compared to the other metals, high values of Hg were registered. This may be alleged to the uses of Hg forms for agricultural inputs. The pollution load discontinuously increases along the river from the upstream to downstream in all seasons. Winter samples recorded greater values than the summer and autumn (1.42 ± 0.35). All the experimental results of Hg are significantly ($p = 0.043$, $p < 0.05$) greater than the WHO/FAO set standards for fresh water (0.05mg/l) and maximum acceptable DW for livestock (0.003mg/l). These observed values depicted that River Mojo water is severely polluted and unsafe for the uses of domestic purposes.

Furthermore, the concentration of Pb has been observed to varying from 0.001 to 2.39mg/l in the study area. Relatively the results are low indicating that the solubility of Pb in alkaline conditions is less, viz, Pb interacts with pH, alkalinity and hardness and is most soluble in acidic and soft waters. The analytical results pointed out that more than half the analyzed results are above the maximum permissible limit of WHO for DWG (0.01mg/l) and all are below FAO guideline standard for irrigation water (5.0mg/l). Four results are above maximum acceptable DW for livestock (0.1mg/l) and the mean value (0.539 ± 0.8mg/l) revealed that the river water is unsafe for watering of livestock. The concentration of Pb in the research river water has higher values during winter period at all sites. Different from the others, the high Pb concentration was recorded at control site, S_o, and the least values are registered during summer and autumn. The increased Pb level during winter season may be reasoned out that the dilution potential of the water is decreasing due to the stop of rainfall. All the results analyzed are below WHO and FAO Guideline for surface water used for irrigation (5.0mg/l) (Table 6).

Correlation analysis

Correlation analysis was carried out for inter-metallic, inter - physico – chemicals and inter – metal - physicochemical parameters association to understand the significance ($p = 0.01$, $p = 0.005$, $p < 0.05$) of association among the metals and the other physico – chemical parameters. The statistical description on the outputs of the analysis pointed out that the parameters are negatively and positively associated. Out of 148 matrixes, 77 parameters are positively correlated. A correlation coefficient (r) value of more than 0.7 indicates high level of significance at p=0.01; between 0.5 and 0.7 is moderately significant at 0.05 level and less than 0.5 is insignificant.

The Pearson correlation coefficient matrix for trace heavy metals (AS, Cd, Cr, Hg and Pb) and physicochemical parameters in River Mojo is presented in Table 8. The relationship between the heavy metals studied offer remarkable information on the sources and pathway of the heavy metals. Arsenic was significantly positively correlated with Hg (r = 0.906), this may foretell that both have common sources. Cd, Cr and Pb have weak negative correlation with As and Hg. DO is only positively correlated with sulphate (r = 1.0, perfect correlation) and Hg (r = 0.574). TDS is associated positively with all parameters whereas temperature and DO are negatively correlated (r = -0.790) and Pb is positively correlated with S^{-2} (r = 0.926) because both react together and precipitate as PbS. pH is negatively correlated with all parameters except for DO. DO is negatively associated with COD and BOD (r = -0.471, r = -0.971) because in rich DO conditions, COD and BOD oxidize to CO_2 and water. DO is also negatively correlated with Cd (r = -0.991). Cd is positively related to Cr, Pb, and SO_4^{2-} (r= 0.982, 0.77, 0.992 (Table 6) for the reasons that all might have similar sources.

Table 8: Correlation coefficient matrix for physicochemical parameters of River Mojo during the period of summer (October 2013), n = 3.

	pH	Temp	DO	EC	TDS	RP	Nitrate	Sulfate	TA	COD	BOD	S^{-2}	Pb	Cr	Cd	Hg	As
pH	1																
Temp	-.785	1															
DO	.887	-.790	1														
EC	-.851	.429	-.852	1													
TDS	-.814	.429	-.877	.992	1												
RP	-.544	.934	-.688	.215	.254	1											
Nitrate	-.591	.045	-.614	.920	.918	-.149	1										
Sulfate	-.899	.802	1.000	.852	.873	.692	.607	1									
TA	-.773	.328	-.813	.991	.993**	.137	.958*	.809	1								
COD	-.481	-.113	-.471	.849	.838	-.315	.985*	.464	.896	1							
BOD	-.886	.640	-.971*	.951*	.966*	.494	.784	.969*	.929	.669	1						
Sulfide	-.860	.855	-.990*	.769	.799	.784	.496	.990*	.722	.341	.926	1					
Pb	-.814	.963	-.851	.328	.404	.954	-.007	.857	.272	-.178	.661	.926	1				
Cr	-.876	.598	-.956*	.965*	.979*	.445	.818	.954*	.948	.709	.998**	.904	.609	1			
Cd	-.916	.737	-.991	.911	.925	.597	.698	.992**	.874	.568	.991**	.964*	.770	.982*	1		
Hg	.318	.035	.574	-.744	-.806	.047	-.863	-.554	-.824	-.830	-.700	-.488	-.269	-.726	-.610	1	
As	-.093	.298	.267	-.392	-.484	.172	-.597	-.239	-.507	-.592	-.372	-.204	-.269	-.397	-.276	.906	1

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

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

5. Conclusion

The local informant explained that before 40 - 50 years back from today, in River Mojo, different species of fish and other organisms were living. But at present all are absent and the water cannot serve for the living habitat of living organisms. Thus, this study strengthens this fact which the results of the analysis came out that manifests high pollution load of River Mojo with trace heavy metals (As, Cr, Cd, Hg and Pb) and the analyzed physicochemical parameters that exceeds the set WHO/FAO standards. The results of analysis pointed out that the pollution nature varies temporarily and spatially. The sources can be from agricultural and industrial activities and municipal wastes. Thus, the River Mojo water is not in a safe position to be used for drinking, irrigation and livestock watering.

Additionally, the analyzed physicochemical parameters results show the levels of trace heavy metals in water from the majority of sampling sites exceeded permissible limit set by WHO/FAO and Ethiopian National Drinking Water Quality Guideline (ENDWQG, 2002) for drinking water. Variations in heavy metal concentrations in water are a consequence of a wide range of human activities on the river. Much precaution has to be taken especially on the use of water from River Mojo as it may pose risks to the users as it is mainly used as a major source of water for vegetable irrigation, livestock watering and for different domestic uses by the local dwellers.

6. Recommendation

The specific pollution sources should be identified and remedial solution should be taken. Each industrial plant has to establish modern treatment and/or search the reuse and recycle waste technologies. The concerned bodies should conduct the stringent follow - up on environmental protection concerns and bring to the ground the set environmental laws. Further investigation on the soil of irrigable farmlands and irrigated vegetables on concentration of the aforementioned trace heavy metals is highly needed

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