



Heavy Metals and Pathways of Incorporation in the Soil, Sediments and Water Matrices of River Nzoia, Kenya

*Tarus S. J., Kituyi J. L. and Segor F. K.

Department of Chemistry and Biochemistry, University of Eldoret,
P.O. Box 1125-30100, Eldoret, Kenya

*Corresponding author's email address: chepkoechta@yahoo.com

Abstract

For prudence in the management of lotic ecosystems, vital information on the degree of pollutant load is required. Several human activities are practiced within the River Nzoia catchment area, most of which result in heavy metals and/or their compounds most of which end up in different matrices of the river's bio-system. Since metals cannot biodegrade, most of them will therefore exist in forms, thus affecting the biosphere of the river. This study was conducted to monitor spatial and temporal variations in the concentrations of heavy metals in water, soil and sediments of River Nzoia, in Western Kenya. The heavy metals analysed by atomic absorption spectrophotometer (AAS) were; zinc (Zn), lead (Pb), copper (Cu), chromium (Cr) and cadmium (Cd) from a total of eight stratified sampling stations located along the River Nzoia from Cherangani to Mumias. Sampling was done twice capturing the variability during the dry and rainy seasons in February 2007 and June 2007. Heavy metal levels were Zn [1.7789 ± 0.2982 mg/L], Pb [0.9409 ± 0.0076 mg/L], Cu [0.7041 ± 0.1026 mg/L], Cr [0.917 ± 0.00827 mg/L] and Cd [0.1748 ± 0.00414 mg/L] exceeded the WHO limits (0.05 mg/L for Zn, Pb and Cu, 0.01 mg/L for Cr and Cd), in all the sites sampled. This showed that Nzoia River's water is dangerously contaminated by these heavy metals. The catchment area was affected by temporal variations with higher values of heavy metals recorded during the rainy season.

Keywords: Heavy metals, Soil, Sediments, Pollution, Ecosystem, Temporal Variability, Poverty Alleviation

INTRODUCTION

Nzoia River Basin Ecosystem has supported and nurtured human communities for several millennia. The restoration, protection and management of the basin guarantee the survival and well being of the people. Gaining and consolidating access and control over the basins' natural resources is essential for socially and economically deprived and vulnerable communities who depend directly on these resources for their livelihoods. Stakeholders in the Nzoia River basin are increasingly noticing declining water quantity and quality due to environmental degradation. The way in which water is managed is a critical factor in achieving poverty alleviation, improving local people's health, food security, economic development, protecting a range of natural resources and the industrial base in Western Kenya, and generally ensures a sustainable development in this basin. In order to address these challenges, it is important that the contaminant load of Nzoia River be determined (Nzoia river basin management initiative, 2006).

The Nzoia River is a 160-mile (257 km) long river rising from Cherangani hills, downstream to Lake Victoria. Sampling sites were located on the river network as shown in Figure 1. The basin is approximately 12,000 km² and lies entirely within western Kenya along the border with Uganda. It is bounded by the latitudes: 34° - 36° East, longitude: 0°03' - 1°15' North, and lies between 1134 - 27000 m above sea level. It is characterized by three

physiographic regions: the highlands, characterized by Mount Elgon and the Cherangani Hills; the upper plateau, which includes Eldoret and Kitale; and the lowlands including Busia, which experiences the majority of the flooding that occurs in the basin (USGS EROS Data Center, 2003). It flows south and then west, eventually flowing into Lake Victoria near Port Victoria, Busia. The region receives an average of 1350 mm/year of rain and is an important cereal and sugarcane farming region of Kenya producing at least 30% of the national output of both maize and sugar. Potential major sources of pollution for the river are the agricultural chemicals, urban effluents of Eldoret (population 234,000), Kitale (pop. 88,100), Bungoma (pop. 32,900), Webuye (pop. 45,100), Kakamega (pop. 86,500) and Mumias (pop. 32,900). The river absorbs industrial wastes of the Pan-paper pulp mills at Webuye, textile factories in Eldoret, coffee factories scattered in the higher regions, sugar industries mainly at Mumias, Kakamega and Bungoma districts, and tea factories in Cherangani which might contribute immensely to the pollution of River Nzoia. The pollution role played by any of these factors is unknown (USGS EROS Data Center, 2003).

MATERIALS AND METHODS

Sampling

Water, soil and sediment samples were collected from eight different sites across six districts namely; Kitale East, Uasin Gishu, Kitale West, Lugari, Bungoma, and Butere Mumias, which are a representative of the region. These sites were selected on the basis of the different agricultural and industrial activities.

Sampling was done during the dry season (Nov-March) and wet season (April-June). For soil samples, three field points were selected randomly near river banks at which soil cores were dug to depth of 30 cm using a 2 cm internal diameter soil corer. The samples were then mixed thoroughly and divided into three replicates of about 500 g. Water samples were collected (sub- surface and $\frac{3}{4}$ below surface) and mixed thoroughly then divided into three replicates and stored in clean 100 ml plastic containers and transported back to the laboratory.

The sites sampled were;

Site 1: Kitale (Koitobos Bridge near the road).

Site 2: Cherangani (Naigamut Bridge near tea factory and tea farms).

Site 3: Uasin Gishu (Nzoia Karara farm, way before the flower farms in Moi's Bridge).

Site 4: Moi's bridge (At the bridge just after the flower farms and the town.).

Site 5: Lugari (Near Nzoia water treatment intake).

Site 6: Webuye (Before the effluent from the Factory but near the town).

Site 7: Pan- Paper (After the effluent from the Factory)

Site 8: Mumias (Downstream of Mumias sugar factory)

Sample Preparation

In the laboratory the soil and sediment sub-samples were air dried, homogenized and crushed in a mortar with a pestle then sieved through a 5 mm pore size and then digested using the wet digestion method, as follows;

A sample of 1.0 g was transferred into a conical flask and 5 mL of conc. nitric acid added then shaken for 2 minutes followed by 2 mL of conc. HCl while shaking. The flask was inserted onto a hot plate and covered with a watch glass and heated for 2 hours until no fumes evolved maintaining temperature at 70°C. The sample was not allowed to dry by adding HNO₃, then cooled, filtered and diluted to 50 ml and taken for atomic absorption spectroscopy (AAS) analysis (spectrAA 100/200 model). Water samples were not digested in order to determine the available heavy metals.

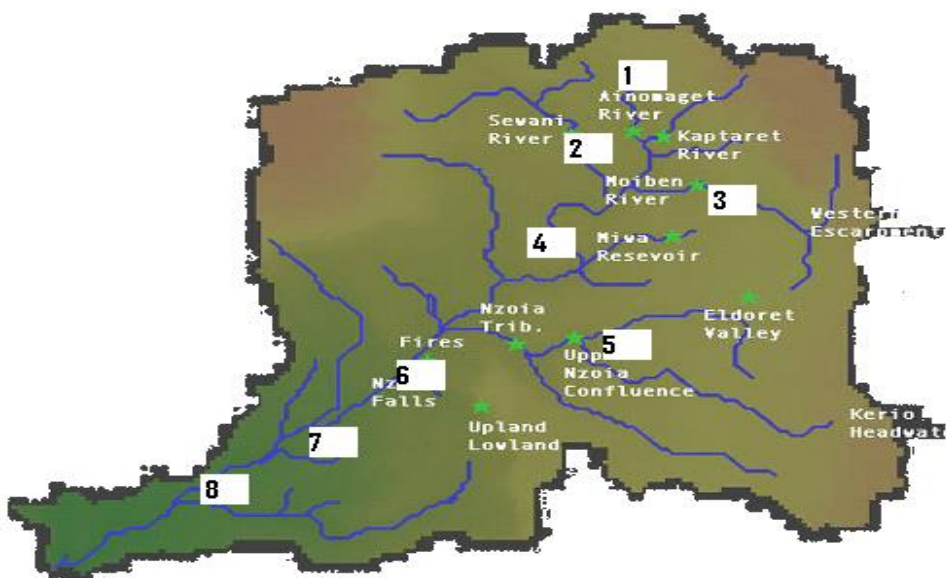


Figure 1: Map of Nzoia River catchment showing the sampled sites

Calibration Curves and Reproducibility of Instruments Used

The standard stock solutions of 1000 ppm were used and the calibration graphs had a correlation coefficient being $R^2 \geq 0.9$. Readings were done in triplicates and mean absorbance calculated for case.

Recovery Tests

The reliability of the AAS method in the determination of the elements studied was assessed by carrying out recovery studies using standard sediment samples. Known quantities of each metal standard solution were added to the sediment prior to the digestion step. To samples of sediments weighing 30 g were separately added standard solutions of each metal and then digested, results compared and analyzed for the respective elements and the percentage recoveries worked out. The recovery percentage for the heavy metals were; Pb 94%, Cu 91%, Cr 97%, Zn 96% and Cd 95%.

RESULTS AND DISCUSSION

Spatial Variations in Concentration of The Selected Heavy Metals in Water, Soil and Sediments

The mean overall concentration levels (ppm) of the heavy metals in soil, water and sediments from the eight sites in the entire sampling period are shown in Figure 2. Zn levels were the highest and ranged from a minimum of 0.741 mg/L in Uasin Gishu to a maximum of 3.601 mg/L in Mumias. This was followed by Pb ranging from a minimum concentration of 0.650 mg/L in Uasin Gishu to a maximum of 1.425 mg/L in Pan-Paper. The third most abundant heavy metal was Cr, which ranged from 0.811 mg/L in Cherangani to 1.651 mg/L in Pan-Paper. Cu was fourth and ranged from 0.186 mg/L in Uasin Gishu to 1.683 mg/L in Moi's Bridge. Cd was the least abundant among the heavy metals studied and ranged from a minimum of 0.048 mg/L at Uasin Gishu to a maximum concentration of 0.474 mg/L, and the metal distribution in the Nzoia was in the order $Zn > Pb > Cr > Cu > Cd$.

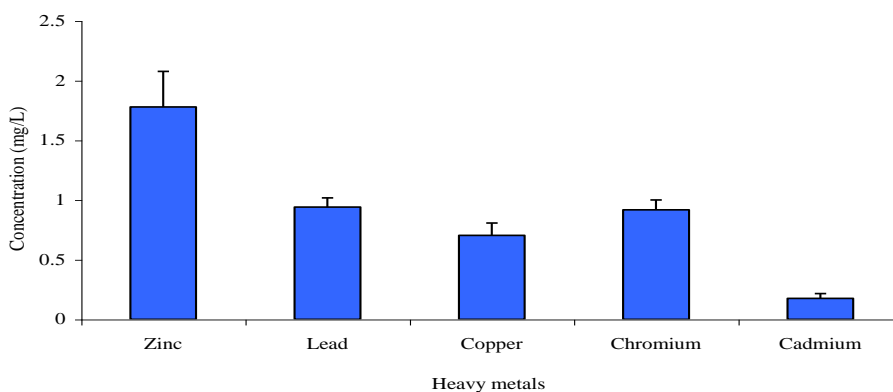


Figure 2: Mean concentration of heavy metals during the entire sampling period

The mean concentrations of the heavy metals analyzed in the three environmental media (water, soil and sediments) are presented in Table 1.

Table 1: Heavy metal concentrations (mg/L) in the water, soil and sediments in Nzoia

Heavy Metals	Concentration in mg/L		
	Water	Soil	Sediment
Zn	0.019 ± 0.002	1.702 ± 0.048	2.340 ± 0.075
Pb	0.010 ± 0.0001	0.594 ± 0.010	1.359 ± 0.091
Cu	0.010 ± 0.001	0.310 ± 0.006	0.145 ± 0.011
Cr	0.036 ± 0.003	0.451 ± 0.020	0.042 ± 0.002
Cd	0.002 ± 0.001	0.027 ± 0.001	0.037 ± 0.001

All analyzed heavy metals were significantly ($P < 0.05$) lower in water as compared to other environmental media with exception of Pb and Cd. Except for Pb and Cu, other heavy metals were significantly ($P > 0.05$) higher in soil samples. This could be because metals tend to bind to soils thereby increasing in concentrations (Bruemmer *et al.*, 2007), a consequence of long-term disposal of sludge and effluents from the factories.

In water, concentrations of all the heavy metals were lower than other environmental matrices, which signify the ability of heavy metals to accumulate in the environment where they have higher static resident time. Metal concentrations can also be lower in water in comparison to other environmental matrices possibly through the water self-cleansing processes, which conforms to the findings of Kondoro and Mikidadi (1998) who attributed the decline of the concentration of heavy metals in water to dilution with unpolluted water and the fact that heavy metals tend to adsorb to sediments more than water.

The present results conform to the hypothesis that in areas where higher industrial activities abound, higher concentrations of heavy metals are likely to occur. Higher concentrations of Zn and Pb have possible origins from the numerous industrial sources within the catchment area. The results of the spatial heavy metal concentration in water during the study period are shown in Figure 3.

The differences in concentrations of Zn (0.6156 ± 0.1087) [overall mean \pm SEM] mg/L among the eight sampling stations were significant (ANOVA; $F = 9.813$, $df = 4$, $P < 0.001$). Its highest levels in water occurred in Mumias, Pan-Paper and Moi's Bridge. In Pan-Paper, and Mumias, the presence of effluents from sugar factories provides conditions necessary for the dissolution of Zn compounds.

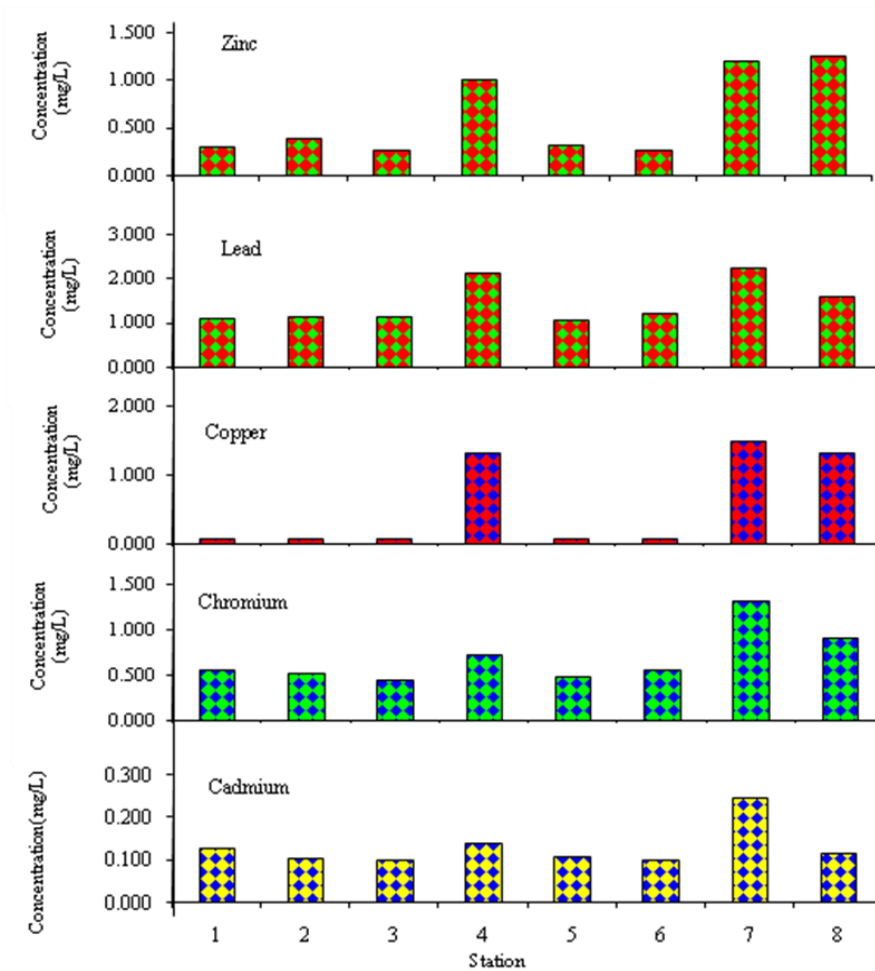


Figure 3: Spatial variations in heavy metal concentrations in water among the eight sampled stations during the study period

Settlement wastes from Moi's Bridge and downstream movement of River Nzoia provide the linkage in Zn transport that eventually increases its levels in water in these sites. There are also numerous non-point sources of pollutions that can provide Zn above the natural background levels like metamorphosis of rocks, which were numerous at the Pan-Paper site. The land along the river in this area is topographically steep, hence easy wash down from soil. Zinc concentration in Uasin Gishu was the lowest followed by Webuye while Kitale, Lugari and Cherangani had moderate levels. The concentration of Zn in natural surface waters is usually below 10 µg/L (Alloway, 1990) and the acceptable level in water is quite flexible but more than 3 mg/L may be undesirable (WHO, 1996).

Comparatively, concentrations of Pb in water were lower than those of Zn, apart from Moi's Bridge, Webuye and Mumias, which were significantly different ($p < 0.05$). There were no significant (ANOVA; $F = 0.456$, $df = 4$, $P = 0.977$) differences recorded in the concentration of Pb (1.4363 ± 0.1222 [overall mean \pm SEM] mg/L) among the other sampling stations within the Nzoia. In areas where there are activities that have no major significant contributions to heavy metals in the environment, their overall levels are likely to be much lower and the spatial distributions are likely to be uniform (Alloway, 1990). The concentration of Pb was much lower than that of Zn in water because of fewer activities that are unlikely to increase its concentration in water in comparison to the Zn levels. This suggests that even though several industrial effluents can be deposited in the environment by

numerous human activities that spread in the spatial scale within these areas, there are fewer threats from Pb contamination of water than zinc. However, the levels of Pb in all the sampling sites were higher than 0.05 mg/L and in comparison, to WHO (1996) guidelines on its presence in water; the water of Nzoia area is also not safe for drinking.

Concentration of Cu in water (0.5475 ± 0.1674 [mean \pm SEM] mg/L) was significantly different (ANOVA; $F = 442.356$, $df = 7$, $P < 0.001$) among the eight sampling stations. Its lowest concentrations were recorded in Kitale, Cherangani, Uasin Gishu, Lugari and Webuye, which were all significantly ($P < 0.05$) lower than Cu concentrations in Moi's Bridge and Mumias. Highest copper levels, however, occurred in Pan-Paper (1.4800 ± 0.2121 mg/L). This can be explained by the fact that Pan-Paper has higher density of metal work garages and several workshops as well as motor vehicles and waste metal recycling plants.

A lot of mining activities have also been carried out around Moi's Bridge, Mumias and Pan-Paper since 1990s. Many locals have been conducting sand mining activities for some time despite the existence of Nzoia municipal by laws that prohibit such mining activities (Kondoro and Mikidadi, 1998). Seepages of the natural Cu levels from these mining sites can find their way into the water and lead to increased levels of Cu in water, which results in all the sites recording values higher than the recommended values for water of 0.05 mg/L (WHO, 1996).

The level of Cr (0.6804 ± 0.0709 [mean \pm SEM] mg/L) in water exhibited significant (ANOVA; $F = 63.056$, $df = 7$, $P < 0.001$) differences among the sampling stations. The highest concentration was recorded in Webuye, which was significantly ($P < 0.05$) higher than its concentrations in other stations. This could be due to water logging nature of the surrounding soils, which accounted for much of the increased Cr levels. In waterlogged soils, aeration of organic matter is lacking and therefore, humic acid formed in the process of decomposition during long periods of water logging, results in increased levels of adsorption of heavy metals in the sediments, which consequently sink to the water table and eventually contaminates the water table (Järup, 2003). Concentration of Cr in Kitale, Uasin Gishu, Cherangani and Lugari were statistically similar ($P > 0.05$) but significantly ($P > 0.05$) lower than the levels in Moi's Bridge and Mumias. Its levels in natural waters vary between 1 and 2 $\mu\text{g/L}$ but can be elevated in areas with natural sources (WHO, 1996). The maximum acceptable WHO level of Cr of 0.01 mg/L was, however, exceeded in all the sampled sites.

The amount of Cd (0.1262 ± 0.0146 [overall] mg/L) in water was significantly different among the sampled stations (ANOVA; $F = 6.608$, $df = 7$, $P = 0.001$). Highest levels, however, occurred in Pan-Paper. This could be due to the dissolution of minerals and ores and from industrial effluents from Pan-Paper factory. Its intermediate levels in water were recorded in Cherangani, Uasin Gishu and Lugari, which were all statistically similar ($P > 0.05$) but significantly ($P < 0.05$) lower than the concentrations in Kitale, Moi's Bridge, Webuye and Mumias. These areas have a lot of industrial activities whose effluents end up in the river. The levels of Cd in river waters vary between 1 and 2 $\mu\text{g/L}$ but can be elevated in areas with natural sources (WHO, 1996). The maximum acceptable WHO level of Cd of 0.01 mg/L was, however, exceeded in water in all the sites implying that the water is highly polluted from Cd. The results of the heavy metal concentrations in soils among the eight sampled stations within Nzoia during the entire study period are shown in Figure 4.

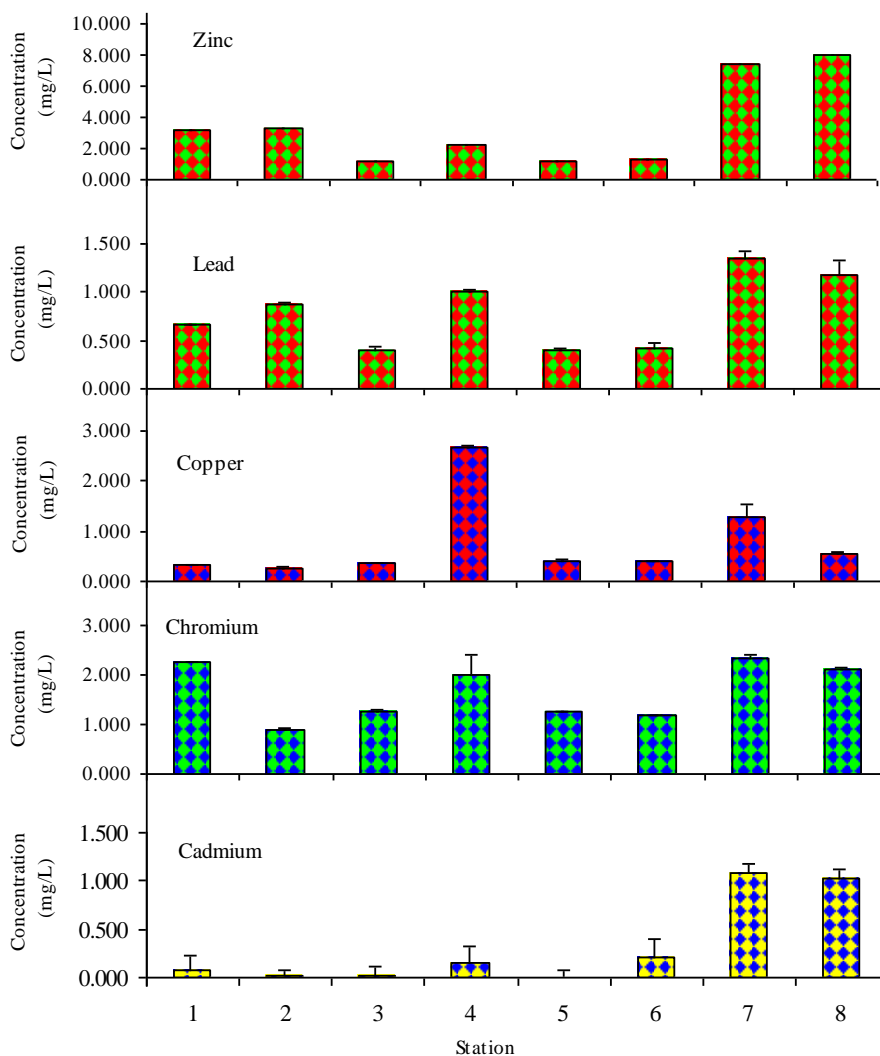


Figure 4: Spatial variations in heavy metal concentrations in soils among the eight sampled stations during the study period

The differences in concentrations of Zn (3.4881 ± 0.6644 [overall mean \pm SEM] mg/L) among the eight sampling stations were significant (ANOVA; $F = 9.828$, $df = 7$, $P < 0.001$). Significantly ($P < 0.05$) higher concentrations were obtained in Pan-Paper and Mumias than all the other stations studied. In these two stations, the presence of factories in close vicinity discharging their effluents into the river provides conditions necessary for the deposition of Zn and its compounds to the surrounding soils. However, it is not only the factory effluents that increase its amounts to the soils but also presence of numerous non-point sources of pollutants including cattle dips, livestock centres and abattoirs, which can enhance increased levels of Zn into the soil.

There is also the effect of downstream movement of River Nzoia, whose banks can spill over to the soils within the area and provide base for higher Zn loading in the soil. Due to intensive farming in Mumias and Webuye, the chemicals used can find their way into the soil and could accumulate over a period of time. Increased flooding frequency of the river around this area could also cause enrichment of the flood plain soil by heavy metals, predominantly Zn.

Concentrations of Pb (0.7869 ± 0.0913 [mean \pm SEM] mg/L) in the soils demonstrated significant ($F = 3.005$, $df = 7$, $P = 0.022$) spatial variations among the sampled stations. Significantly ($P < 0.05$) higher concentrations were recorded in Cherangani, Moi's Bridge, Pan-Paper and Mumias in comparison to those in other sampling stations. This could be attributed to exhaust emissions from motor vehicles in the busy urban centres of Moi's Bridge, Pan-Paper and Mumias in addition to effluents from factories in these areas. Intermediate levels were obtained in Uasin Gishu and Webuye, however, Lugari reported the lowest levels in soil within the entire region. This is because Lugari is mainly rural and with no industrial activity coupled with very little traffic density.

Levels of Cu in soils (0.7762 ± 0.2015 [mean \pm SEM] mg/L) were significantly different ($F = 6.327$, $df = 7$, $P < 0.001$) among the eight sampling stations. Significantly ($P < 0.05$) higher levels were reported in Moi's Bridge, Pan-Paper, and Mumias, in relation to those in other sampling locations, which were statistically similar ($P > 0.05$) in Cu concentration. These areas practice large scale farming and many people grow sugar cane and are involved in small scale agriculture. In Moi's Bridge there are numerous greenhouses for production of tomatoes, and floricultural products that all use water and other chemicals to operate especially pesticides, which could be bound to Cu. These chemicals find their way outside the greenhouses into the soil through seepage and runoff and could accumulate over time. There are also higher chances that Cu can be transported downstream to stations of Pan-Paper and Mumias and be deposited in the soils in these sites. Seepages from sand mining sites in these areas can in essence increase its levels in soils.

Amount of Cr in soils of Nzoia (1.6620 ± 1.1378 [mean \pm SEM] mg/L) exhibited highly statistically significant ($F = 26.667$, $df = 7$, $P < 0.001$) differences among the sampling stations. The highest concentrations were recorded in Kitale, Moi's Bridge, Pan-Paper and Mumias, which were significantly ($P < 0.05$) higher than Cr concentrations in other stations. In Kitale high levels could be linked to the high density of metal workshops. Another source of elevated Cr in Kitale area could be the extensive use of seed protectants in the numerous seed companies found in this area that could find their way into soil through seepage. In Moi's Bridge, much of it could be from other chromium related products such as fungicides, which are used extensively at the flower farms and wood preservatives (*Hibiscus esculentus*, 2013). In Pan-Paper and Mumias apart from the hospitals, there are effluents from the factories and the use of wood preservatives especially around Pan-Paper area. However, least concentration of Cr occurred in Cherangani.

Concentration of Cd (0.3233 ± 0.1102 [overall mean \pm SEM] mg/L) in soils of the Nzoia was significantly different among the sampled stations ($F = 31.276$, $df = 7$, $P < 0.001$). Highest levels in soils occurred in Pan-Paper and Mumias. Once again, the presence of Pan-Paper and Mumias factories and their mode of deposition of their effluents could have contributed to the high levels. Since these two areas have higher levels of agricultural activities, especially large-scale sugarcane farming, there are possibilities that these higher levels could be attributed to high levels of Cd in the basin, which arise from remote sources in agricultural fields where there is high propensity in the use of mainly phosphate fertilizers. However, intermediate levels in soil were recorded in Kitale, Moi's Bridge and Webuye, which were all statistically dissimilar ($P > 0.05$) in Cd concentration but, all significantly ($P < 0.05$) higher than Cherangani, Uasin Gishu and Lugari. These concentrations could be from natural sources since they are not alarmingly high.

The results of the concentrations of heavy metals in sediments among the eight sampled stations within the Nzoia during the entire study period are shown in Figure 5.

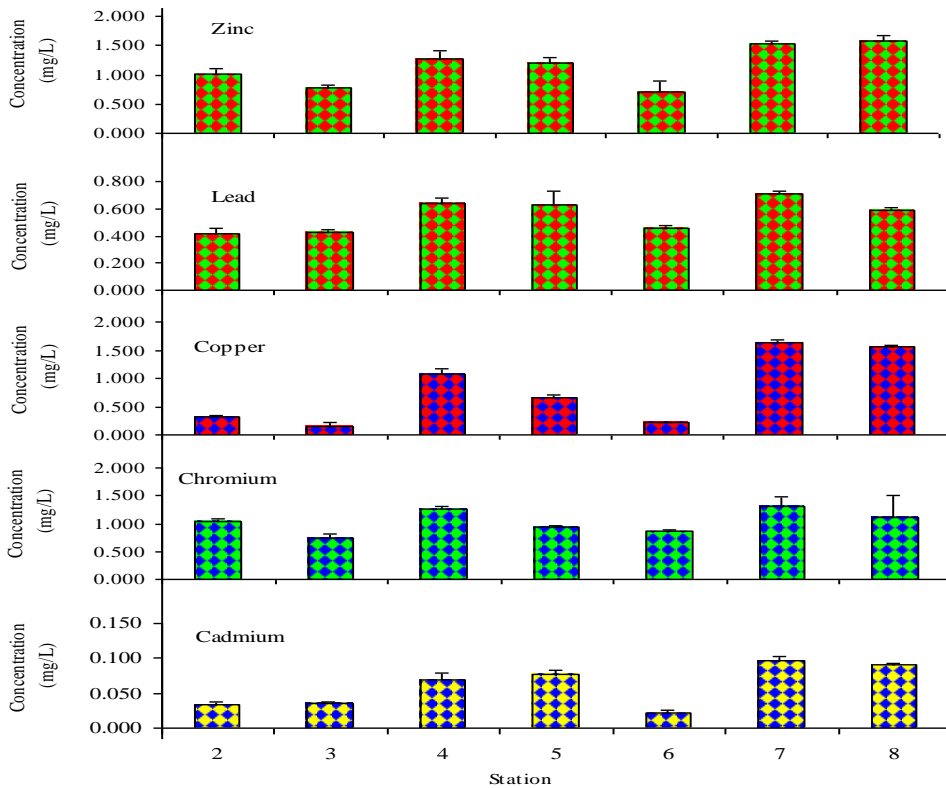


Figure 5: Spatial variations in heavy metal concentrations in sediments among the eight sampled stations during the study period

Levels of Zn (1.1550 ± 0.0876 [overall mean \pm SEM] mg/L) showed significant (ANOVA; $F = 1.382$, $df = 7$, $P = 0.255$) differences among the eight sampling stations within the Nzoia. Highest levels were recorded in Pan-Paper and Mumias, followed by Uasin Gishu and Moi's Bridge. Again, the presence of the two factories seems to be a major contributing factor to Zn pollution in the sediments in Pan-Paper and Mumias. Other sources could be from the effect of flooding, downstream movement, hence, transport of Zn, and its adsorption to the sediment particles due to long term accumulation.

Levels of Pb (0.5507 ± 0.0299 [overall mean \pm SEM] mg/L) in the sediments demonstrated highly significant ($F = 104.879$, $df = 7$, $P < 0.001$) spatial variations among the sampled stations within Nzoia. Significantly ($P < 0.05$) higher values were recorded in Uasin Gishu, Moi's Bridge, Pan-Paper and Mumias in comparison to those in other sampling stations. Uasin Gishu and Moi's Bridge stations are near the Eldoret-Kitale highway so the Pb contribution could be from exhaust emissions from motor vehicles and runoff from the busy urban Moi's Bridge 'Jua Kali' area. Pan-Paper and Mumias Pb pollution could again be from the factory effluents and petroleum products from machinery in the factories and the busy surrounding urban areas of the two places. Moderate concentrations were obtained in Cherangani and Lugari while those in Kitale were the lowest within the entire region. These areas are surrounded by non-busy roads and little urban settlement activity, hence, the lower Pb pollution.

Concentration of Cu (fig 5) in sediments (0.8007 ± 0.1612 [overall mean \pm SEM] mg/L) was significantly different ($F = 16.347$, $df = 7$, $P < 0.001$) among the eight sampling stations within Nzoia. Its values were highest in Uasin Gishu, Pan-Paper and Mumias, which were significantly ($P < 0.05$) higher than those in the other stations. The levels in Moi's Bridge were intermediate followed by Kitale and Webuye while the lowest were in Cherangani. This could be due to the fact that there are extensive agricultural practices in Uasin Gishu, Pan-Paper and Mumias involving use of a wide variety of farm chemicals including fungicides, which usually contain Cu compounds. In Cherangani, no Cu related compounds are used in agriculture since the pesticides used for tea farming do not contain Cu.

The level of Cr (fig 5) in sediments of Nzoia (1.0370 ± 0.0528 [overall mean \pm SEM] mg/L) exhibited highly statistical significant ($F = 31.963$, $df = 7$, $P < 0.001$) differences among the sampling stations. The highest levels were recorded in Moi's Bridge, Pan-Paper and Mumias in relation to those sampled from other stations. In Moi's Bridge, much of it could be from Cr related products such as fungicides, which are used extensively at the flower farms and wood preservatives.

In Pan-Paper and Mumias apart from the hospitals, there are effluents from the factories and the use of wood preservatives especially in Pan-Paper area. These are easily deposited in sediments and could easily accumulate over the years. Downstream transport by the river could also contribute to the fact that the concentration is higher downstream than upstream. The samples from Lugari and Webuye had intermediate levels while those from Cherangani had the lowest relative to the sampled locations. Again, in Cherangani use of Cu based farm chemicals are minimal since it is mainly a tea and maize growing area.

Amounts of Cd in sediments (0.0605 ± 0.0078 [overall mean \pm SEM] mg/L) were significantly different ($F = 16.347$, $df = 7$, $P < 0.001$) among the eight sampling stations within Nzoia. The values were highest in Moi's Bridge, Lugari, Pan-Paper and Mumias, which were significantly ($P < 0.05$) higher than in other stations. Cherangani and Uasin Gishu recorded intermediate values while the lowest were obtained in Webuye. This again could be due to the factory effluents from Pan-Paper and Mumias factories. Webuye, however, recorded the least possibly due to the fact that the river has a higher flow rate at this point.

Temporal variations in concentrations of the selected heavy metals in water, soil and sediments

Temporal variations in concentrations of the heavy metals studied in Nzoia are shown in Figure 6.

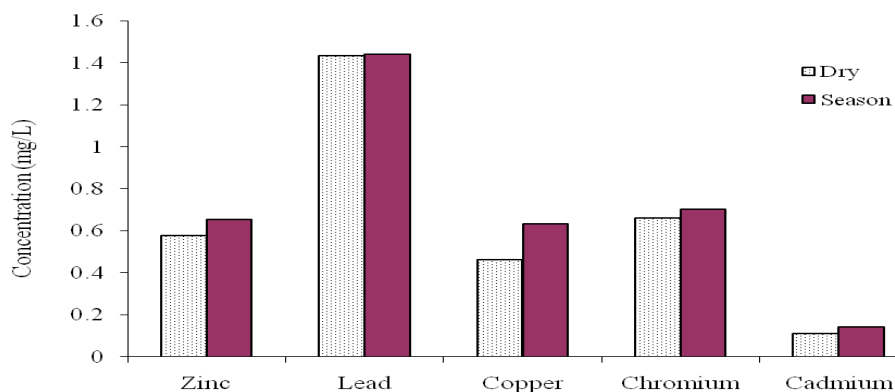


Figure 6: Mean temporal variation of metals between dry and rainy season in different areas during the study period

The level of Zn was significantly ($t = 5.542$, $P < 0.001$) higher during the rainy season (1.658 ± 0.068 mg/L) than in dry season (1.792 ± 0.085 mg/L). No significant differences ($t = -1.922$, $P = 0.560$) in concentrations were recorded for Pb between rainy season (0.935 ± 0.084 mg/L) and dry season (0.940 ± 0.016 mg/L). Likewise, concentrations of Cu were significantly ($t = 5.871$, $P < 0.001$) higher in rainy season (0.578 ± 0.042 mg/L) than in dry season (0.723 ± 0.029 mg/L). Significant differences ($P < 0.05$) were also recorded for Cr and Cd within the environment of Nzoia. Cr concentration was significantly ($t = -3.050$, $P = 0.002$) lower in dry season (0.781 ± 0.016 mg/L) when compared to rainy season (1.006 ± 0.024 mg/L), so did statistical significance ($t = 5.253$, $P < 0.001$) of Cd in dry season (0.104 ± 0.016 mg/L) in comparison to the wet season (0.200 ± 0.016 mg/L). These could be attributed to enhanced runoff during rainy seasons, which could transport more heavy metals into the environment. Levels of Pb, however, did not change probably because Pb has the highest resident time especially in soil and sediments than all the other heavy metals analysed. Cd level was also quite low during both seasons possibly due to minimal use.

Concentrations of all the analyzed heavy metals in water were significantly ($P < 0.05$) higher in the rainy season than in the dry one within Nzoia. No significant differences ($P = 0.951$, $P = 0.988$, respectively) in concentration values were recorded for chromium and cadmium between rainy and dry seasons in soil samples, but those of zinc, lead and copper were significantly ($p < 0.05$) higher in the rainy season than in the dry season.

Likewise, concentrations of all the analyzed heavy metals in sediments were significantly ($P < 0.05$) higher in the rainy season than in the dry season. All the heavy metals showed a slight increase in the rainy season in soil, water and sediments possibly due to enhanced runoff from storm water, which wash away all the heavy metals from municipal areas, paints, garages, leaded gasoline or fuel from tarmac roads and other non-point sources into the river.

CONCLUSION AND RECOMMENDATION

Water quality data collected for surface waters of River Nzoia indicated that the quality of the river waters, which is mainly agriculturally and industrially influenced was found to be polluted by heavy metals (Zn, Pb, Cu, Cr and Cd), which exceeded the limits in all the sites sampled. It was also established that contamination of the soils, sediments and water of river Nzoia catchment area is affected by temporal variations and was particularly higher during the rainy season compared to the dry season. Generally, Pan Paper and Mumias were the most polluted stations. Therefore, control measures should be taken within the catchment area to avoid the river manifesting serious environmental pollution.

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