

The Concentrations of Heavy Metals (Ni, Cd, Cu, As and Pb) from the Selected Sampling Points along River Molo Wood Treatment Sites

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Abstract:- Humans and hydrological systems interact at the point where water resources are managed, and this has profound effects on human settlement patterns and economic growth. The wood treatment plants around Nakuru County area accumulated over time could pose serious health problems to the residents living around River Molo and its environs. Wood treatment could contribute heavily on the accumulation of heavy metals. Therefore, research on the determination of physico-chemical characteristics, Geochemical speciation of heavy metals and heavy metals in water and soils from River Molo is very important. Water and soil samples will be gathered during dry and wet seasons from the selected sampling points. The water samples will be analyzed for dissolved oxygen, temperature, dissolved solids, electrical conductivity, PH and heavy metals (Pb, Ni, Hg, As and Cd) using Atomic Absorption Spectrophotometry and scanning electron microscopy (SEM). Atomic Absorption Spectrophotometry (AAS) with Perkin-Elmer 3000 was used for analysis of heavy metals. Lead (Pb) concentration ranged between 0.06 - 10.24 mgkg⁻¹, Cd was within the range of 0.04-0.57 mgkg⁻¹, Ni concentration ranged between 0.29-30.24 mgkg⁻¹, and Zn between 0.1-91.58 mgkg⁻¹ in water from the Nakuru County. Concentrations of Pb and Cd were higher than the permissible limits stipulated by the World Health Organization (WHO) and other international set standards.

Keywords:- Concentration, elements, heavy metals, permissible limits, metal speciation.

I. INTRODUCTION

Rivers are valuable water sources, priceless and irreplaceable assets which are essential for conservation of nature, recreational, and also economic growth. The quality of water in rivers depends on vegetation, land use and geological morphology in the catchment areas (Benamer, 2014). Heavy metals can find way into the environment as micro pollutants through anthropogenic sources such as agricultural, industrial and domestic effluents. Agricultural activities act as sources of heavy metals in water, such as in fertilizers (Cd, Pb, Cr and Zn), pesticides (Pb, Cu, As and Zn), manure and composts (As, Pb, Cd, Cu, Zn and Ni), and sewage sludge (Cu, Cd, Ni, Zn, Pb) (Udeigwe *et al.*, 2015). Metal-induced toxicity symptoms in human beings range from milder ones such as nausea, excessive salivation, vomiting, abdominal pain, diarrhea with bleeding, dizziness, dermatitis, headaches, aggressiveness and hallucinations to very serious ones such

as endocrine disruption, lung disease, liver and kidneys failure, hepatic damage, mutagenic, carcinogenic and teratogenic effects (Oyekunle *et al.*, 2012). In this research several heavy metals, particularly Pb, Cd, Hg, Ni, As and Cr will be investigated. This group consists of the most toxic five metals (Cd, Ni, As, Hg and Pb) which are remarkably dangerous to human health and natural ecosystem (Gunnar *et al.*, 2015).

In trace metal chemistry, trace metal contents in samples of interest are usually quantified as total concentration. This does not give insight about environmental mobility, biogeochemical behavior, toxicity, bioavailability, and risks that are intensely dependent on the chemical composition of heavy metals (Nigam *et al.*, 2015). Considering the enhanced understanding of metabolic, biological and toxicological effects of heavy metals, it is necessary to measure heavy metals as "totals" as well as determine quantitatively different chemical forms of these heavy metals (speciation) (Clough *et al.*, 2013). Information about speciation of heavy metals is conspicuously lacking in River Molo. Previous studies show that the most toxic forms of heavy metals in water are free metal ions, followed by less toxic strong metal complexes (Nystrand *et al.*, 2016). Moreover, it has also been found that Cr (VI) is very toxic while Cr (III) is an essential element, Mn(III) oxidation states are more toxic than +2, +4, +6 and +7 (Nigam *et al.*, 2015) and organometallic compounds of Sn, Hg and Pb are more toxic than their corresponding inorganic forms (Ashraf *et al.*, 2012). In sediments, carbonate bound, metals in exchangeable, and Fe-Mn bound speciation are considered to be more mobile and bioavailable while the organic bound and residual metal fractions are stable and non-bioavailable (Baran & Tarnawski, 2013). In this research different forms (species and oxidation states) will be determined and therefore more information regarding toxicity of heavy metals will be obtained. There are factors in the environment which affect speciation of heavy metals, and should be considered in speciation research. Among the environmental factors is the redox condition which determines the oxidation state of some metals and also affects the toxicity and bioavailability of the element (Pradhanang, 2014). Other physical chemical parameters which affect metal speciation and bioavailability are pH, temperature, water hardness, dissolved organic matter, redox-potential, DO and salinity (Bryn *et al.*, 2016). These parameters are also important in determining the quality of water and therefore they will be determined in this research.

Heavy metals are phototoxic and can act as micro pollutants. Lead, Hg, and As present a serious challenge to human health and natural ecosystems. Such effects may alter the general composition, functionality, and the functional diversity of the microbes in the soil (Chen *et al.*, 2017). Some of these also affect the genetic variation and growth of plants due to high mobility once in the soil (Ashraf *et al.*, 2012). Therefore, soil contamination leads to fundamental bioaccumulation of the metal impurities such as Pb, Hg, and As especially in small organisms which follow the high trophic levels in the food chain. The concentration of these metals may induce toxicity in microbial systems and plants which may ultimately be transferred to humans resulting in totetratogenicity, mutagenicity, and carcinogenicity (Tchounwou *et al.*, 2012). The extend of toxicity of the heavy metals is dependent on the oxidation state of the metals, the organics attached (methyl or ethyl groups), as well as the amounts of the metals that have been absorbed by the soil. Moreover, deposited Pb, Hg, and As on the soil surface from treatment sites are carried by runoff water to other locations away from the treatment sites.

The problem being experienced by the world in the present age is pollution of the environment by inorganic, organometallics and organic substances. The World Health Organization report indicate that in the year 2004, approximately 1.1 billion lacked safe drinking water. Majority of these populations lived in Africa, India and the Middle East. The report also revealed that 42% of Africa lacks safe drinking water. A prediction by experts shows that more than 47% of the world population will face serious water challenges by 2030. Among the possible pollutants of water, heavy metals and persistent organic pollutants (POPs) have attracted a lot of attention because they are toxic even at low concentrations. Heavy metals are non-bio-degradable and tend to accumulate in human and animal bodies to very toxic high levels hence leading to undesirable effects.

II. MATERIALS AND METHODS

A. Sample collection, preparation and treatment

The samples of water will be collected during the dry and wet season from six different sampling points in three replicates (using 2.5 L amber bottles and plastic containers) and concentrated nitric acid will be added to one of the bottle containing water samples for preservation.. Sediments will be collected from the same sampling points as the water samples in two replicates using a core sampler. The samples will be placed into plastic containers (for heavy metals and inorganic samples) and aluminium containers (for organic samples). These samples will be placed in a cold box and transported to the laboratory where they will refrigerated at -10°C awaiting the analysis. Sediment samples will be air dried and pulverized before being refrigerated (Alshikh, 2011). Sampling points will be located using a global information system (GIS).

pH of the water samples will be determined using a pH meter. The PH probe will be rinsed thoroughly using deionized water and calibrated using buffers of pH 7 and pH 9. Since pH values are temperature dependent, the measurements will be at the point of sample collection. The water samples electrical conductivity will be measured using a conductivity meter under standard conditions of temperature and pressure. Measurement of conductivity will be made immediately at the sample collection site because conductivity changes with time. The concentration of chlorides, fluorides, phosphates, sulphates, hydrogen carbonate and total carbonate in surface water will be determined automatically by means of a titroline processor using appropriate reagents. The detailed procedure for analysis of these components is described elsewhere (Zhong-he & Ármannsson, 2005).

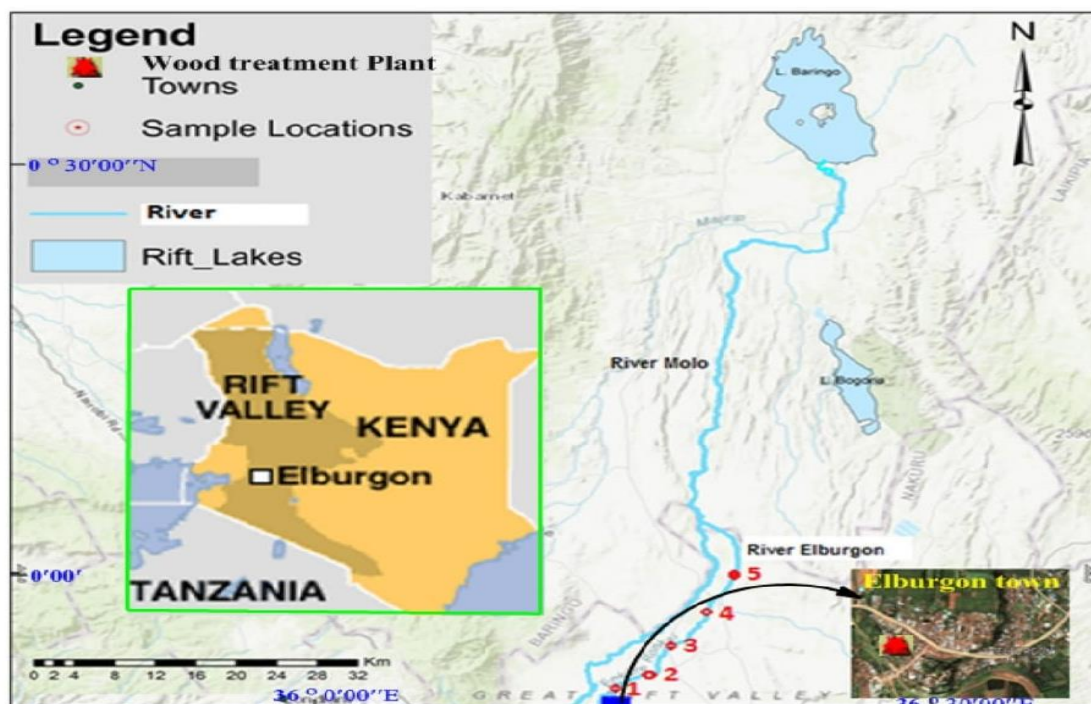


Fig. 1: Map of sampling sites

A. Sample analysis

Solutions of 5.00, 4.50, 4.00, 3.50, 3.00, 2.50, 2.00, 1.50, 1.00 and 0.50 mg/L will be prepared by appropriate dilution of 1000 mg/L of each metal ion solution. These will be used for the calibration of the Atomic absorption spectrophotometer. Water samples will be digested using nitric acid as described elsewhere (Ogoyiet *et al.*, 2011). The levels of Cd, Ni, Pb, K, Ca, Na and Mg in the worked-up samples will then profiled using atomic absorption spectrophotometer (AAS). Mercury and Arsenic will be determined using cold vapour atomic absorption spectrophotometry (Ogoyi *et al.*, 2011).

B. Speciation of heavy metals in sediment

A sample of one gram will be extracted using 1M MgCl₂ (pH 7.0) at a ratio of 1:8, with continuous agitations for 1 hour at room temperature to obtain (fraction1) the exchangeable fraction. The residue will be extracted with 1M NaOAc at a ratio of 1:8. The mixture will then be agitated for 5 hours to obtain (fraction 2) the carbonate bound form. The fraction bound to iron and manganese oxides (fraction 3) will be extracted by reacting the residue obtained in fraction 2 with 0.04 M NH₂OH.HCl in 25% (v/v) HOAc with agitation for 6 hours. The residue from fraction 3 will be extracted by adding to it 3 mL of 0.02 M Nitric(v)acid and 5 ml of 30 % hydrogen peroxide and pH adjusted to pH 2.0 with HNO₃. The solution will then be agitated at 96 °C for 2 hours and 3 mL of 30 % H₂O₂ will be added and sample will be agitated for 3 hours. After cooling, 5 mL of 3.0M ammonium acetate in 20% (v/v) HNO₃ will be added. The sample will then be diluted to 20 mL and agitated continuously for 30 minutes. After each successive extraction, the supernatant will be separated by centrifuging 7000 rpm for 30 minute. The supernatant will be filtered through a 0.45 micron filter paper. The result is the fraction

B. The Physico-chemical properties of water samples

Table 1: Physiochemical properties of water samples in River samples around wood treatment sites(Mean +SD)

Sample	pH		DO		Temperature		conductivity		salinity	
	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry
Q ₁	8.3300+ 0.146*	7.0200+ 0.013*	6.4500+ 0.061 ^a	5.9000+ 0.000 ^b	26.4000+ 0.214*	29.5000+ 0.000*	40.0400+ 5.405 ^b	22.2000+ 0.000 ^c	0.0100+ 0.000	0.0150+ 0.000
Q ₂	8.2850+ 0.031*	6.8960+ 0.008*	5.9000+ 0.112 ^b	6.1000+ 0.000 ^a	25.5000+ 0.242*	29.5000+ 0.000*	69.0000+ 4.7800 ^a	24.7000+ 0.000 ^c	0.0400+ 0.000*	0.0190+ 0.000*
Q ₃	8.4200+ 0.180*	6.7250+ 0.006*	5.8600+ 0.112 ^b	6.1000+ 0.000 ^a	25.6000+ 0.000*	29.5000+ 0.000*	22.6500+ 2.444 ^c	18.2000+ 0.000 ^c	0.0300+ 0.014	0.0220+ 0.000
Q ₄	8.5050+ 0.123*	6.2800+ 0.000*	6.4000+ 0.131 ^a	5.8000+ 0.000 ^b	25.5500+ 0.606*	28.8000+ 0.000*	19.1000+ 3.243 ^d	32.4000+ 0.000 ^a	0.3100+ 0.000*	0.150+ 0.000*
Q ₅	8.2100+ 0.131*	6.9500+ 0.000*	6.0000+ 0.131 ^a	6.1000+ 0.000 ^a	25.8000+ 0.131*	28.5000+ 0.000*	15.8500+ 0.919 ^e	25.7000+ 0.000 ^b	0.0150+ 0.007	0.0170+ 0.000
FEPA	6.9	6.9	5.0	5.0	40	40	1	1	n/s	n/s

C. Heavy metals concentration in water

The concentration of someHM was found to be greater than that of the WHO. The concentration indicated no difference (p>0.05) with reference to the location or season. There was also insignificant (p>0.05) location-season

bound to organic matter and sulfide (fraction 4). The residue from fraction 4 will be digested with HF/HNO₃/HClO₄ mixture (in the ratio 7:3:1) at 120 °C for 2 hours to obtain the residual fraction (fraction 5). The filtrate obtained in each step of the extraction will be analyzed for heavy metals. (Pradhanang, 2014).

C. Quality control/Quality assurance (QC/QA)

Control sample (distilled water and sediment) will be analyzed for heavy metals, essential elements, carbonates, fluorides, chlorides, phosphates and organic pollutants prior to the analysis of water samples and sediments from River Molo. Standard concentrations will be prepared in such a way that it will be within the bracket of components in the water and sediment sample. This is termed the analysis range. The analyses of samples will be conducted in replicates to enhance the validity and reproducibility of the results. To one sample out of 20 samples, a known concentration of the analyte will be added and the recovery checked. If a recovery of ~95% is obtained then this will be good enough in order to proceed with analysis (Zhong-he & Armannsson, 2005).

III. RESULTS AND DISCUSSION

A. The Physico-chemical properties of sediments and water samples

The measurement of physiochemical properties with influence in toxicity and environmental mobility of heavy metals is as shown in the Table 1 below. For different sampling seasons, there was a significant variation (p<0.05) in conductivity and DO. Furthermore, salinity, temperature and pH for the sampling sites showed seasonal difference at p<0.05.

interaction over the regimes of sampling. Nonetheless, there was a non-statistical variations in the arsenic concentration in the water samples but there was variability due to numerical differences (Q₁> Q₂> Q₃> Q₄> Q₅). The results are as indicated in Tables below:

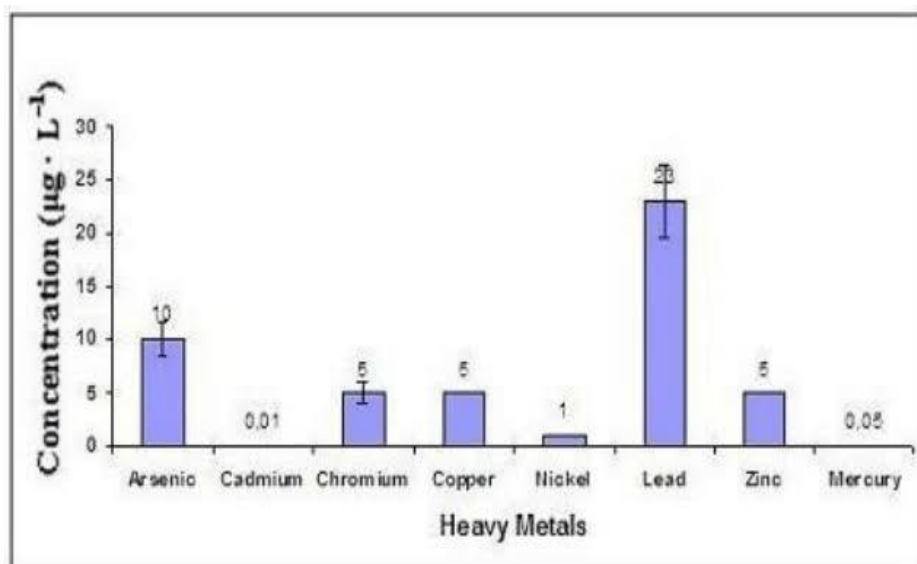


Fig. 2: Concentration of heavy metals

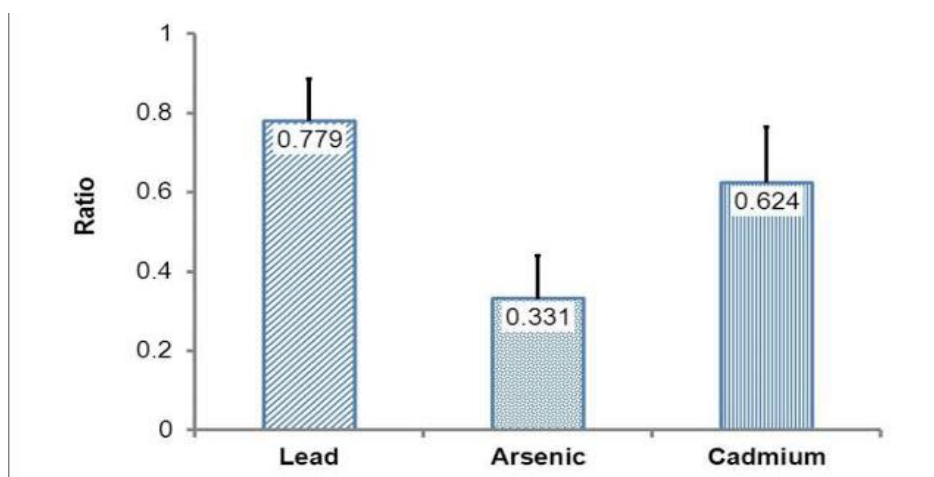


Fig. 3 :Ratio of concentrations of Pb, As and ,Cd

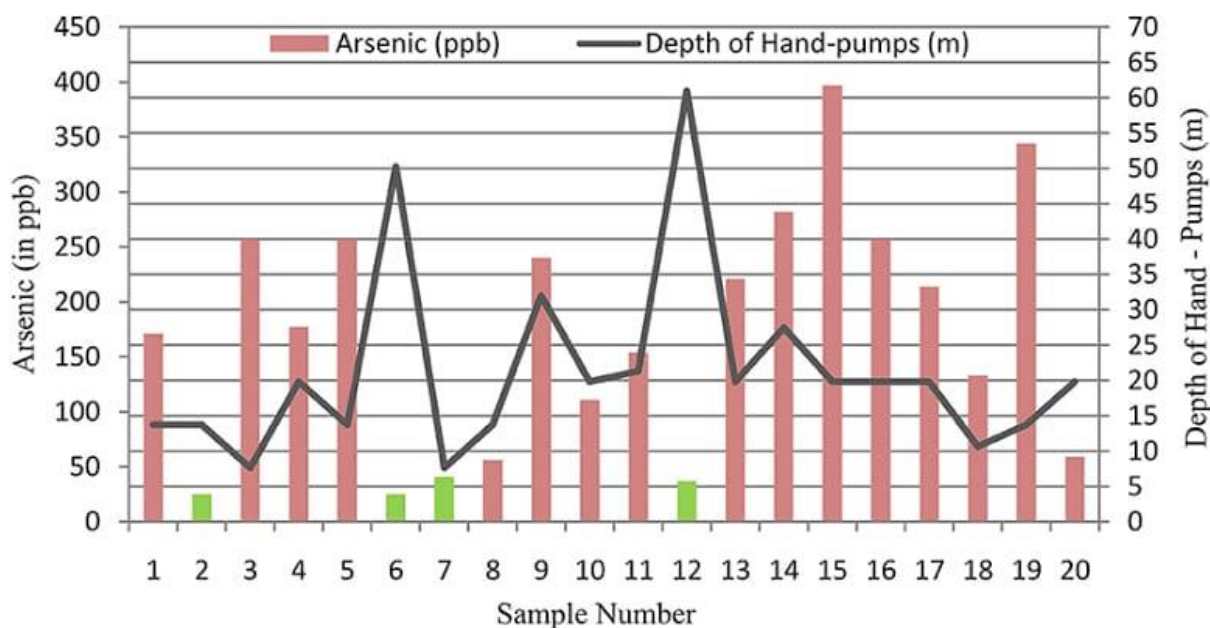


Fig. 4: Graph of Arsenic concentration at different hand depths

D. Concentration of Heavy Metals (Ni, Cd, Cu, As and Pb) ion water samples around wood treatment sites

Table 2: Mean (+SD) mg/L Arsenic concentration in the WATER samples around wood treatment sites

Sample location	Conc. (Rainy)	Conc. (Dry)
Q ₁	0.7850 + 0.001	0.5705 + 0.000
Q ₂	0.8560 + 0.000	0.5000 + 0.000
Q ₃	0.2459 + 0.001	0.6700 + 0.000
Q ₄	0.4200 + 0.000	0.8900 + 0.000
Q ₅	0.8000 + 0.000	0.6500 + 0.000

Table 3: Mean (+SD) mg/L Lead concentration in the WATER samples around wood treatment sites

Sample location	Conc. (Rainy)	Conc. (Dry)
Q ₁	0.4550 + 0.001	0.3660 + 0.000
Q ₂	0.4155 + 0.000	0.5523 + 0.000
Q ₃	0.3234 + 0.001	0.7500 + 0.000
Q ₄	0.5100 + 0.000	0.9450 + 0.000
Q ₅	0.6555 + 0.000	0.7435 + 0.000

Table 4: Mean (+SD) mg/L Chromium concentration in the WATER samples around wood treatment sites

Sample location	Conc. (Rainy)	Conc. (Dry)
Q ₁	0.6050 + 0.001	0.5211 + 0.000
Q ₂	0.5340 + 0.000	0.5140 + 0.000
Q ₃	0.7450 + 0.001	0.6600 + 0.000
Q ₄	0.8100 + 0.000	0.7650 + 0.000
Q ₅	0.8023 + 0.000	0.7000 + 0.000

Table 5: Mean (+SD) mg/L Copper concentration in the WATER samples around wood treatment sites

Sample location	Conc. (Rainy)	Conc. (Dry)
Q ₁	0.6654 + 0.001	0.4560 + 0.000
Q ₂	0.4560 + 0.000	0.4000 + 0.000
Q ₃	0.7645 + 0.001	0.4789 + 0.000
Q ₄	0.6200 + 0.000	0.4900 + 0.000
Q ₅	0.5900 + 0.000	0.5500 + 0.000

Table 6: Mean (+SD) mg/L Nickel concentration in the WATER samples around wood treatment sites

Sample location	Conc. (Rainy)	Conc. (Dry)
Q ₁	0.3550 + 0.001	0.3500 + 0.000
Q ₂	0.2260 + 0.000	0.3050 + 0.000
Q ₃	0.2200 + 0.001	0.2400 + 0.000
Q ₄	0.4120 + 0.000	0.3200 + 0.000
Q ₅	0.1900 + 0.000	0.1000 + 0.000

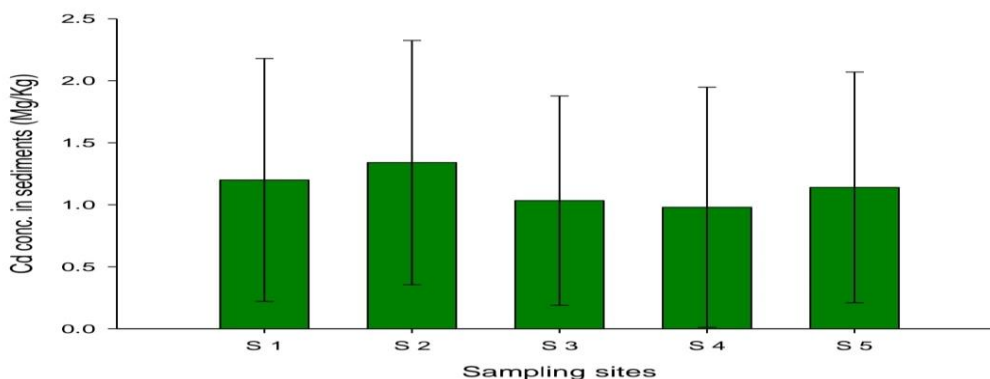


Fig. 5: Cd concentration in different sampling sites

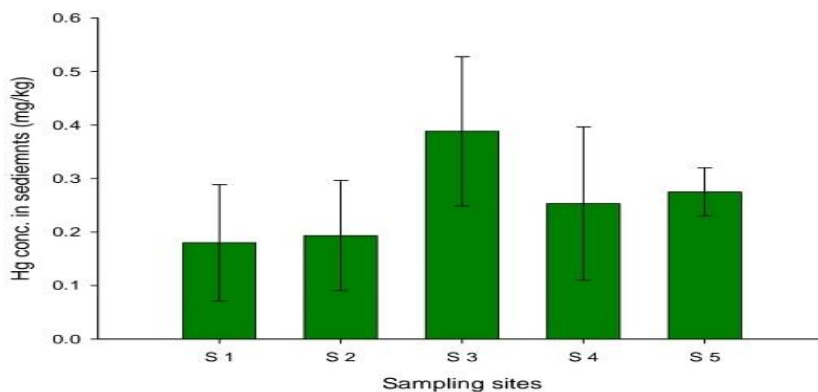


Fig. 6: Hg concentration in different sampling sites

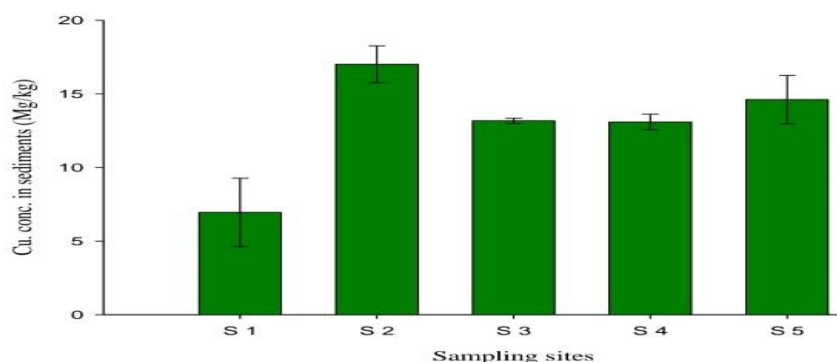


Fig. 7: Cu concentration in different sampling sites

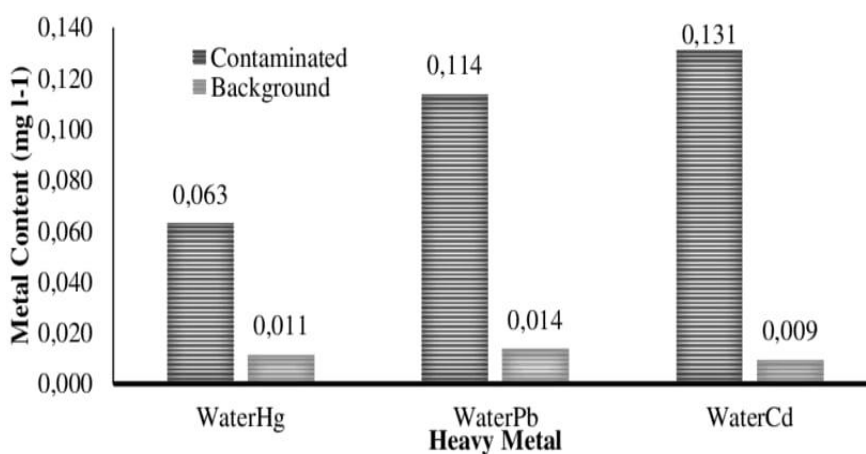


Fig. 8: Heavy metal concentration and background concentration

IV. CONCLUSION

The water samples were found to have a significant ($p < 0.05$) high levels of **Ni, Cd, Cu, As and Pb**. This was attributed to the use of wood treatment chemicals in the treatment of wood around the area. The high concentration was beyond the maximum permissible concentration for **Cd, and Pb** in the water as per WHO and other international set standards. It was also noted that the concentration of arsenic in the soils during dry season was significantly high as compared to the rainy season. Dry season has low leaching effect of the HM used during wood treatment and this is the reason for high **Ni, Cd, Cu, As and Pb** concentrations during dry season.

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