

Quantification and Speciation of Lead, Cadmium and Chromium in Dandora Dumpsite Soils

P. M. Kahara^{1*}, J. Murungi², J. K. Kiptoo¹ and G. Nyaga¹

¹*Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology, P.O.Box 62 000-00200, Nairobi, Kenya.*

²*Department of Chemistry, Kenyatta University, P.O.Box 43844-00100, Nairobi, Kenya.*

Authors' contributions

This work was carried out in collaboration among all authors. Author PMK designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors JM, JKK and GN reviewed the experimental design and all drafts of the manuscript. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2020/v29i330166

Editor(s):

(1) Thomas P. West, Texas A&M University-Commerce, USA.

Reviewers:

(1) Gilbert Feuyit, University of Yaounde I, Cameroon.

(2) Adefarati Oloruntoba, Bioresources Development Center, Nigeria.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/55298>

Original Research Article

Received 11 January 2020

Accepted 17 March 2020

Published 30 March 2020

ABSTRACT

Open dumpsites are one of the main sources of heavy metals and as a result, lots of research has been undertaken on the pseudo-total content of heavy metals in dumpsite soils, but little research on the forms in which they exist. The current research was carried out to determine levels of chromium, lead and cadmium in the various fractions of Dandora dumpsite soil and how they are fractionated in the topsoil and subsoil horizons. Samples were obtained from eight sites with depths of (0-30 cm) and (30-60 cm) for topsoil and bottom soils respectively. The modified Community Bureau of Reference (BCR) sequential extraction procedure was used and metal analysis performed using flame atomic absorption spectrophotometry. The metals (lead, chromium and cadmium) total concentration ($\mu\text{g/g}$) in the upper soil profile ranged from 42.22 to 1096.21, 38.26 to 180.60 and 11.23 to 44.22 while the lower soil profiles were 54.19 to 239.28, 30.56 to 76.48 and 9.47 to 22.56, respectively. The concentration of lead in various fractions of the upper soil profile followed the order; reducible > oxidisable > residual > exchangeable, while that of chromium was residual > oxidisable > reducible > exchangeable. Cadmium followed the order exchangeable > residual > reducible > oxidisable. The percentage of the metals in non-residual fraction were Pb

*Corresponding author: E-mail: pekta7219@gmail.com;

(78%), Cr (58.7%) and Cd (70%). Their mobility factors were (Pb) 39.7 (Cr) 7.75 and (Cd) 5.02 in the upper soil profiles. Thus, the results suggest that Dandora dumpsite is highly polluted with the selected heavy metals.

Keywords: Open dumpsites; sequential extraction; community bureau of reference; heavy metals.

1. INTRODUCTION

Modernization, high rate of industrialization coupled with population growth have immensely resulted in the generation of tonnes of solid wastes; ranging from hazardous to non-hazardous waste. Pollution of dumpsite soils with heavy metals is due to improper disposal of solid wastes such as electronic devices, used batteries, papers and even clothes. A continuous buildup of solid wastes from various sources leads to undesirable enrichment of metalloids or heavy metals in dumpsite areas. In effect, the toxic elements find their way into groundwater and soils posing severe environmental challenges.

It has been identified that metals such as lead and cadmium do not possess any biological importance while trace amounts of metals such as vanadium, manganese, iron, chromium or nickel do possess biological importance. The environmental challenge associated with heavy metals is that upon exceeding a certain concentration limit they tend to possess toxic effects on living organisms also they remain undeterred the breakdown of organic waste.

The knowledge of the binding of metals with different soil phases and components is of major interest to assess the connections with other biotic and abiotic elements of the environment. Nevertheless, metal speciation is a more complex task than the total metal contents. Several factors influence the concentration of heavy metals on and within plants. These factors include climate, atmospheric deposition, nature of the soil on which the plant is grown and degree of maturity of the plant. The nature of the soil is one of the most important factors determining the heavy metal content in plants [1].

Speciation is defined as the identification and quantification of the different defined species or forms or phases in which an element occurs. It is essentially a function of the mineralogy and chemistry of the soil sample examined [2]. Quantification is done using chemical solutions of varying but specific strength and reactivity to release the metals from the different fractions of the examined soil. In terms of metal availability to plants, various species of metals are more biologically available in the ecosystem. Bioavailability and the mobility of metals are also related to each other, the higher the concentration of mobile, toxic metals (Pb, Cd and Cr) in the column, the higher the potential for plant uptake and animal/human consumption.

Sequential extraction procedures have been developed to differentiate amongst various soil metal fractions, and are considered useful for evaluation of bioavailability of metals in soils. Bioavailability is a concept defined the degree to which chemicals present in the soils may be absorbed or metabolized by human or ecological receptors or are available for interaction with biological systems. Sequential extraction involves subjecting a given mass of sample to extraction with reagents possessing different chemical properties. These chemicals dissolve metals associated with a specific phase with all the metal species bonded to it. The geochemical fractions include exchangeable, carbonate bound, iron and manganese oxides bound, organic bound and residual [3].

2. MATERIALS AND METHODS

2.1 Study Area

The study area shown in Fig. 1 (GPS coordinates 1.2483°S, 36.8963°E) is situated in Embakasi,

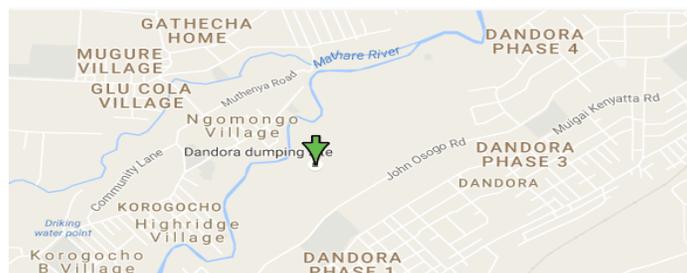


Fig. 1. Map of Dandora dumpsite

Nairobi County. Surrounding neighborhoods include Korogocho, Kariobangi, and Baba Dogo. It is one of Africa's biggest dumpsite occupying 30 acres.

2.2 Sample Collection and Pre-treatment

Soil sampling was carried out at depths of 0-30 cm and 30-60 cm for upper and lower soil profiles respectively. Upon grinding, the soil samples were then sieved (0.1 mm). After 24 hours of oven drying (150°C) of the sieved samples, 5 ml perchloric acid and nitric acid mixture in the ratio of 1:3 was then added to 1 g of the soil sample in a conical flask, followed by its digestion in a hotplate. Recovery of the metals was achieved by adding 10 ml of 0.5 M HCl followed by heating to boiling point. The resultant mixture was thereafter filtered. Preparation of blank then preceded. The soils' total organic carbon, pH and texture was determined based on procedure proposed by [4].

2.3 Fractionation Analysis

Metal fractionation analysis was carried out according to the procedure modified from the Standards, Measurement and Testing (SM&T, formerly referred to as the (BCR) procedure of the European Union according to [5]. Application of the procedure aimed at sequentially dissolving metals soluble in various extracting agents is summarized in Table 1.

Table 1. Extracting agents used in fractionation analysis

Fraction	Extracting agent
Exchangeable	0.11 M acetic acid
Reducible	0.5 M hydroxyl ammonium chloride
Oxidisable	Hydrogen peroxide
Residual	3:1 HCl: HNO ₃ (Aquaregia)

2.4 Statistical Analysis

Statistical analysis of the data obtained involved the determination of the mean and standard deviation. Variations within sampling stations and between the means involved one-way analysis of variance ($p \leq 0.05$) at 95% confidence level. Establishment of (r^2) correlation, involved analysis of Pearson's product correlation analysis moment.

3. RESULTS AND DISCUSSION

3.1 Selected Physio-Chemical Characteristics of Dandora Dumpsite Soils

The results for pH, total organic carbon and soil texture are presented in Table 2 in form of (mean± standard deviation).

The soil pH ranged from slightly acidic (5.92) to almost neutral (6.94). The most acidic soils were collected from site 2 which is 100 m from the centre of the dumpsite and site 8 which is 700 m away from the centre. This acidity might be attributed to the dumping of acidic wastes such as expired acidic fertilizers, expired acids in laboratory wastes or from bacterial activities. The values for (TOC) ranged from 8.72% in site 8 which is 700 m from the centre to 15.02% in site 1 which is at the centre of the dumpsite. The values reduced as the distance from the centre of dumpsite increased. There was a significant difference in TOC values within the sites. These values were higher than those reported by other workers [6]. This could be attributed to the fact that the type of soils and the activities of the study areas were different. The soil texture was mainly sandy except in sites 3 and 6 where it was clayish. Total organic carbon has been found to influence soil metal content through immobilization or promotes its mobility due to the formation of more soluble complexes [7].

3.2 Pseudo-total Heavy Metal Concentration

Mean and standard deviation of Cr, Pb and Cd concentrations are presented in Table 3.

For the three metals, concentrations increased to a maximum in the soils collected from the centre of the dumpsite and decreased away from the centre. Generally, the concentration decreased in the lower soil profiles. From Table 3, levels of lead in the upper soil profile were ranging between 42.11±2.01 ug/g to 1096.21±21.35 ug/g (centre of the dumpsite). In the bottom soil profile, it ranged from a mean of 37.30±4.53 ug/g 700 m away from the centre to 239.28±13.89 ug/g at the centre. The results suggest that there was a significant difference between measurements obtained from depths of 0-30 cm and those from 30-60 cm. since $p \leq 0.001$ at $\alpha = 0.05$. Over the same range, chromium levels were between 38.26±3.12 ug/g and 180.60±19.19 ug/g in the upper soil profile while in the lower soil profile it was between 27.08±1.07 ug/g to 81.02±9.01 ug/g. The results

revealed that chromium had the second-highest concentration among the metals under study. Amongst the three metals under study cadmium had the lowest total concentration ranging between 11.23 ± 0.48 ug/g to 44.22 ± 1.37 ug/g in the upper soil profile. Bottom soil profiles showed similar results but with lower concentrations ranging from 9.47 ± 0.31 to 44.22 ± 1.37 ug/g to 22.56 ± 0.75 ug/g. The results also showed a significant difference in concentrations within the various distances away from the centre and in the depths of 0-30 cm and 30-60 cm.

3.3 Forms of the Selected Heavy Metals in the Dumpsite Soils

The mean \pm standard deviation levels of the various forms of the three heavy metals in the two horizons were obtained from average mean levels of each horizon for the eight sites in the dumpsite at depths of (0-30 cm and 30-60 cm.) The results are presented in Table 4.

From Table 4, the mean levels of lead in the various forms in the upper soil profile (0-30 cm) ranged from 0.50 ± 0.05 ug/g to 4.54 ± 0.39 ug/g. The levels decreased in the order Reducible > Oxidisable > Residual > Exchangeable. In the bottom profile, the levels ranged from 0.48 ± 0.09 ug/g to 3.22 ± 0.29 ug/g. They decreased in the order Reducible > Residual > oxidisable > Exchangeable. The exchangeable fraction was the lowest in both upper and bottom soil profiles. However, the results suggest that there was a significant difference between the various fractions $p \leq 0.001$ but depth-wise Pb levels did not differ significantly. The low value of an exchangeable lead indicates that availability and tendency for environmental pollution and toxicity to biological organisms will be low [8]. The amount of lead associated with the reducible fraction is the highest 4.54 ug/g in the upper profile and 3.22 ug/g in the bottom profile. This may be due to formation of stable complexes with acetate like $[Pb(CH_3)_4]$. Although the predominant form of lead in the environment is Pb^{2+} , the higher oxidation state of Pb^{4+} has been reported to be incorporated in clay minerals and the Fe/Mn oxides structures [9], which would account for the percentage of the metal in the reducible fraction.

Levels of chromium ranged from 0.26 ± 0.01 to 1.15 ± 0.11 ug/g in the upper profile. They decreased in the order Residual > oxidisable > Reducible > Exchangeable. In the lower soil profile levels ranged from 0.26 ± 0.02 to 1.32 ± 0.09 ug/g hence decreasing in the order Reducible >

oxidisable > Reducible > Exchangeable. For chromium the soluble fraction (Exchangeable) is very low, this could be due to losses from leaching, erosion and plant uptake since this represents the fraction that is most bioavailable and mobile in the soil [10]. Although the total percentage of chromium in the soil was very high (Table 2) most of it was bound to the residual fraction and therefore largely immobile. A very small fraction 0.26 ug/g in the upper soil was associated with the exchangeable fraction while a fairly larger fraction (1.13 ug/g) was associated with the oxidisable fraction. Mean levels of cadmium ranged from 0.11 ± 0.04 ug/g to 0.26 ± 0.05 ug/g in the upper soil profile. They decreased in the order Exchangeable > Residual > Reducible > Oxidisable. In the bottom profile the levels ranged from 0.07 ± 0.03 ug/g to 0.15 ± 0.05 ug/g thus decreasing in the order Residual > Exchangeable > Oxidisable > Reducible. From the Table 4, a high percentage of cadmium was associated with non-residual fractions meaning that it can easily be transferred into the food chain through water reservoirs, uptake by plants from the soils or any other mechanism [11]. The appreciable cadmium content associated with the exchangeable fraction (0.26 ug/g) shows that its availability is susceptible to pH or ionic composition changes in the environment [12]. This creates environmental pollution concerns since Cd is a cumulative poison for mammals. Sources of Cd include wastes from Cd-based batteries, incinerators and runoff from agricultural soils where phosphate fertilizers are used since Cd is a common impurity in phosphate fertilizers. Its main ways of entering into the environment are from metal refining, electroplating, phone batteries and paint industries [13]. Previous studies by [14] indicate relative ease of uptake of Cd from the soils by the plant.

3.4 Mobility Factors for Lead, Chromium and Cadmium

Mobility of metals in soils may be assessed based on the absolute and relative content of the fractions weakly bound to soil components. The relative index of metal mobility was calculated as mobility factor (M.F) [15] based on the following equation.

$$M.F. = \frac{F_1}{F_1 + F_2 + F_3 + F_4} \times 100$$

Where M.F is the mobility factor, F_1 is the 1st fraction (exchangeable), F_2 is the 2nd fraction (reducible), F_3 is the 3rd fraction (oxidisable)

Table 2. Mean physicochemical parameters of the dumpsite soil (n=8)

Parameter	Site							
	1	2	3	4	5	6	7	8
pH	6.33±0.11	5.89±0.23	6.40±0.29	6.51±0.01	6.89±0.37	6.58±0.91	6.53±0.44	6.00±0.22
TOC(%)	15.48±0.26	14.11±0.33	12.19±0.55	11.62±0.17	9.60±0.98	9.25±0.17	11.370 ±0.56	8.15±0.30
Texture	Sandy	Sandy	Clay	Sandy	Sandy	Clay	Sandy	Sandy

Table 3. Mean levels of Pb, Cr and Cd in the dumpsite soil in ug/g (n=8)

Site	Chromium		Lead		Cadmium	
	Upper soil profile	Lower soil profile	Upper soil profile	Lower soil profile	Upper soil profile	Lower soil profile
1	180.60±19.19	76.48±8.68	1096.21±21.35	239.28±13.89	44.22±1.37	22.56±0.75
2	168.54±11.27	81.02±9.01	979.83±49.90	243.41±37.84	29.47±3.18	19.27±1.50
3	140.26±15.66	73.98±10.63	802.44±52.43	181.14±33.67	20.42±3.24	18.41±1.10
4	121.15±9.39	43.28±2.80	320.55±34.12	92.40±20.19	22.54±2.50	13.98±1.45
5	92.63±1.24	31.23±1.99	237.34±22.12	91.08±13.72	24.73±1.22	13.07±0.78
6	71.42±4.45	40.47±1.40	102.10±11.20	101.82±23.94	18.25±1.37	10.46±0.33
7	46.97±1.14	27.08±1.07	69.44±3.17	37.30±4.53	12.48±1.08	10.42±0.08
8	38.26±3.12	30.56±2.28	42.11±2.01	54.19±11.85	11.23±0.48	9.47±0.31

Table 4. Forms of Cd, Cr and Pb in the dumpsite soils (µg/g)

	Depth	Exchangeable	Reducible	Oxidisable	Residual	Total
Cd	0-30 cm	0.26±0.05	0.15±0.04	0.11±0.04	0.21±0.06	0.62±0.14
	30-60	0.13±0.05	0.07±0.03	0.10±0.04	0.15±0.05	0.53±0.15
Cr	0-30 cm	0.26±0.01	0.73±0.04	1.13±0.11	1.51±0.11	3.15±0.20
	30-60	0.26±0.02	0.68±0.04	1.04±0.10	1.32±0.09	2.73±0.23
Pb	0-30 cm	0.50±0.05	4.54±0.39	1.94±0.13	2.60±0.13	8.40±0.62
	30-60	0.48±0.09	3.22±0.29	1.65±0.11	2.31±0.14	6.90±0.47

while F_4 is the fourth fraction (residual). The study reveals that cadmium had the highest mobility factor in the two soil profiles with a mean of 39.70 ± 4.32 in the upper profile and 34.09 ± 8.30 in bottom profile. It was followed by chromium while lead had the lowest mobility. These high mobilities indicate that the metals are mobile and bioavailable. A high mobility factor for heavy metal has been interpreted as evidence of relatively high lability and biological availability [16].

Table 5. Mobility factors (Mean \pm SD) for cadmium, chromium and lead in the dumpsite soils

Depth	Cadmium	Chromium	Lead
0-30 cm	39.70 ± 4.32	7.75 ± 0.45	5.02 ± 0.23
30-60 cm	34.09 ± 8.30	8.40 ± 0.57	5.48 ± 0.61
p-value	0.521	0.373	0.484

4. CONCLUSIONS

The increasing amount of total metal content in the dumpsite soil could be due to human activities. The main source is the uncontrolled disposal of solid wastes in the dumpsite. The results revealed that there is a significant difference in levels of Pb, Cr and Cd in the eight sampling points. A high percentage of all the metals were associated with non-residual fractions which indicates that all these metals were mobile and potentially bioavailable. The levels of lead in the fractions from highest to lowest followed the order, reducible, oxidisable, residual and exchangeable while chromium was in the order residual, oxidisable, reducible and exchangeable and cadmium was in the order exchangeable, residual, reducible then oxidisable. Mobility factors for Pb, Cr, and Cd were 39.7, 7.75 and 5.2 respectively.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Bäckström M, Nilsson U, Håkansson K, Allard B, Karlsson S. Speciation of heavy metals in road runoff and roadside total deposition. *Water, Air and Soil Pollution*. 2003;147(1-4):343-366.
- Tokaloğlu S, Kartal S, Elçi L. Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. *Analytica Chimica Acta*. 2000;413(1-2):33-40.
- Chisti Y. Biodiesel from microalgae. *Biotechnology Advances*. 2007;25(3):294-306.
- Burt R, Wilson MA, Keck TJ, Dougherty BD, Strom DE, Lindahl JA. Trace element speciation in selected smelter-contaminated soils in Anaconda and Deer Lodge Valley, Montana, USA. *Advances in Environmental Research*. 2003;8(1):51-67.
- Greenway GM, Song JQ. Heavy metal speciation in the composting process. *Journal of Environmental Monitoring*. 2002;4(2):300-305.
- Yuan CG, Shi BJ, He B, Liu FJ, Liang LN, Jiang GB. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environment International*. 2004;30(6):769-783.
- Pagnanelli F, Esposito A, Toro L, Veglio F. Metal speciation and pH effect on Pb, Cu, Zn and Cd biosorption onto *Sphaerotilus natans*: Langmuir-type empirical model. *Water Research*. 2003;37(3):627-633.
- Gümgüm B, Öztürk G. Chemical speciation of heavy metals in the Tigris River sediment. *Chemical Speciation & Bioavailability*. 2001;13(1):25-29.
- Nemati K, Bakar K, Abas R, Sobhanzadeh E. Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. *Journal of Hazardous Materials*. 2011;192(1):402-410.
- Dong B, Liu X, Dai L, Xiaohu D. Changes of heavy metal speciation during high-solid anaerobic digestion of sewage sludge. *Bioresource Technology*. 2013;131:152-158.
- Kosobucki P, Kruk M, Buszewski B. Immobilization of selected heavy metals in sewage sludge by natural zeolites. *Bioresource Technology*. 2008;99(13):5972-5976.
- Kumar A, Ramanathan LA. Speciation of selected trace metals (Fe, Mn, Cu and Zn) with depth in the sediments of Sundarban mangroves: India and Bangladesh. *Journal of Soils and Sediments*. 2015;2476-2486.
- Davutluoglu OI, Seckin G, Kalat GD, Yilmaz T, Ersu BC. Speciation and implications of heavy metal content in

- surface sediments of Akyatan Lagoon–Turkey. Desalination. 2010;260(1-3):199-210.
14. Luo M, Jianqiang L, Weipeng C, Maolan W. Study of heavy metal speciation in branch sediments of Poyang Lake. Journal of Environmental Sciences. 2008;20(2): 161-166.
15. Abollino O, Aceto M, Malandrino M, Mentasti E, Sarzanini C, Petrella F. Heavy metals in agricultural soils from Piedmont, Italy. Distribution, speciation and chemometric data treatment. Chemosphere. 2002;49(6):545-557.
16. Cai QY, Mo CH, Wu QT, Zeng QY, Athanasios K. Concentration and speciation of heavy metals in six different sewage sludge-composts. Journal of Hazardous Materials. 2007;147(3):1063-1072.

© 2020 Kahara et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
<http://www.sdiarticle4.com/review-history/55298>