Bull Environ Contam Toxicol (2010) 85:318–323
DOI 10.1007/s00128-010-0033-x

Distribution of Cd and Zn Levels in Soils and *Acacia xanthophloea* Benth. from Lake Nakuru National Park Kenya

N. Dharani · J. M. Onyari · J. I. Kinyamario · D. M. Maina · K. M. Mavuti

Received: 24 August 2009 / Accepted: 12 May 2010 / Published online: 11 July 2010

Abstract Cadmium and zinc from anthropogenic sources in Lake Nakuru were investigated. High metal levels (mg/kg) in soils (Cd $\leq$ 16.3 and Zn $\leq$ 280) and Acacia *xanthophloea* (Cd $\leq$ 32 and Zn $\leq$ 310) were observed at polluted sites. Significant variations in metal values were evaluated using ANOVA (*F* test) and student's *t* test at $p < 0.05$ and metal correlations studied. High levels of metals in soils and unhealthy/dying *Acacia* were obtained at polluted sites. Significant positive correlation was obtained between Cd and Zn in soils and plants. Acacia sp are effective biomonitor of environmental quality in areas subjected to pollution.

Keywords Cadmium · Zinc · Soils · Acacia

Environmental pollution with toxic metals continues to be a serious global concern. Pollution of the Environment includes soils and water resources with toxic trace metals have increased considerably since the onset of industrialization and urbanization (Nriagu 1979, 1990; Senwo and Tazisong 2004). Trace metals either derived from natural inputs and anthropogenic emissions are ubiquitous in the global environment (Blackmore 1998; De Wolf et al. 2001; Muohi et al. 2003; Dharani et al. 2007). Certain toxic metals including cadmium (Cd) and zinc (Zn) are regularly mentioned as potentially toxic to living terrestrial and aquatic ecosystem (USEPA 1995).

Heavy metal pollution in the soils and plants has been reported by a number of scientists. Elemental values in soils of Brazil (Campos 2003), Florida (Ma et al. 1997), Kenya (Wandiga and Onyari 1987; Maskall and Thornton 1996; Dharani et al. 2007), India (Kuhad et al. 1998), China (Chen et al. 1991), Canada (Frank et al. 1976), Syria (Khuder et al. 1998), and South Carolina (Franklin et al. 2003) have been investigated. Heavy metals data has also been reported along the Kenyan Coast (Wandiga and Onyari 1987; Everaarts and Nieuwenhuie 1995; Williams et al. 1996; Muohi et al. 2003), and sediments in Lake Victoria, Kenya (Urasa and Onyari 1996; Orata 2003). According to Muohi et al. (2003), the high concentrations of Zn and Cd reported in sediments along Kenyan coast, and Orata (2003) from sediments in Winam Gulf in Lake Victoria in Kenya, are primarily attributable to various anthropogenic inputs that includes industrial effluents, sewage, urban/domestic wastes and car washing activities.

Pyatt (1999, 2001) reported heavy metal concentrations in pine needles and in acacia tree (*Acacia retinoides*) from Cyprus. The plants were found to act as effective bioaccumulators of heavy metals. Metal concentrations have also been investigated in soils and plants (Bowell and Ansah 1994) in Ghana. Botanical materials such as fungi, lichens, tree bark, tree leaves and tree rings of higher plants, have been used to detect the deposition,

N. Dharani (✉)
Kenyatta University, P.O. Box 13800,
00800 Nairobi, Kenya
e-mail: ndbonsai@gmail.com

J. M. Onyari
Department of Chemistry, College of Biological and Physical Sciences, University of Nairobi, P.O. Box 30197,
Nairobi, Kenya

J. I. Kinyamario · K. M. Mavuti
School of Biological Sciences, College of Biological and Physical Sciences, University of Nairobi, P.O. Box 30197,
Nairobi, Kenya

D. M. Maina
Institute of Nuclear Science, University of Nairobi,
P.O. Box 30197, Nairobi, Kenya

accumulation and distribution of metal pollution. Hence, the most economical and reasonable method for monitoring the heavy metal levels in the atmosphere is using vegetation. Scots pines (Yilmaz and Zengin 2004) and acacia (Aksoy et al. 2000a) and other plants (Aksoy et al. 2000b) have been used for biomonitoring of heavy metal levels in ecosystems. Lake Nakuru National Park is a closed drainage basin and the catchment areas include a highly agricultural community surrounding the park, an urban area with a fast growing human population and an industrial sector (Raini 1995). The major vegetation type of the park is *A. xanthophloea* woodland, an important habitat for many wild animals, providing nesting places and shelter for many resident and migratory birds. The woodland also provides forage for large herbivores, mainly the Rothschild's Giraffe (*Giraffa camelopardalis rothschildi*) and Black Rhinoceros (*Diceros bicornis*). In recent years, *Acacia xanthophloea* trees have been undergoing unexplained die back in Lake Nakuru National Park. This study was therefore undertaken to assess the current levels of copper and lead, identify the sources in Lake Nakuru National Park and suggest some conservation measures to alleviate the serious ecological pollution problems facing the lake.

Materials and Methods

Lake Nakuru National Park (Fig. 1) lies in the eastern arm of the Great Rift Valley and its altitude ranges from approximately 1,760 to 2,080 m above sea level. Lake Nakuru occupies roughly 42 km^2 at its lowest point in a wider catchment basin of approximately 1,800 km^2. Water flows into the lake through rivers, Makalia and Nderit. The lake also receives water through a series of fresh water springs along the northern and eastern shorelines. It is also fed through direct precipitation and subsequent runoff from Nakuru town. The soil samples were collected from four different sites (A, B, C and D) during the rainy and dry seasons. Soils samples were taken at different depths (0–20, 20–40 and 40–60 cm). Site A was selected from Bahraini springs area on the eastern shoreline where acacia trees are dying. Samples collected were A1 (0–20 cm), A2 (20–40 cm) and A3 (40–60 cm). Site B was selected opposite pelican corner on the western shoreline where acacia trees are healthy. Samples collected were B1 (0–20 cm), B2 (20–40 cm) and B3 (40–60 cm). Site C is near Naishi headquarter in the southern part of the park where acacia trees are healthy. Samples collected were C1 (0–20 cm), C2 (20–40 cm) and C3 (40–60 cm). Site D was selected from Njoro river sewage area in the north-western part of the park where acacia trees were dying. Samples collected were D1 (0–20 cm), D2 (20–40 cm) and D3 (40–60 cm).

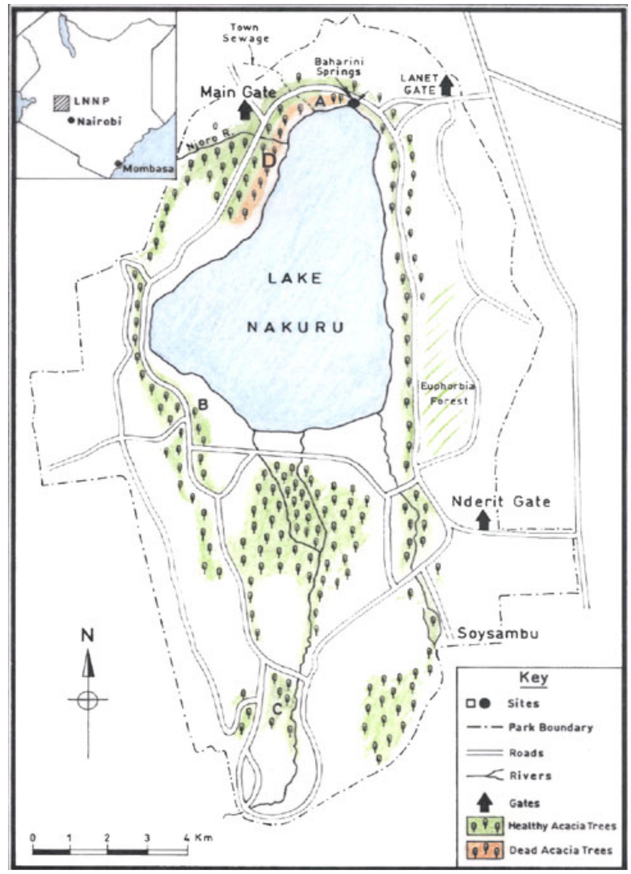


Fig. 1 Lake Nakuru National Park's map showing the Baharini springs, the swamps near Baharini springs, Town, Njoro river sewage, and Nakuru town industrial area

Soil samples were dried in an oven at 105°C for 24 h, then ground and sieved. The fraction of the soil material, which passed through <63 μm sieve was collected. For analysis, 1.0 ± 0.1 g triplicate of the fine soil samples were weighed in labeled digestion tubes. After the addition of 20 mL conc. Hydrochloric acid, the samples were digested for 3 h at 100°C in an aluminum heating block. The digestion mixture was cooled to room temperature and 1 mL hydrogen peroxide carefully added. The digestion tubes were heated for a further 30 min. The digests were allowed to cool and quantitatively transferred into 50 mL volumetric flasks and made up to mark using deionized water. The digestion mixture was transferred into 50 mL polypropylene bottles ready for analysis. Reagent blanks were prepared in a similar manner for every batch of sample to cater for matrix effects.

The plant samples were dried in an oven at 70°C for 24 h. The dried samples were then cut into small pieces using a stainless steel knife. They were further ground using a leaf grinder to obtain a fine powder. For analysis, 2.0 ± 0.05 g of the ground samples were weighed in digestion tubes and 15 mL of conc. nitric acid and 5 mL of conc. perchloric acid

($HClO_4$) were added. The mixture was kept for at least 24 h for initial digestion process and subsequently digested in a digestion block at a temperature of 130°C for 1.5 h (until the brown fumes ceased, resulting in a clear and colorless solution). The digests were filtered through glass wool, into 50 mL volumetric flasks and the filtrate diluted to volume using deionized water. The digests were then transferred into polypropylene bottles ready for analysis. Reagent blanks were prepared in a similar manner for every batch of sample to cater for matrix effects.

Acacia xanthophloea plant samples were collected from different sites as listed below:

P1 = Bark collected from healthy mature trees from site B (opposite pelican corner).
P2 = Bark collected from unhealthy trees from site A (Baharini springs area).
P3 = Bark collected from unhealthy trees from site D (Njoro river sewage area).
P4 = Leaves and twigs from healthy trees from site B (Opposite pelican corner).
P5 = Leaves and twigs from unhealthy trees from site A (Baharini springs area).
P6 = Leaves and twigs from unhealthy trees from site D (Njoro river sewage area).

Evaluation of the accuracy of the analytical method was done using SOIL-7 and *Bowen kale* leaves certified reference materials obtained from International Atomic Energy Agency (IAEA). The results indicated good accuracy between experimental and IAEA certified values. Two techniques were used for comparison, Atomic Absorption Spectrophotometer and Energy Dispersive X-ray Fluorescence (EDXRF).

Analytical results were evaluated using SPSS (version 9.0). The standard deviation values of the means were calculated using the Excel for windows 2000, to compare the site categories. Student's *t*-test and ANOVA (*F*-test) were performed using the software SPSS (version 9.0). Student's *t*-test were also conducted to determine the significant differences in metal content during rainy and the dry seasons. ANOVA (*F*-test) was performed to compare the different sites studied.

Results and Discussion

Table 1 gives the AAS and EDXRF analytical results obtained for IAEA *Bowen kale leaves* Certified Reference Material. The results shown indicate good agreement between experimental and certified values. Dharani et al. (2007) reported the typical XRF spectra for *Acacia xanthophloea* from Lake Nakuru National Park showing the presence of zinc.

Table 1 Observed and certified values* (mg/kg) for IAEA Soil-7 CRM

Technique		Zn	Cd
AAS	Observed	92.2 ± 0.06	2.3 ± 0.05
EDXRF	Observed	99 ± 5.28	–
*	Certified	101–113	1.1–2.7 (NC)

NC Not certified. ≤ = less than or equal to the detection limit

Table 2 Comparative analysis of zinc levels (mg/kg) soils collected from Lake Nakuru National Park (sites *A*, *B*, *C*, *D*) using AAS and EDXRF

Samples	Elements	AAS	EDXRF
Soils			
B1	Zn	178 ± 11.4	170 ± 2.5
B3	Zn	175 ± 10	181 ± 24
D1	Zn	157 ± 5.0	145 ± 6.7

Table 3 Comparative analysis of zinc levels (mg/kg) in *Acacia xanthophloea* collected from Lake Nakuru National Park (sites *A*, *B*, *C*, *D*) using AAS and EDXRF, respectively

P1	Zn	18 ± 1.0	16.7 ± 2.2
P3	Zn	310 ± 16	325 ± 24
P5	Zn	167 ± 5.5	160 ± 6.0

The data shown in Tables 2 and 3 demonstrate good agreement between the two techniques employed, attesting to the good accuracy of the procedure used for analysis of the samples. Cadmium could not be analyzed using XRF since the primary X-ray excitation source used was radioactive ^{109}Cd.

The mean zinc and cadmium concentrations measured in soils obtained from the sites investigated are shown in Figs. 2, 3, 4, 5.

The mean cadmium and zinc concentrations measured in soils obtained from various sites both in rainy and dry seasons investigated are shown in Figs. 2 and 3, respectively. Our results reveal a high content of cadmium in soils from Baharini springs (9.6 ± 1.0 to 12.2 ± 2.2 mg/kg) and Njoro river sewage area (12 ± 1.3 to 16.3 ± 2.3 mg/kg) in both seasons. Normal average concentration of cadmium in soils ranges from 0.01 to 2.0 mg/kg (Alloway 1990). However, concentrations of Cd were found to be lower in soils located opposite pelican corner (site B) and near Naishi headquarter (site C) in both seasons. Inputs of Cd to the environment are derived from various diffuse sources. According to Boeham and Schaefers (1994), primary materials containing Cd and their concentrations (mg/kg) are zinc ore concentrates

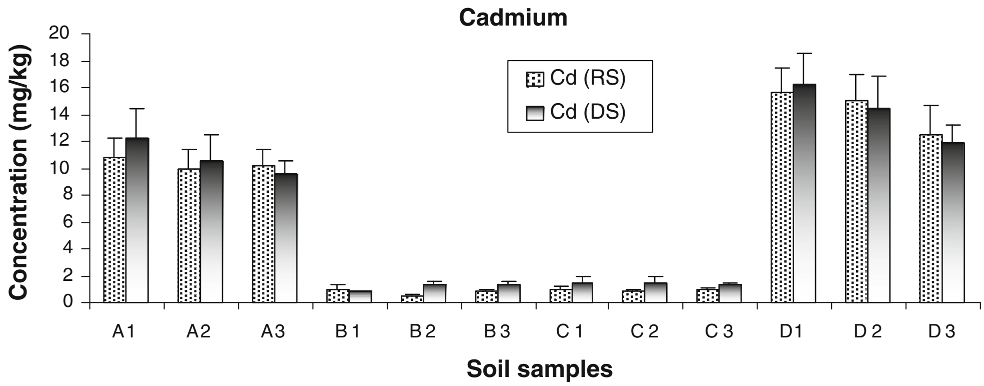


Fig. 2 Concentration (mean ± SD) of cadmium in soil samples collected from. Sites *A*, *B*, *C* and *D* during the rainy season and the dry seasons

Fig. 3 Concentration (mean ± SD) of zinc in soil samples collected from sites. *A* to *D* during the rainy season and the dry seasons

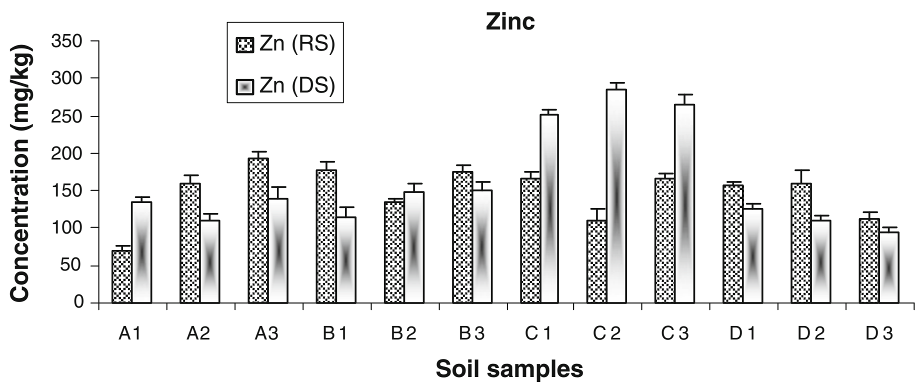


Fig. 4 Concentration (mean ± SD) of cadmium in *Acacia xanthophloea* samples

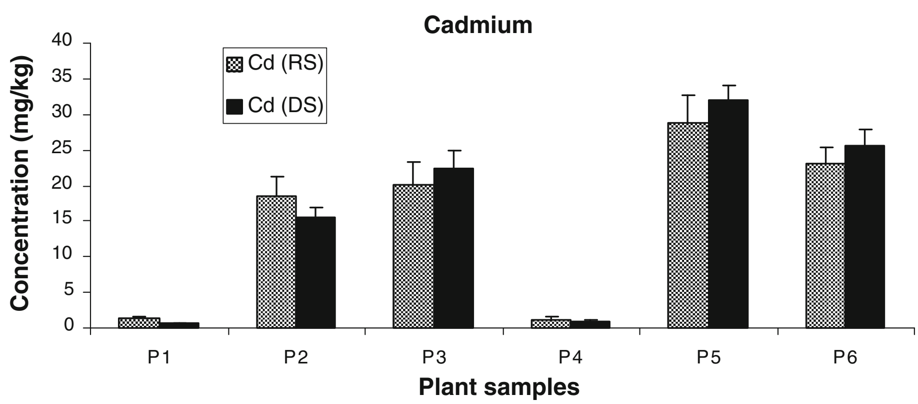
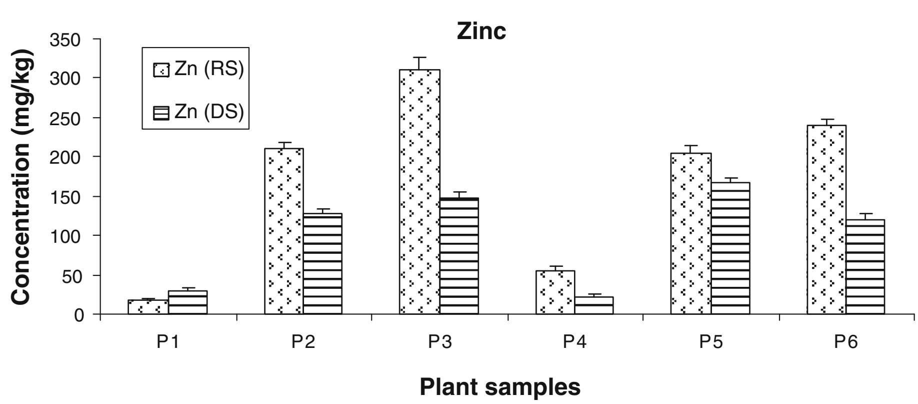


Fig. 5 Concentration (mean ± SD) of zinc in *Acacia xanthophloea* samples



(1,000–12,000), lead ore concentrates (3–500), copper ore concentrates (30–1,200), iron ore (0.12–0.30), hard coal (0.50–10.0), heavy oil (0.01–0.10), phosphate ore (0.25–80) and soils. The higher level of Cd obtained in soils samples might be due to contribution from other anthropogenic sources such as agricultural runoff where fertilizers are used in addition to possible release of soil bound-metal. Sources of Cd include waste from industrial toxic waste, Cd-based batteries, incinerators and runoff from agricultural soils where phosphate fertilizers are used. Cadmium is a common impurity in phosphate fertilizers. High levels of Cd have also been reported in sediments from Winam Gulf in Lake Victoria in Kenya by Orata (2003) and in Mombasa, Kenya coast (Wandiga and Onyari 1987; Onyari 1985; Muohi et al. 2003).

Results of trace metal analyses for plant samples are presented in Figs. 4 and 5. Zinc in higher plants, ranges from between 10 and 120 mg/kg of dry matter at its normal average concentration. A concentration greater than 120 mg/kg is considered to be an excess or toxic to plants. Conversely, if the concentration of Zn is less than 10 mg/kg, it is thought to be deficient (Marschner 1997 and Chen et al. 2001). A considerably high mean concentration of zinc above toxic level was found in samples from Baharini springs ranging from 128 ± 6.3 to 210 ± 7.9 mg/kg and 167 ± 5.5 to 205 ± 8.7 mg/kg for samples P2 and P5, respectively. Also, plant samples from Njoro river sewage area showed high levels of Zn (148 ± 6.8 to 310 ± 16) for sample P3 and 120 ± 7.9 to 239 ± 7.8 mg/kg for sample P6. The leaves and bark from unhealthy *A. xanthophloea* trees demonstrated very high values of Zn in their tissues. The high content of Zn can be attributed to anthropogenic activities inputs to Lake Nakuru through the industrial wastes discharged into the town effluents, Njoro river sewage, and storm drainage during the heavy rainfall. Industrial effluents mainly arise from the battery industry (zinc chloride, tin, and zinc oxide), paint manufacturing industry (paint additives), galvanized metals and zinc containing products that are significant sources of Zn to Lake Nakuru.

In higher plants, cadmium usually ranges from 0.05–0.2 mg/kg at its normal average concentration. In general, plants are considered to be toxic when Cd levels rise above 3 mg/kg (Kamugi 1990; David 1998). Whereas, the bark and leaves samples collected from opposite pelican corner (P1 and P4) exhibited low concentration of all toxic metals including Zn and Cd, very high mean concentration of Cd in leaf and bark tissues of *A. xanthophloea* trees collected from Baharini springs ranging from 15.5 ± 1.5 to 2.6 ± 1.8 mg/kg for sample P2 and 28.8 ± 4.0 to 32 ± 2.0 mg/kg for sample P5. The results obtained in this study indicate a very high mean concentration of Cd in leaf and bark tissues of unhealthy and sick *A. xanthophloea* trees in Lake Nakuru. High levels of Cd in plant tissues are probably influenced by industrial waste pollution that is introduced in the Lake ecosystem through sewage sludge and industrial drainage. Heavy use of chemical fertilizers and manure in agricultural farming also add Cd pollutants to Lake Nakuru. According to Celik et al. (2005), the death of *Robinio pseudo-acacia* L. in Denizli, Turkey occurred due to high concentrations of heavy metals in the plant that were attributed to their close proximity to industrial areas and in urban roadsides. Nevertheless, it should be remembered that many plant species thrive in metal-contaminated soils and are used as phytoremediating plants (Celik et al. 2005). Deng et al. (2004) reported that the concentrations of Pb, Zn, Cu and Cd accumulated in the root tissues of wetland plant species *Leersia hexandra*, *Juncus effuses* and *Eqisetum Ramosisti* were investigated in field conditions of China. According to their study some plant species could accumulate relatively high metal concentrations (far above the toxic concentrations to plants).

Significant seasonal variations in the mean Cd and Zn values were demonstrated by ANOVA (F test) and student's t test at $p < 0.05$ for all sites investigated. Significant elemental correlations were calculated by Pearson's correlation coefficient (r). Elemental concentrations calculated for soils collected from sites A and D showed that Cd correlated positively to Zn. A significant positive correlation was also found between Cd and Zn in the soils and plants collected from sites A and D. The level of other heavy metal pollutants like Pb and Cu in the soils and in *Acacia xanthophloea in* Lake Nakuru National Park Kenya, were investigated by Dharani et al. (2007) and the results obtained indicated high levels of Pb and Cu in both soil and plant samples. This is attributable to various anthropogenic activities in Nakuru town and the surrounding areas, mainly from industrial effluents, automobile emissions, roadside garages, farming (pesticides) etc. Ochieng et al. (2007) reported some of the sites investigated in Lake Nakuru, had relatively higher concentration levels of heavy metals Cd, Co, Cu, Pb, Ni, and Zn in the water which points to anthropogenic addition. Consequently there is need for continuous monitoring and surveillance of toxic heavy metal pollutants and persistent organic pollutants (POPS) in the catchments studied so as to provide knowledge of the inputs, and ecological effects of such pollutants. Knowledge of such data is critical in formulation of sound management strategy for Lake Nakuru National Park, which is an important habitat for flamingoes and tourism activities.

Acknowledgments We wish to thank Mr Bore of Mines and Geology Department for permission to use AAS and the Director of Wildlife Services Kenya, the Chief Scientist and the Senior Warden of Lake Nakuru National Park for granting us permission to work in the park.

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