

**SPECIATION OF CADMIUM AND LEAD IN GARAGE
SOILS FROM NGARA- NAIROBI AND THEIR LEVELS IN
NEARBY VEGETABLES AND WATER**

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ABSTRACT

Mismanagement of chemical wastes from light industries and motor vehicle garages results to pollution of the natural environment and poses substantial danger to public health and welfare. The present study reports levels and forms of Pb and Cd in garage soils obtained from Ngara-Nairobi and their levels in vegetables and water bodies found nearby. The concentration levels of cadmium obtained ranged from 0.40-4.80 mg/kg and a mean of 2.95 ± 0.14 mg/kg. Its concentration levels were highest in the residual, followed by exchangeable, then oxidisable and least amount in the reducible bound fraction. Thus, a high percentage of cadmium is associated with non-residual fractions and can easily be transferred into the food chain through water reservoirs or uptake by plants growing in the soils. The concentration levels of lead were found to be within the range of 22.00-313.60 mg/kg and had a mean of 128.36 ± 6.51 mg/kg. Its concentration levels in the fractions from highest to lowest followed the order; reducible, residual, oxidisable and exchangeable. The mobility factor of cadmium was found to be 33.4405 while that of lead was 7.05. Concentration levels of cadmium in nearby kales ranged from 0.73 to 1.50 mg/kg while those of lead ranged from 10.25 to 19.60 mg/kg. In spinach the concentration levels of cadmium and lead ranged from 0.84 to 1.75 and 7.83 to 20.53 mg/kg respectively. Concentration levels in water samples ranged from 0.77 to 1.50 mg/L for cadmium and 4.60 to 8.89 mg/L for lead. These high concentration levels of the metals in water and vegetable pose great danger to human health as their consumption can lead to serious depletion of some essential nutrients in their bodies thus leading to decrease in immunological defenses. This calls for proper waste management procedures, continuous education and training to the artisans and efficient soil remediation programs at the sites.

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Background information

The presence of toxic metals such as lead and Cadmium in the environment is a source of worry to many environmentalists, government agencies and health practitioners. This is because they are associated with many health complications (Tyler, 1981; Borgmann, 1983). Their concentration in soils is associated with biological and geographical cycle as well as anthropogenic activities such as agricultural practices, transport, industrial activities and waste disposal (Abollino *et al.*, 2002).

Knowledge of their total concentration levels in the soil provides limited information about their potential behavior and bioavailability. In fact it is well known that they exist in various forms in soils. Further, their reactivity, mobility and bioavailability depends on the form they exist (Kabata and Pendias 1992; Ahumada *et al.*, 1999; Kabala and Singh, 2001; Abollino *et al.*, 2002). The water-soluble forms spontaneously participate in ion exchange reactions and are therefore very mobile and available to plants. The metals contained in the reducible forms are usually incorporated into the crystalline lattices of clays and are relatively inactive (Kabala and Singh, 2001) while the ones in the oxidizable forms are mainly complexed to organic matter and are relatively active or firmly bound depending on the combination of physical and chemical properties of the soil. Therefore the soil components such as available organic matter, Fe-Mn oxides and clays as well as its pH are important factors that determine the lability, mobility and biological uptake of the heavy metals it contains (Maand Rao, 1997; Norwa *et al.*, 1999; Kabala and Singh, 2001).

Selective sequential extraction (S.S.E.) procedures are commonly used to predict the chemical mobility and bioavailability of heavy metals in soil. These procedures involve subjecting a solid sample (soil or sediment) to successive reaction steps with reagents that possess different chemical properties (acidity, redox potential, or complexing properties) in which each step extracts a part of the metal associated with a particular form within the soil sample. Consequently the procedures are able to provide both the concentration levels of the metals and also qualitative information on the forms, associations, effects, bioavailability and potential harmful effects of soil metals and guide in the choice of remedial technologies.

Materials and Methods

Description of study area

This study was conducted at the Ngara open-air motor vehicle workshop which is located in the capital city of Kenya, Nairobi. The motor vehicle workshop is located near Kirinyaga road and opposite Globe Cinema. The drainage from the garage flows from the workshop into the nearby Nairobi River.

Sampling and Sample Pre-treatment

Ten sampling points each 4m x 4m quadrants were chosen with reference to potential sources of the heavy metals. Each quadrant was subdivided into twenty cells (20cm by 20cm) denoting a sampling point. Soil samples from ten randomly selected cells of each quadrant were collected at depths of 0-10cm and mixed to obtain a representative composite sample. This was done twice in the rainy month of April ten days apart. The samples obtained were placed in separate labeled polyethylene bags and transported to the laboratory at room temperature on the same day. In the laboratory extraneous materials were removed, the soil samples air-dried and homogenized by grinding. They were then oven-dried to a constant mass for 48 hours at 50°C, cooled and sieved using size 600 μm mesh to remove large undesired particles sizes. The sieved soil samples were then ground to powder form using an agate mortar and pestle to particle sizes of nanometres range. The resultant powder was stored in clean labeled polyethylene bags in a desiccator until analysis

Analysis

Heavy metals in the soil were extracted using the modified BCR chemical sequential extraction. The exchangeable and acid soluble fractions (F1), was extracted by shaking about 1.0g soil sample in a 40mL solution of 0.11 M CH_3COOH for 16 hours at room temperature. The reducible fractions (F2), was extracted by shaking the residue from (F1) in a 40mL solution of 0.1 M $\text{NH}_2\text{OH.HCl}$ at pH 2 for 16 hours at room temperature. The residue from (F2) was treated twice with 8.8 molL^{-1} hydrogen peroxide, evaporated to near dryness, 50 mL of ammonium acetate was added and the pH was adjusted to 2 using nitric acid and shaken overnight. The mixture was then centrifuged to separate (F3), the extract representing the oxidizable fraction. The residual fraction was extracted by digesting residue from (F3) using 20mL of aqua-regiasolution. Similarly extract for total metal concentration (bulk soil analysis) was obtained by

extracting about 1.0g of soil sample with about 20mL of aqua-regiasolution. The concentration of metal in the various fractions was determined using a flame atomic absorption spectrophotometer (Model Buck Scientific210 VGP). The levels of Pb and Cd obtained in the various fraction and bulk were used to calculate their concentrations in the fractions and bulk soil respectively.

The recovery of the sequential extraction was obtained as a percentage of the sum of four fractions over directly measured total, $[(\text{sum of fractions}/\text{total metal})\times 100]$. All analysis was done in triplicate and the three absorbance readings averaged. Quality checks were also performed on the instrument by checking the absorbance after every ten sample runs.

Spinach, kales seedlings and water

Water, kales seedlings and spinach samples were collected from ten sampling sites which were selected based on their proximity to the garage. Therefore, a total of ten water samples were collected. Similarly, vegetables (ten spinach and ten kales seedlings) were purchased directly from a farmer who grows them there. Sample containers were thoroughly washed with detergent, rinsed with water and then with distilled water before soaking in 5% HNO₃ for about 24 hrs. Containers were finally rinsed with distilled water before being used for sampling. Water samples were collected following the procedure recommended by American Public Health Association (APHA *et al* 1994). Water samples were kept cooled *en route* to the laboratory and stored at 4 °C in a refrigerator until analyzed. Vegetable samples were placed in polyethylene bags, labeled and taken to the laboratory. Plant samples were thoroughly rinsed with water and with distilled water to remove any attached soil particles and they were oven – dried at 60 °C. The dried vegetables were ground into fine particles using a clean acid – washed blender.

Results and discussions

Concentration levels of Cd in soil

The total concentration levels of Cd in the soil are shown in table 1. The average concentration of Cd in bulk soil was 2.95±0.14mg/kg and ranged from 0.40 to 4.80mg/kg. Though the mean of total concentration did not exceed the maximum allowed concentrations for Cd in soils set at 3mg/kg, it is clear from the range that some sites exceeded it. From the results on Table 1 the

exchangeable fraction of Cd ranged from 0.20 to 3.20 mg/kg with a mean of 1.04 ± 0.08 mg/kg which was 32.4% of the mean pseudo-total concentration constituting a mobility factor of 32.4. This fraction contains the most active and presumably the most mobile and bioavailable metals (Xian, 1989).

Table 1: Average concentration levels and ranges of cadmium in soil and in the various fractions

FRACTIONS	MEAN \pm SE n=40	RANGE
Exchangeable	1.04 ± 0.08^a	0.20-3.20
Reducibles	0.38 ± 0.06^c	0.00-3.40
Oxidisable	0.74 ± 0.06^a	0.00-2.40
Residual	1.05 ± 0.08^b	0.20-3.60
Total	2.95 ± 0.14^d	0.40-4.80

*Mean \pm SE values followed by different small letters within the same column are significantly different ($p < 0.05$ at $\alpha = 0.05$)

This high percentage of cadmium associated with the exchangeable and hence high mobility factor is worrying for it can easily be transferred into the food chain through water reservoirs and uptake by plants growing in the soil (Kartal and Birol, 2003).

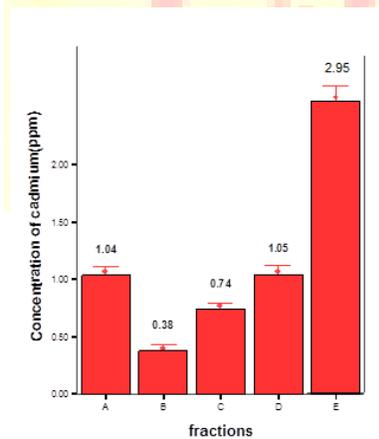


Figure 1: mean concentration levels of cadmium in the fractions

A-Exchangeable, B-Reducibles, C-oxidisable, D-residuals and E-Total

Table 2 shows the average concentration and ranges of lead in the bulk soil and also in the four fractions; exchangeable, reducible, oxidisable and residual.

Table 2: Average concentration levels and ranges of lead in soil and in the various fractions

FRACTIONS	MEAN±SE n=40	RANGE
Exchangeable	9.73±0.47 ^c	4.40-31.40
Reducible	91.01±7.31 ^a	9.00-448.00
Oxidisable	22.53±2.63 ^b	0.00-136.40
Residual	14.72±0.62 ^c	5.00-37.40
Total	128.36±6.51 ^d	22.00-313.60

*mean±SE values followed by different small letters within the same column are significantly different (p<0.05 at α=0.05)

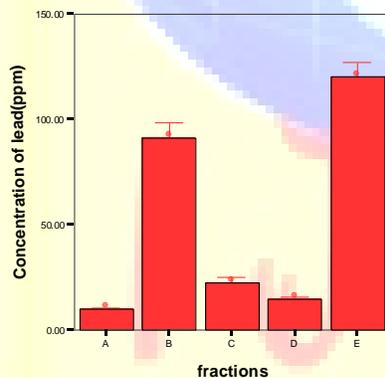


Figure 2 mean levels of lead in the fractions

A-Exchangeable, B-Reducibles, C-oxidisable organics and sulphides, D-residuals and E-Total

The concentration of lead in bulk soil ranged from 22.00 to 313.60mg/kg and averaged at 128.36±6.51mg/kg. This exceeds the maximum allowed concentrations for lead set at 100 mg/kg. The average concentration levels of lead in the various fractions from highest to lowest followed the order; reducible(66%), oxidisable(16.3%), residual(10.7%) and

exchangeable(7.1%). The low concentration levels of exchangeable lead obtained (7.1% of pseudo-total) is consistent with other reports (Sheppard and Thibault, 1992, Kartaland Birol, 2003, Kabala and Singh, 2001, Yusuf, 2007). Lead found in the reducible fraction where 66% of the pseudo-total was bound can be readily mobilized under reducing conditions (Bourg and Vedy, 1986). It has also been reported that un-extracted lead in the exchangeable fraction desorbs in the reducible fraction (Ryan *et al.* 2002). Lead in the oxidisable fractions where 16.3% was bound is known to increase mobility in acid soils (Jorgensen and Willems, 1987). The lead contained in the residual fraction is a relatively stable and weakly (Sheppard and Thibault, 1992; Ramos *et al.*, 1994; Karczewska *et al.*, 1998; Ahumada *et al.*, 1999; Kabala and Singh, 2001). Mobilizing it requires the use of aggressive extracting solutions (Zauyahet *et al.*, 2004).

Table 3: Average concentration levels of cadmium and lead in the kales seedlings obtained from 10 sample sites

Sites	Cadmium in mg/kg		Lead in mg/kg	
	Mean±SE	n = 30	Mean±SE	n = 30
1	0.87±0.01		12.71±0.27	
2	0.82±0.03		13.29±0.33	
3	0.83±0.01		10.25±0.00	
4	1.07±0.02		19.60±0.27	
5	0.80±0.03		13.23±0.10	
6	0.73±0.03		13.72±0.06	
7	1.04±0.05		13.99±0.03	
8	0.93±0.03		18.90±0.23	
9	1.42±0.02		15.18±0.05	
10	1.50±0.03		12.84±0.33	

Concentration levels of cadmium and lead in kales seedlings

The average concentration levels of cadmium and lead in the nearby kales seedlings are shown in Table 3. They ranged from 0.73 to 1.50 mg/kg and 10.25 to 19.60 mg/kg for Cd and Pb respectively. As expected from high mobility factor of Cd and high concentration levels of Pb in the soil, their levels were found to be higher than WHO maximum allowed limits of 0.2 µg/g Cd and 0.3 mg/kg Pb for vegetables (WHO, 1995).

Table 4: Average concentration levels of cadmium and lead in spinach obtained from 10 sample sites

Site	Cadmium		Lead	
	Mean±SE	n = 10	Mean±SE	n = 10
1	1.69±0.02		8.18±0.00	
2	0.85±0.02		8.95±0.08	
3	0.84±0.01		7.83±0.02	
4	0.95±0.03		8.93±0.17	
5	0.94±0.03		11.92±0.14	
6	1.35±0.02		12.69±0.10	
7	1.55±0.03		12.28±0.14	
8	1.75±0.05		13.57±0.33	
9	1.29±0.03		17.28±0.03	
10	1.67±0.02		20.53±0.15	

Table 4 shows the average concentration levels of cadmium and lead in the nearby spinach. They ranged from 0.84 to 1.75 mg/kg and 7.83 to 20.53 mg/kg for Cd and Pb respectively. These results are consistent with lead levels in literature report by Leelhaphuntet *et al.*, 1994. However, cadmium

levels are much higher than those reported by Denmark National Food Agency (Benkoetal., 1995)

Concentration levels of cadmium and lead in water samples

Concentration levels of cadmium and lead in the water samples from the drainage near the garage are shown in table 5.

Table 5: Average concentration levels of cadmium and lead in water obtained from 10 sites

Site	Cadmium	Lead
	Mean±SE n = 10	Mean±SE n = 10
1	0.96±0.02	5.50±0.07
2	1.25±0.02	5.85±0.09
3	0.77±0.02	5.89±0.01
4	1.09±0.03	6.44±0.13
5	1.09±0.03	4.60±0.00
6	0.93±0.01	8.89±0.09
7	1.33±0.02	6.25±0.00
8	1.15±0.05	4.95±0.15
9	1.50±0.02	6.62±0.02
10	1.27±0.01	7.13±0.14

Concentration levels of cadmium in the water samples ranged from 0.77 to 1.50mg/kg while those of lead ranged from 4.60 to 8.89 µg/g. These levels are significantly higher than the WHO standard value of maximum safe limits for drinking water of 0.03 µg/g for cadmium and 0.01 µg/g for lead. This is an indication that there is considerable lead and cadmium contamination when compared to natural unpolluted water systems (UNEP, 2004). One

probable source of lead pollution in the water is the leaching from soil that is found next to busy highways into the water system (USEPA, 2003). Once lead falls onto the soil, it usually attaches to the soil, from where small amounts may be leached into rivers, lakes and streams as the soil particles are moved by rainwater (Mahaffey *et al.*, 1982). Contamination of groundwater by lead may also result from the dissolution of lead from soil and earth crust, where it is usually present in a form of carbonate and hydroxide complex, with varying degree of solubility (WHO, 1995).

Conclusion

This study established that the levels of lead in the soils were very high but had fairly high mobility factors while those of Cd were fair high with extremely high mobility factors. Consequently their concentrations in the nearby water pools and vegetables were higher than the maximum allowed levels. Therefore there is urgent need for strict enforcement of proper waste management procedures, continuous education and training to the artisans with emphasis on environmental implications of poor waste management and efficient soil remediation programs at the sites.

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