ORIGINAL ARTICLE

Heavy Metals in Sediments of Gilgel Gibe I Hydroelectric Dam Reservoir and its Tributaries

Kassim Kedir*, Abera Gure and Fuad Abduro

Department of Chemistry, College of Natural Sciences, Jimma University, Ethiopia

*Corresponding Author: kassimkedir08@gmail.com

ABSTRACT

Aquatic ecosystems are susceptible to pollution with heavy metals arising from anthropogenic and natural sources. In this study the pH, organic matter content, and concentrations of selected heavy metals (Cd, Pb, Cu, Cr, Co) in the sediments of Gilgel Gibe I Hydroelectric Reservoir and its tributaries were investigated. Sediment samples were taken by grab sampling from 5 sample sites. Microwave digestion was used for the extraction of the samples prior to quantitative determination of the target heavy metals by Flame Atomic Absorption Spectroscopy (FAAS).The obtained concentrations of the heavy metals were varied from 0.80 ± 0.46 - 10.4 ± 0.68 mg/kg (Cd), 0.80 ± 0.46 - 10.4 ± 0.68 mg/kg (Pb), 17.26 ± 1.94 - 28.38 ± 0.30 mg/kg (Cr);0.55 ± 1.38 - 9.74 ± 0.45 mg/kg (for Cu); and 7.53 ± 0.51 - 18.50 ± 1.11 g/kg (Co). One-way ANOVA ($p < 0.05$) indicated that the concentrations the studied heavy metals were significantly different among the sediment samples collected from the dam reservoir and its tributaries. The dam reservoir sediment accumulate higher concentration of Cd (i.e., 10.4 ± 0.68 mg/kg) and this value is above the sever effect level of National Oceanic and Atmospheric Administration (NOAA) and Canadian interim sediment quality guideline. Nada Kala contribute highest amount of metal accumulation compared with other tributaries. The degree of metal pollution was analyzed in terms of contamination factor and Cd has showed moderate contamination of reservoir sediment. Generally, the obtained findings demonstrated that the studied sediments have high concentrations of target heavy metals. Speciation study is recommended to determine the desorption tendency of the heavy metals towards water column as well as their risk on aquatic ecosystems.

Keywords: Flame atomic absorption spectroscopy; Gilgel Gibe Reservoir; Heavy metals; Microwave digestion; Sediment samples

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INTRODUCTION

Sediments, as basic components of our environment, provide nutrients for living organisms and also serve as a sink and reservoir for a variety of environmental contaminants (Latifah and Met, 2014). It has been recognized that aquatic sediments adsorb persistent and toxic chemicals like toxic heave metals at the levels many times higher than in the water column (Latifah and Met, 2014; Rod bell et al., 2014). In aquatic ecosystem, the concentrations of

heavy metals are often increased due to natural processes like geological weathering of nearby rocks, airborne dust, forest fire and vegetation as well as anthropogenic activities such as draining of sewages, dumping of domestic wastes, recreational activities and application of agrochemicals such as fertilizers and pesticides (Rosenberg et al., 1997; Loska et al., 2002; Moore et al., 2011; Adebayo, 2017).

Heavy metals such as Cu, Zn, Fe, Mn, Cr and Ni are essential metals since their presence in trace amounts play a significant role in biological systems. However, when their intake is excessively higher, they may produce toxic effects (Ong et al., 2013). On the other hand, heavy metals such as Cd, Pb, As and Hg are toxic at even trace concentrations levels (Ong et al., 2013).They have been labeled as very harmful chemicals in drinking water and other food products since they can disturb enzyme function, cause cancer, damage organ and nervous system, and death of living organisms (Nzeve et al., 2014).

In aquatic ecosystems, heavy metals are usually monitored by measuring their concentration levels in sediments. Because, sediment is considered as the important sink for heavy metals (Latifah and Met, 2014). It also plays a significant role in the remobilization of the heavy metals in aquatic systems under favorable conditions and in interactions between water and sediment (Shoaei et al., 2015). Heavy metals are persistent and thus, they may be either adsorbed on sediment particles or accumulated in aquatic organisms (Adebayo, 2017). Generally, the levels of the heavy metals in sediment are often several orders of magnitude higher than in the overlying water column (Fonsea et al., 2011).

Gilgel-Gibe I hydroelectric dam was constructed on Gilgel Gibe River in Jimma Zone, Southwest Ethiopia and has been operated since 2004 to generate 184 MW hydroelectric power (Yewhalaw et al., 2009). The reservoir formed by the dam receives the incoming water from four major tributaries including Gilgel Gibe, Nada Guda, Nada Qalla and Nadhi rivers. Nowadays, the reservoir is also used for fishing and recreation for the surrounding communities. Because of intensified agricultural activities; domestic wastes from the surrounding towns (Danaba and Asandabo); exhausted vehicle gas released from the nearby cross country main road and other activities during the construction of the dam, the sediment of the reservoir is expected to contain higher levels of heavy metals. Thus, investigation of the levels of heavy metals in sediments of the dam reservoir and its tributaries is important. Therefore, in this study, the levels of selected heavy metals including Cd, Pb, Cu, Cr and Co in the sediments of the Gilgel-Gibe I Hydroelectric dam reservoir and its tributaries were determined using flame atomic absorption spectroscopy (FAAS).

MATERIAL AND METHODS

Study area

Gilgel Gibe (I) Hydroelectric Power Dam is located in Jimma Zone, Oromia Regional State, at about 260 km from Addis Ababa in southwest Ethiopia. It was constructed at latitude of$7^o54'31.88"$N and longitude of $37^o22'24.33"$E geographical location. It is located at about 57 km in north east of Jimma city and has maximum reservoir capacity 917,000,000 m^3, which can cover more than 54 km^2 of land (Legese et al., 2017).
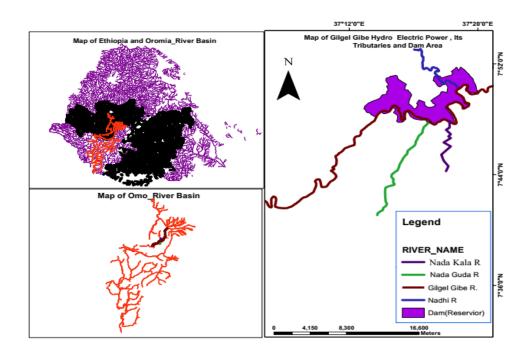
Figure 1. Map of the study area

Sampling and sample pre-treatment

Sediment samples were collected by grab sampling from the upper section (0 - 10 cm) during dry season from March – May, 2017 using soil auger. From the reservoir, 25 samples were taken from different sampling points which were randomly selected in all directions of the lake and its center. Similarly, from each tributary (Nada Guda, Nada Kala, Gilgel Gibe and Nadhi rivers), 12 samples were collected at each river mouth following the standard procedure (Robert and Christopher, 2001). The samples were collected in pre-cleaned polyethylene bags. At the sampling site, the samples were mixed (homogenized) by spreading on plastic sheet and totally, 5 composite samples, i.e., 1 composite sample for the Dam Reservoir, and each tributary were separately taken for the subsequent analysis. Then, the obtained composite samples were transported to Jimma University, Analytical Chemistry Research Laboratory, where the samples were air-dried at room temperature by spreading on flat plastic tray. Finally, the samples were ground using ceramic mortar and pestle and sieved using 2 mm mesh size sieve. The ground samples were stored in polyethylene bags and stored in refrigerator until the next digestion procedure.

Analysis of pH and organic matter

The pH of sediment samples was determined using the standard method (Van Reeuwijk, 2002). Soil organic matter contents (%OM) of the samples were also estimated by the Walkley-Black wet oxidation method (Walkley and Black, 1934).

Digestion of sediment samples

The samples were digested using microwave (BERGHOF-speed wave digester) digestion procedure earlier reported (Esen and Balci, 2008). Accordingly, 0.5 g of sediment sample was accurately weighed and transferred into the microwave vessel. The sample was then moisturized with deionized water. Then, after addition of 2 mL 40% HF, 4 mL 68% HNO_3 and 1 mL 30% H_2O_2 the sample was digested for 15 min at 210 ℃ fixing the pressure at 200 psi. Subsequently, after cooling for 30 min, 25 mL H_3BO_3 was added and then, the content was irradiated again for 15 min. Finally, the digested sample was filtered and transferred to 50 mL volumetric flask and the remaining volume was then filled to the mark with deionized water to make ready for FAAS analysis.

Metal determination

Quantitative determination of the heavy metals were performed by FAAS (Analytic model AA nova AA 330) equipped with hallow cathode lamp as a source of radiation for individual elements. Before, real sample analysis,

the instrument was calibrated by preparing series of concentrations of the standard solutions of each analytic. After, constructing the calibration curves, the analyses of the concentrations of the heavy metals in the sediment samples were separately carried out.

Statistical Analysis

Data were analyzed using one-way ANOVA to determine variations in the concentrations of heavy metals among the studied sediment samples. SPSS software (version 23) was used for the statistical analysis and difference was considered statistically significant at $p < 0.05$".

RESULT AND DISCUSSION

Concentration of the heavy metals

The obtained pH, %OM and concentrations of the heavy metals (Cd, Pb, Cr, Cu and Co) in sediments of Gilgel Gibe I hydroelectric dam reservoir and its potential tributaries such as Nada Kala, Nada Guda, Gilgel Gibe and Nadhi Rivers are shown in Table 1.

Table 1. The pH, %OM and concentrations of the studied heavy metals in the sediments of Gilgel Gibe I hydroelectric reservoir and potential tributaries (Mean ± SD, n = 6).

Sample site	Heavy metals concentration (mg/kg dry weight)					pH	%OM	Reference
	Cd	Pb	Cr	Co	Cu			
Nada Guda River	9.17 ± 0.45^a	21.69 ± 0.94^a	23.24 ± 0.94^a	9.10 ± 0.53^a	6.20 ± 1.29^b	5.00 ± 0.01	3.25 ± 0.20	
Dam Reservoir	10.4 ± 0.68^a	19.59 ± 0.12^a	22.93 ± 0.96^a	10.10 ± 1.16^b	9.74 ± 0.45^a	6.51 ± 0.50	6.98 ± 0.80	
Nadhi River	8.59 ± 0.45^a	22.26 ± 0.12^a	27.5 ± 0.57^b	7.53 ± 0.51^a	4.55 ± 1.38^b	5.53 ± 0.88	3.41 ± 0.35	
Gilgel Gibe River	8.81 ± 0.55^a	17.26 ± 1.94^a	30.13 ± 0.71^b	9.53 ± 0.97^a	9.37 ± 1.75^a	5.73 ± 0.95	3.82 ± 0.25	
Nada Kala River	0.80 ± 0.46^b	28.38 ± 0.30^b	38.76 ± 1.00^c	18.50 ± 1.11^c	7.42 ± 0.91^a	6.05 ± 0.56	2.04 ± 0.05	
Sever Effect Level	10.00	250.00	110.00	55.30	110.00	-	-	NOAA, 2009
Lowest Effect Level	0.60	31.00	26.00	-	16.00	-	-	NOAA, 2009
ISQG (2002)	0.60	35.00	37.30	-	35.70			Desta et al., 2012
Tekeze Dam, Ethiopia	1.00	12.75	33.00	17.00	36.00	-	-	Desta et al., 2012
Avisar Dam, Turkey	0.76±0.40	2.44±2.20	14.48±4.40	-	29.98±4.70			Öztürk et al., 2009

Mean values with similar superscript within a column are not significantly different ($p > 0.05$); NOAA, National Oceanic and Atmospheric Administration, %OM, Percent Organic Matter; ISQG (Interim Sediment Quality Guidelines

The obtained results demonstrated that, the sediments of the Gilgel Gibe I hydroelectric dam reservoir and its tributaries accumulate considerable amount of the target heavy metals in varied concentrations. The order of their accumulations is Cr > Pb > Co > Cd > Cu across all the sediment samples. Dam reservoir sediment accumulates relatively higher concentrations of Cd and Cu than the rest sample sites.

The concentrations of Cd in the studied samples were ranging from 0.80 ± 0.46 - 10.4 ± 0.68 mg/kg, which are all above the maximum limit set for the lowest effect level of Cd (i.e., 0.6 mg/kg) in the sediment (NOAA, 2009and SQG, 2002). The lowest and highest concentrations were observed from sediments of Nada Kala River (0.80 ± 0.46 mg/kg) and the dam reservoir (10.4 ± 0.68 mg/kg). Cd has strong cation exchange capacity with element such as calcium in the mineral structure like calcium carbonate and non-competitive sorption and retention due to organic matter functional group like organic acids, phenols and surface charges (Dekunet.al. 2013). The occurrence of Cd in natural soils is largely influenced by the amount of Cd in the parent rock (Heike, 2004). The lowest concentration of Cd at Nada Kala accounts 0.80 ± 0.46 mg/kg can be due to less in source contribution of Nada Kala River even though; this tributary contributing high amount of selected target metals. Except for Cd concentration, the concentrations of other studied metals in sediment collected from Nada Kala have not exhibited significant variations with the rest sample sites. As stated by Heike 2004, Cd solubility decrease as pH increase with the values for calcareous soils (pH approximately 8.4), precipitation of $CdCO_3$ to occur with low cation exchange capability, low content in organic matter controls Cd solubility but the pH values obtained in all the samples are not in a safe

side to facilitate the combined state of Cd. For these reason continuous monitoring the reservoir environment and biota is mandatory due to the total Cd concentration indicating bad signal for the environment.

The chemistry of Pb in sediment is affected by factors like specific adsorption, precipitation of stable compounds and formation of complex compounds with soil organic matter (Heike 2004). Total metal concentrations in soil/sediment are further influenced by geochemical and biogeochemical processes where metals may be redistributed to different parts of the soil profile (Rieuwerts et al., 1998). Maximum concentration of total Pb (28.38 ± 0.30 mg/kg) was recorded in Nada Qalla sediment sample in which less amount of organic matter was obtained. Other tributaries: Gilgel Gibe, Nada Guda, and Nadhi rivers had contributed to a considerable amount of Pb to the dam reservoir. The presence of relatively low concentration of Pb in the dam reservoir sediment might be attributed to some signal of leaching as mobile fraction to water column (Kedir et.al. 2017). One-way ANOVA ($p < 0.05$) revealed that Pb concentration in Nada Kala is significantly high and different from the other sample sites. Low to medium molecular weight OM can provide dissolved ligand for metals to form soluble complexes (Chang et al. 2014). Acidic range of sediment pH value also facilitate the free metal form instead of forming a complex in basic environment and the pH values of the studied sample is in acidic region and the determined amount of organic matter is an implication for the need of continuous monitoring to look for the future fate of the reservoir aquatic environment and biota.

Adsorption and precipitation behavior of Cr in sediment is controlled by a variety of

factors such as redox potential, oxidation state, pH, soil minerals, competing ions and complexing agents (Heike, 2004). Studying the behavior of Cr is more pronounced by the precipitation of Cr in a wider pH range from acidic to basic region (Ghorbel-Abid and Trabelsi-Ayadi, 2015). From all the studied metal in Gibe I hydroelectric dam reservoir and its potential tributaries sediments, the highest concentration of total Cr was determined in Nada kala river sediment which might be due to the sediment surface immobile all forms of Cr through complexion and significant variation were observed in the concentrations of Cr among different sample sites.

Distribution of Cu between different soil constituents is mostly influenced by the presence of soil organic matter and Mn and Fe oxides. The maximum concentration of Cu (9.74±0.45 mg/kg) was recorded from the sediment of Dam Reservoir and the minimum (4.55±1.38 mg/kg) was observed from Nadhi River sediment, which is below the lowest Effect Level. As compared to the concentration of Cu (36 mg/kg) recorded in Tekeze dam sediment the result obtained in Gilgel Gibe I reservoir sediment and its tributaries were lower. Various literatures have witnessed as Cu shows a strong affinity for soil organic matter so that the organic-fraction and soil Fe and Mn oxides serve as a sink for Cu, however; their stability depends on the pH. At higher pH it strongly adsorb to the organic matters, but in acidic range Cu is desorbed to the solution and become environmental concern(Chang et al. 2014).

The maximum concentration of Co18.50±1.11 mg/kg determined at Nada kala is an indication for requiring detailed analysis which can be due to an association with other metals obtained in high concentration of Pb and Cr along with high pH values responsible in facilitating metals to exist more in combined state with the surface of the sediment.

The accumulation of target heavy metals in sediment of studied sample followed the following order at each specific sample site: Nada Guda: Cr > Pb > Cd > Co > Cu. Dam Reservoir: Cr > Pb > Cd > Co > Cu. Nadhi River: Cr > Pb > Cd > Co > Cu. Gilgel Gibe: Cr > Pb > Cd > Cu > Co. Nada kala: Cr > Pb > Cd > Cu > Co. Probably, one of the most important natural factors controlling to the spatial variations of the heavy metals in the sediment is sorption and adsorption phenomena (Aprile&Bouvy,2008) which is influenced by sediment physicochemical properties.

Heavy metals in water-sediment interface can be combined with different organic and inorganic group and then, form an association between the metallic ion with the functional group and surface phenomena along with various physicochemical factors influencing the velocity of this association rate and decomposition processes (Aprile and Bouvy, 2008). As can be observed from Table 1, the target heavy metals have been accumulated in the sediments the dam reservoir and the studied potential tributaries. This may indicate that the heavy metals entered the sediments from various sources like natural geological weathering and anthropogenic contribution such as agrochemicals, municipal wastes, release from machineries and heavy trucks during dam. Generally; the studied sediments contain high concentration of the target metals indicating the need for continuous monitoring along with their source so as to take the right intervention mechanisms.

Contamination factor

The contamination factor (CF) of target heavy metals was calculated based on

various literature (e.g. Min et al., 2013; Ferati et al, 2015; Kerolli-Mustafa et al., 2015). It is used to evaluate the contamination level of the individual heavy metal based on average world back ground reference concentration ($C_{ireference}$) (Burton, 2002; Chakravarty and Patgiri, 2009).

$$CF = \frac{Ci\ sample}{Ci\ reference}$$

Where: CF = is the contamination factor

$C_{isample}$ = sample concentration

$C_{ireference}$ = reference background values for heavy metals in sediment

Table 2. Contamination factor (CF) of the studied heavy metals

Target Analyte	Cd	Pb	Cr	Co	Cu
Max. CF	1.04	0.14	0.36	0.68	0.18
Sample	Reservoir	Gilgel Gibe	Nada Kala	Nada Kala	Reservoir

As indicated by maximum contamination factor (Table 2), the Gilgel Gibe Reservoir sediment accumulated Cd and Cu, Gilgel Gibe river sediment accumulated Pb and Nada Kala river sediment accumulated Cr and Co metals. According to Håkanson (1980) classification of sediment contamination level CF<1 points to low contamination, 1≤CF<3 moderate, 3≤CF<6 considerable and CF≥6 very high contamination factor (Ferati et al, 2015) and the dam reservoir sediment of accumulate Cd metal having a contamination factor that range in moderate contamination an indicator to continuous monitoring and the remaining metals are in a low contamination range.

Accuracy of the method and validation of the result were checked by the recovery test spiking known concentration target metals standard solution and the obtained percentage recovery data for Cd 86%, Pb 105%, Cr 98%, Co 108% and Cu 102% indicating in the acceptable range of accuracy and the result is valid.

CONCLUSION

Gilgel Gibe I hydroelectric dam was built to serve 50-70 years but sustaining its environment depends up on regular monitoring and proper intervention mechanism. Considerable amount of heavy metals load such as Cd, Pb, Cr, Co and Cu are contributing by main tributaries and accumulating to the reservoir sediments. Maximum concentration of Pb, Cr and Co was observed in Nada Qalla sediment sample and this might be due to the geochemical, physicochemical nature of the sediment along with the anthropogenic contributions. The contamination factor of the target Pb, Cr, Co and Cu clearly indicating some signal of metal accumulation which is not in bad situation but cadmium accumulation is alarming having a contamination factor in a range of moderate contamination requiring critical follow up. All the tributaries are long running rivers crossing extensive farming like coffee plantation, agricultural land utilizing varies agrochemicals and leachate of municipal open dumpsites the studied metals can be sourced from varies sources so; the obtained result is informing as the need of upstream environment analysis is mandatory. The comparison of mean concentrations of the target metals with the

sediment quality standards indicates that, all target metals were below sever effect level except Cd and Cr metals are almost above lowest effect level for sediment quality standard. For these reason elemental speciation (toxicity analysis) and mobility study has to be carried out in seasonal variation to understand tendency of metal desorption to water column. It is also recommended the necessity of more comprehensive study by considering longitudinal data and other factors such as geochemical and physiographic factors for better insight about heavy metals in the sediments of the Reservoir.

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