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Full Length Research Paper

Impact of anthropogenic activities on copper and lead levels in Kisumu city soils

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The sources of heavy metals in the soil are fertilizers, fuel plastics, pigments, motor vehicles exhausts, oils spilt at motor-vehicle mechanic works and paint chips from buildings. The two majorly known heavy metals are copper and lead which are harmful to biota, animals and human beings. The study was conducted in Kisumu City with the aim of determining the concentrations of Cu and Pb in the nine selected sampling sites. In each site 100 g soil samples were collected in triplicates from a 5 cm deep freshly dug hole. Soil samples were collected in a completely randomized design then oven-dried, ground and digested using aquaragia solution for total metallic content and treated in HCl only for bioavailable metal content. All the analysis was performed in the atomic absorption spectrophotometer. The results showed that the total and bioavailable concentrations of Cu ranged between 1.59 to 31.05 ppm and 0.40 to 28.49 ppm while Pb concentrations varied between 8.69 to 119.12 ppm and 7.09 to 91.85 ppm for total and bioavailable respectively. Positive correlation was observed between Cu and Pb concentrations, R^2 = 0.293 and 0.570 for total and bioavailable concentrations respectively.

Key words: Heavy metals, Kisumu city, total, bioavailable, sampling sites.

INTRODUCTION

Kisumu city is located at the shores of Lake Victoria, which is the second largest fresh water lake in the world with an area measuring 68,800 km^2 (Van Densen and Witte, 1995). It is the third largest city in Kenya after Nairobi and Mombasa. Kisumu city is served by a large population of people, motor vehicles, motorcycles and bicycles. Copper and lead occur naturally in the soil in small amounts but in general, their occurrence in the earth's crust is less than 0.1% with the average contents in the lithosphere being 55 and 14 ppm for Cu and Pb respectively (Baker, 1990; Alloway, 1995). On the contrary, Bowen (1966) showed that their average in the typical normal world surface soil is 20 and 10 ppm respectively.

Reared pigs are common scenes in a number of estates in the city. These animals are always loitering in the estate streets looking for food supplements at garbage disposal points. Slurries resulting from pig farming which are spread on farming soils because they are nutrient rich contain trace minerals including in particular copper. Copper salts are included in pig feeds as additives because they promote immune system function and growth (De la Torre et al., 2000; O'Dell, 1998). Long term intensive manure application can be responsible for elevated copper content in the surface soil. Copper stored in soil can pass in solution during rain events and could join the hydrological system and therefore end up in water wells, rivers and even larger water bodies. In a study carried out in China, it was reported that anthropogenic inputs such as atmospheric deposition and street dust were the main sources of copper and lead in Nanjing urban soils (Lu, 2000). Soil fractions are categorized as the inert fraction (assumed as the non-toxic fraction) and the labile fraction, assumed to be potentially toxic (Rachou and Sauvé, 2008). The soil labile fraction is usually taken into account while determining the availability of heavy metals because it is the bioavailable fraction (Gray et al., 2004). The levels of heavy metals are known to change with geographical area and the activities around that area (Omwoyo et al., 2013; Omwoma et al., 2012).

On the other hand, total concentrations of trace elements

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in any soil can provide background information about the status of metals in the soil (Dornia and Michael, 2005; Albanese, 2008). Nevertheless, this does not provide knowledge about the chemical speciation of the metals with various fractions of the soil (Nale et al., 2007; Ajiboye and Ogunwale, 2008). Speciation is the oxidation state, concentration and composition of each of the species present in a chemical sample while total concentration is the maximum tolerable level of a polluting element in an environmental sample such as biota, river water, sediments or soil (Hersfall et al., 1999; Florence, 1986). The bioavailability of heavy metals depends on the speciation of the metals, soil characteristics and the composite interactions between metals and the environment (Yobouet et al., 2010). Heavy metal contamination in urban soils can be harmful to biota, animals and human beings and this led to extensive investigation in some countries and regions (Das et al., 1997; Stroganova et al., 1998). Total metal analysis do give information about possible contamination of the soil with heavy metal, but it is generally recognized that it is the chemical form of a metal in the soil that determines its mobilization capacity and behavior in the environment. Sequential extraction provides useful information about the differentiation of the relative bonding strength of the metal on various solid phases and on their potential reactivity order, different physico-chemical, environmental conditions and is considered important in evaluating mobility and bioavailability of heavy metals in urban soils and therefore, their potential to contaminate water ways (Ramos et al., 1994; Wilcke et al., 1999). Akbar et al. (2006) reported that heavy metals can destruct vital biochemical processes thus posing a threat to human health. Lead (Pb) for instance is an unnecessary metal with neurological toxin affecting many processes and almost every organ in the human body and affecting children growth and development (Luilo and Othman, 2006). In addition, heavy metal toxicity has harmful consequence on plants such as growth, enzymatic activity, stoma function and photosynthesis activity (Onder et al., 2007; Ayodele and Oluyomi, 2011). Different operations of the road transport have been reported to be potential sources of Cu and Pb released into the atmosphere (Sharma and Prasade, 2010; Zhang et al., 2012).

Hjortenkrans (2003) showed that wear and tear of brake linings and tires contribute more than 85% of the total Cu and Pb emission. Furthermore, Zhang et al. (2012) also established that brake wear contribute to Cu and Pb in the environment. During rain events, leaching by running water can occur easily leading to the deposition of such heavy metals into various water sources e.g. wells, boreholes and lakes which are relied on by the residents of the city; this created a big concern. Heavy metal levels in Kisumu city soils are not known and therefore, the potential risks out of the possible high levels in the urban soils cannot be evaluated. The heavy metal residuals could be ending up in Lake Victoria which is a crucial fish and water resource for the local inhabitants and beyond. This underlined the importance of carrying out this study to evaluate the urban area's potential contribution of the heavy metals to Lake Victoria water. The objective of this study was to determine the concentrations of Cu and Pb in soil samples taken from the Central Business District of Kisumu City.

MATERIALS AND METHODS

Study site and experimental design

The study was carried out in Kisumu City in western Kenya which lies on an altitude of 1,131 m above the sea level with geographical coordinates 0° 60' S 34° 45' E and a population of 394,684 (2009 census). The choice of the sampling sites was based on the heavy vehicle traffic and human activities including welding and motor vehicle mechanic works which are likely to increase the heavy metal load in the Central Business District. The sites which were selected include: Railway Junction Kicomi (RJK), Obote Road Kicomi (ORK), Jomo Kenyatta Sports Ground (JKSG), Oginga Odinga Street (OOS), Jomo Kenyatta Avenue (JKA), Kisumu Bus Park (KBP), Oile Park (OP) and Lake Basin Authority (LBA), which was chosen as the reference or control site since there are no major commercial activities taking place here. The experimental design was completely randomized (CRD) design.

Soil sampling and preparation

Three replicate samples weighing 100 g each were taken at different points in each sampling site from freshly dug 5 cm deep holes with the aid of a plastic tube of size 5 cm in diameter and 72 cm in length then stored at -20°C to wait for processing. The samples were dried to constant mass in an oven at 100°C for 24 h. The oven dried samples were ground to a fine powder with the aid of a pestle and a mortar then sieved through a 45 µm nylon sieve. To determine the dry weight of the soil samples 1 g of semi-dry soil samples were used and this was dried at 100°C to constant mass. Total and bioavailable concentrations were determined according to Tack and Varloo (1995) procedures.

Total digestion

1 g of the sieved soil sample was placed in a 50 mL beaker. A volume of 10 mL concentrated HNO_3 and HCl acids, mixed in the ratio 4:1 respectively, was added to the sample and digestion carried out at 50°C for 3 h. The

Table 1. Wet weight, dry weight and wet weight/dry weight ratio of soils in Kisumu City.

Site	ww (g)	dw (g)	ww/dw
Jomo Kenyatta Sports Ground	1	0.9613	1.0403
Jomo Kenyatta Avenue	1	0.9300	1.0753
Kisumu Bus Park	1	0.9626	1.0388
Lake Basin Authority	1	0.7166	1.3955
Oginga Odinga Street	1	0.9423	1.0612
Oile Park	1	0.9571	1.0448
Obote Road Kicomi	1	0.9687	1.0323
Railway Junction Kicomi	1	0.9426	1.0609
Uhuru Garden	1	0.9634	1.0376

Average ww/dw ratio=1.0874 ww= wet weight, dw= dry weight.

Table 2. Total and bioavailable concentrations of Cu and Pb (in ppm) in different sites.

Metal	Concentration	SITE									
		KBP	ORK	OP	JKA	RJK	OOS	UG	JKSG	LBA	MEAN
Cu	Total	30.46	17.79	15.59	17.69	15.89	31.05	12.33	6.60	1.59	16.55
	CV%				5.49						
	LSD≤0.05				0.74						
	Bioavailable	25.09	14.98	10.12	12.42	14.55	28.49	9.81	2.70	0.40	13.17
	CV%				11.93						
	LSD≤0.05				1.28						
Pb	Total	61.29	79.95	119.12	110.44	55.96	93.37	45.30	48.44	8.69	69.26
	CV%				4.95						
	LSD≤0.05				2.79						
	Bioavailable	36.04	70.66	36.02	19.40	49.46	91.85	40.04	19.40	7.09	41.36
	CV%				12.31						
	LSD≤0.05				4.14						

digest was then filtered through a number 1 Whatman filter paper and the filtrate topped to 25 mL with de-ionized water (Tack and Varloo, 1995).

Bioavailable digestion

1 g of the sieved soil sample was treated with 10 mL of 0.5 N HCl overnight at room temperature, in order to extract the most available fraction of the trace metals in the soil. The extract was filtered through a No. 1 Whatman filter paper and the filtrate made to 25 mL with de-ionized water (Tack and Varloo, 1995).

Sample analysis

Sample analysis was done using Atomic Absorption Spectrophotometer (AAS) at wavelengths of 324.8 and 283.3 nm for Cu and Pb respectively.

Data analysis

The generated data was statistically analysed using Statistical Analysis System (SAS) Version 9.2 (SAS Inc., 2002) as a completely randomized design. Analysis using general linear models (GLM) procedure was performed to determine any significant treatment effects at $p \leq 0.05$ confidence level. Microsoft Office Excel was used to develop linear regressions.

RESULTS

The average wet weight (ww)/dry weight (dw) ratio for the soil samples obtained from the nine sites in the city are summarized in Table 1. The concentrations of Cu and Pb presented are based on dry weight of the soil samples. This ratio is of importance in case there is need to know the concentrations based on wet weight.

The results of total and bioavailable concentrations for Cu and Pb in different sampling sites in Kisumu City are presented in Table 2.

The values recorded for Cu ranged between 1.59 to 31.05 ppm with an average of 16.55 ppm and 0.40 to 28.49 ppm with an average of 13.17 ppm for total and bioavailable concentrations respectively. On the other

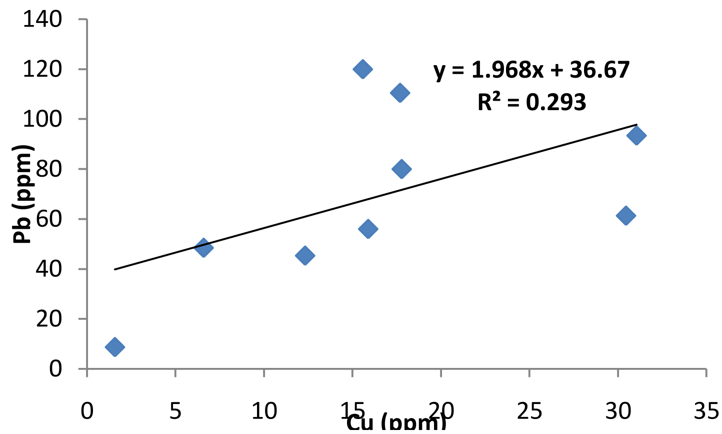

Figure 1. Correlation between Cu and Pb (total concentrations) in the sampling sites.

hand, total and bioavailable concentrations varied between 8.69 to 119.12 ppm with an average of 69.26 ppm and 7.09 to 91.85 ppm with an average of 41.36 ppm respectively for Pb. Oginga Odinga Street (OOS) recorded the highest total Cu concentration and bioavailable Pb concentration. Kisumu Bus Park (KBP) registered the highest bioavailable Cu concentration while the highest total Pb concentration was given by Oile Park (OP). The least total and bioavailable concentrations for both Cu and Pb were obtained in Lake Basin Authority (LBA).

Discussions

Statistical analysis ($p \leq 0.05$) showed significant differences in total and bioavailable concentrations of Cu and Pb within the sites. The high concentrations of Cu and Pb in sites such as Oginga Odinga Street (OOS), Kisumu Bus Park (KBP) and Oile Park (OP) could be associated with the source of pollutants. These sites are engaged with a lot of vehicular operations. Oile Park (OP) is surrounded by three round abouts which are ever busy with motor vehicles, motorcycles and bicycles that are ever using braking systems and tyres. This is in line with the findings made by Hjortenkrans (2003) who showed that brake linings and tyres contribute a larger percentage of total Cu and Pb emissions. Different operations of the road transport are known to be the potential sources of Cu and Pb released into the atmosphere (Sharma and Prasade, 2010; Zhang et al., 2012). Gungshik et al. (2007) also associated the high concentration of Pb in the soil samples with regular influx of automobiles. The low Cu and Pb concentrations recorded by Lake Basin Authority were expected as there are minimal anthropogenic activities going on in and around this place and it is at the outskirts of Kisumu City. This observation is in agreement with the findings made by Albanese (2008) who noted that total concentration of metals is influenced by the surrounding anthropogenic activities in the region.

The results obtained in this study are significantly different with those reported by Baize (1997) for both total Cu and Pb concentrations. He reported Cu and Pb concentrations in the range of 45 to 70 and 13 to 16 ppm respectively in soils from France. However, in this study the concentrations of the two heavy metals were observed to be outside the range and this disparity could be associated with different levels of pollutions and geographic area (Omwoyo et al., 2013). These results further contrast with those established by Baker (1990) and Yobouet et al. (2010) who obtained the average Cu and Pb concentrations in soil to be 55 and 52.02 ppm; 14 and 163.65 ppm respectively. The current findings are in harmony with those published by Bowen (1966) and Baseer (1979) from soils in London and Pakistan respectively.

They obtained that the concentrations were in the range of 2 to 100 ppm and 2 to 100 ppm for Cu and 2 to 250 ppm and 2 to 200 ppm for Pb respectively. These results are also in agreement with those documented by Khattak and Hussain (2007) and Kashif et al. (2009) for Cu concentrations. Their report showed that the average Cu concentration in soils lie in the range 4.44 to 6.20 ppm.

Cu and Pb concentrations correlated positively in all the sampling sites for both total and bioavailable concentrations as demonstrated in Figures 1 and 2. However, the correlation coefficient R^2 for total concentration was non significant. Positive correlation of Cu and Pb concentrations in soils were also reported by Siddiqui and Khattak (2010) in Pakistan soils and attributed the non significant positive correlation in the total metal concentrations to the sources and levels of pollution of the environment. The significant positive correlation in the bioavailable Cu and Pb concentrations

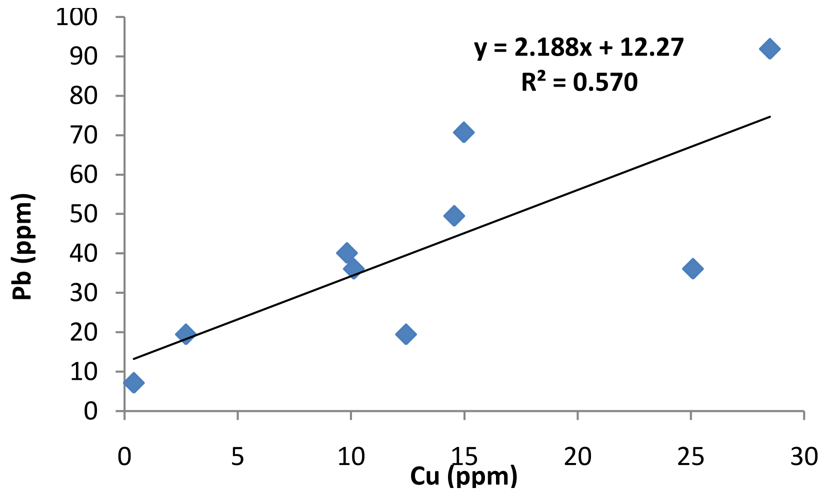

Figure 2. Correlation between Cu and Pb (bioavailable concentrations) in the sampling sites.

can be attributed to different physicochemical and environmental conditions, soil characteristics and the composite interactions between heavy metals and the environment (Wilcke et al., 1999; Yobouet et al., 2010) though this were not determined in this study.

Conclusion

Oginga Odinga Street (OOS) registered the highest total Cu and bioavailable Pb concentrations while the highest total Pb and bioavailable Cu concentrations were recorded by Oile Park (OP) and Kisumu Bus Park (KBP) correspondingly. Least total and bioavailable Cu and Pb concentrations were observed in Lake Basin Authority (LBA). In this regard the heavy metals are associated with the activities around the area. This will in turn end up in Lake Victoria thus increasing the metal loads in the waters. It is thus necessary to device a mechanism that will curb the metals in the soils from the leaching effect.

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