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The Distribution of Cu and Pb Levels in Soils and *Acacia xanthophloea* Benth. from Lake Nakuru National Park Kenya

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Environmental pollution with toxic metals continues to be a serious global concern. Pollution of soils with toxic trace metals have increased considerably since the onset of industrialization and urbanization (Nriagu, 1990; Senwo and Tazisong, 2004). Trace metals, either derived from natural inputs or anthropogenic emissions, are ubiquitous in the global environment (Blackmore, 1998; Muohi et al., 2003). Metals such as copper (Cu) and lead (Pb) are potentially toxic to living terrestrial and aquatic ecosystems (USEPA 1995). Although heavy metals are naturally present in soils, contamination comes from local sources, mostly industrial effluents, agricultural activities, urban/domestic wastes, fossil fuels and other anthropogenic activities (Aksoy et al., 2000a).

Heavy metal pollution in soils and plants has been reported in Brazil (Campos, 2003), Florida (Ma et al., 1997), Kenya (Wandiga and Onyari, 1987; Maskall and Thornton, 1996), India (Kuhad et al., 1989), China (Chen et al., 1991), Canada (Frank et al., 1976), Syria (Khuder et al., 1998) and South Carolina (Franklin et al., 2003). Elevated soil Pb, As and Cu levels have been reported in orchard soil (Francek, 1997; Aten et al., 1980; Peryea and Kammereck, 1997). Pyatt (1999, 2001) reported heavy metal concentrations in pine needles and in acacia trees (*Acacia retinoides*) from Cyprus and these plants were found to act as effective bioaccumulators of heavy metals. The metal concentrations were also investigated in the 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, accumulation and distribution of metal pollution. Plants are suitable for monitoring the heavy metal levels in the environment and consequently Scots pines (Yilmaz and Zengin, 2004), 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, which provides nesting places and shelter for many resident and migratory birds. The woodland also provides forage for large herbivores, mainly Rothschild's giraffe (*Giraffa camelopardalis rothschildi*) and black rhinoceros (*Diceros bicornis*). In recent years, *Acacia xanthophloea* trees have been undergoing unexplained dieback 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, Kenya, and suggest some conservation measures to alleviate the serious ecological pollution problems facing the lake.

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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 1760 m to 2080 m above sea level. Lake Nakuru occupies roughly 42 km^2 at its lowest point in a wider catchment basin of approximately 1800 km^2. Water flows into the lake through the Makalia and Nderit rivers. The lake also receives water through a series of fresh water springs along the northern and eastern shorelines. Additionally, it is 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 the Baharini 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 headquarters 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 the Njoro river sewage area in the northwestern part of the park where acacia trees are dying. Samples collected were D1 (0–20 cm), D2 (20–40 cm) and D3 (40–60 cm).

Soil samples were dried in an oven at 105°C for 24 hours, 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 triplicates of the fine soil samples were weighed in labeled digestion tubes. After the addition of 20 ml concentrated hydrochloric acid, the

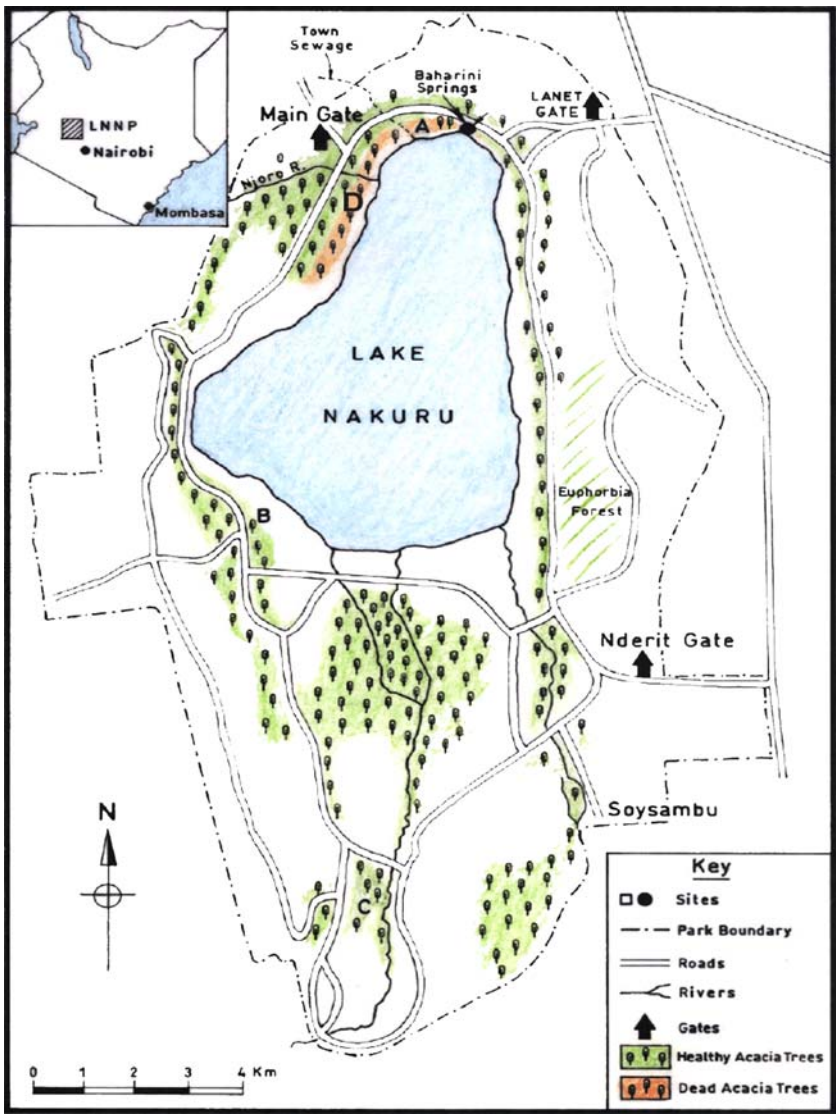

Fig. 1 Lake Nakuru National Park's map showing the Baharini springs, the swamps near Baharini springs, town, Njoro river sewage, and the Nakuru town industrial area

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 minutes. The digests were allowed to cool and quantitatively transferred into 50 ml volumetric flasks and made up to volume 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 samples to cater for matrix effects.

The plant samples were dried in an oven at 70°C for 24 hours. 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 ± 0.05g of the ground samples were weighed in digestion tubes and 15ml of concentrated nitric acid and 5 ml of concentrated perchloric acid ($HClO_4$) were added. The mixture was incubated for at least 24 hours, for the initial digestion process, and subsequently digested in a digestion block at a temperature of 130°C for 1.5 hours (until the brown fumes ceased, resulting in a clear and colorless solution). The digests were filtered through glass wool, into 50ml 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 samples to cater for matrix effects.

Acacia xanthophloe 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 spectrophotometry (AAP) 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). The student's *t* test was also conducted to determine the significant difference in metal content during rainy and the dry seasons. ANOVA (*F* test) was performed to compare the different sites studied.

Table 1 Observed and certified values (mg/kg) for *Bowen kale* leaves (CRM- IAEA)

Method		Cu	Pb
AAS	Observed	4.9 ± 0.62	2.0 ± 0.04
EDXRF	Observed	4.1 ± 0.22	2.3 ± 0.7
*	Certified	5.0	2.5 (NC)

NC, not certified; ≤ = less than or equal to the detection limit

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. Figure 2 shows XRF spectra for *Acacia xanthophloea* in Lake Nakuru National Park.

As shown in Fig. 2, besides copper and lead, other elements are also present. The data show good agreement between the two techniques employed, attesting to the accuracy of the procedure used for analysis of the samples. The mean copper and lead concentrations measured in soils obtained from the sites investigated are shown in Figs. 3–6.

As shown, copper levels were particularly high in soil samples collected from Baharini springs (site A). Typical values varied from 56.7 ± 5.2 to 89.6 ± 7.0mg/kg, whereas copper levels at Njoro river sewage (site D) ranged from 55.4 ± 3.2 to 67.0 ± 6.0mg/kg. Metal-rich mine tailing, metal smelting, battery recycling, fuel burning and fuel production, intensive agriculture, and sludge dumping are the most important human activities leading to soil contamination with large quantities of metals (Celik et al., 2005). Figures 5 and 6 shows the copper and lead levels, respectively, in the studied *A. xanthophloea* samples. The plant samples represent P1 (healthy bark collected from an area opposite pelican corner), P2 (unhealthy bark collected from Baharini springs area), P3 (unhealthy bark collected from Njoro river sewage area), P4 (healthy leaves collected from an area opposite pelican corner), P5 (unhealthy leaves collected from Baharini springs area) and P6 (unhealthy leaves collected from Njoro river sewage area) during rainy and the dry seasons. The average concentration of Cu in soil generally ranges between 20–30 mg/kg, and soil containing a Cu concentration below 2 mg/kg are said to be

deficient since it is an essential trace metal to life (Alloway, 1990; Barber, 1995). The average concentration of Pb in soils is normally found to range from 10–30 mg/kg (Alloway, 1990; Dharmanda, 2002). The slightly higher concentration of Pb in the studied soil is attributable to various anthropogenic activities in Nakuru town and the surrounding areas, mainly from industrial effluents, seed company operations/farming (i.e., pesticides), automobile emissions, roadside garages, leaded gasoline and car wash activities. Tetraethyl lead is used as a petrol additive, however unleaded petrol was introduced in Kenya late 2005 to conform to Dakar protocol that required phasing out of leaded petrol in Africa. Our results suggest anthropogenic sources of lead and copper since the concentrations were notably higher at some sites, and lower in soil located opposite pelican corner (site B) and near Naishi headquarter (site C). Marschner (1997) and Chen et al. (2001) reported that the normal concentration of Cu in plants ranges from 2.0–25 mg/kg of dry matter. Concentration of Cu greater than 30 mg/kg is phytotoxic, whereas levels less than 2.0 mg/kg is considered a deficiency in plants. High Cu levels were observed in *A. xanthophloea* at sites where the trees are unhealthy (P2, P3, P5 and P6). The bark and leaf samples of *A. xanthophloea* collected from Baharini springs (P2 and P5) exhibited high levels of Cu in their tissues varying from 66 ± 6.0 to 128 ± 2.0 and 51 ± 4.0 to 146 ± 16 mg/kg, respectively. Also high concentrations of Cu were obtained in the plant samples located along the Njoro river sewage area, between 54.6 ± 6.5 to 95.5 ± 15 and 62 ± 6.2 to 119 ± 5.8 mg/kg for samples P3 and P6, respectively. The *A. xanthophloea* bark and leaf samples collected from unhealthy trees from Baharini springs and Njoro river sewage areas yielded high levels of Cu.

Whereas the normal concentration of Pb in higher plants varies from 5–10 mg/kg of dry matter, the element is regarded to be in excess and toxic to plants if it exceeds 30 mg/kg (Kamugi, 1990). Pb was found to be higher in *A. xanthophloea* tissues collected from Baharini springs. Typical values ranged from 42.8 ± 5.0 to 51 ± 6.5mg/kg and 36 ± 3.6 to 42 ± 4.3 mg/kg for samples P2 and P5, respectively. The concentration of Pb in plant tissues from the Njoro river sewage area ranged from 31.5 ± 3.5 to 34.7 ± 5.0 mg/kg for sample P3 and 38.4 ± 4.1 to 40.2 ± 3.6 for sample P6 (Fig. 6). The main sources of metal pollution in Lake Nakuru include industries such as battery, tannery, auto-parts manufacturing, farm activities,

Table 2 Comparative analysis of soil and *Acacia xanthophloea* samples collected from Lake Nakuru sites A, B, C, and D (concentration values in mg/kg, dry weight)

Sample	Element	AAS EDXR
Soil		
A1	Cu	62.8 ± 4.0
		59.3 ± 5.3
A3	Cu	68.5 ± 2.5
		71.0 ± 2.08
A2	Pb	43.5 ± 4.2
		41.4 ± 1.2
B1	Pb	16.0 ± 1.0
		17.0 ± 4.2
B3	Pb	20.0 ± 1.1
		18.5 ± 1.85
C3	Pb	16.0 ± 1.3
		15.8 ± 5.15
Acacia xanthophloea		
P1	Cu	1.5 ± 0.61
		1.1 ± 0.5
P3	Cu	95.5 ± 15
		86.2 ± 6.5
P1	Pb	6.2 ± 2.1
		5.7 ± 1.2
P6	Pb	40.2 ± 3.6
		42.3 ± 4.2

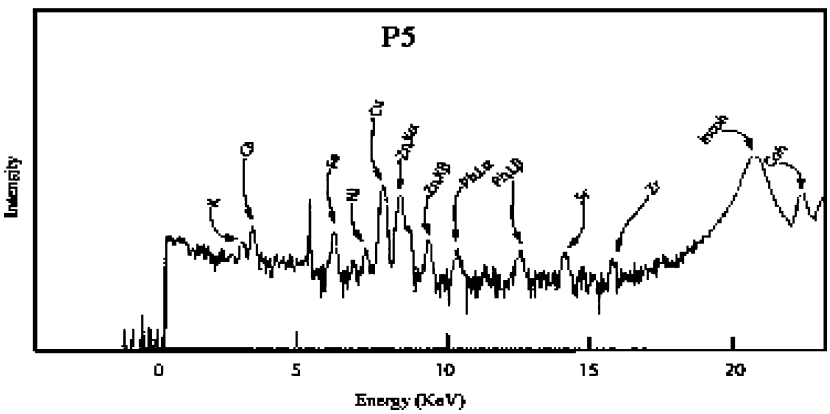

Fig. 2 XRF elemental spectrum of leaves of *A. xanthophloea* collected from Baharini springs in Lake Nakuru National Park Kenya

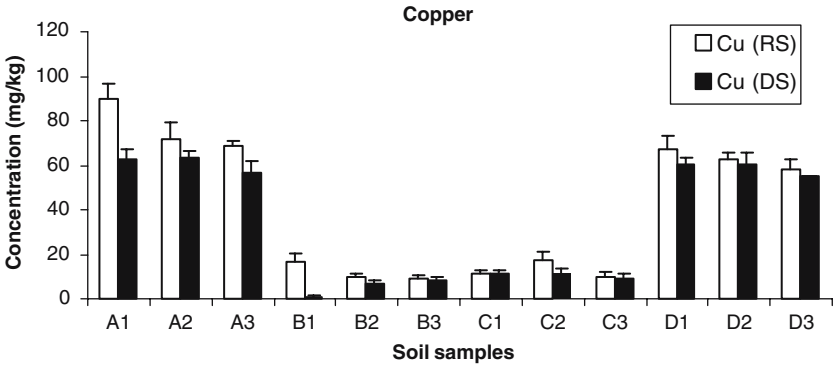

Fig. 3 Concentration (mean ± SD) of copper in soil samples collected from sites A, B, C and D during the rainy season and the dry seasons

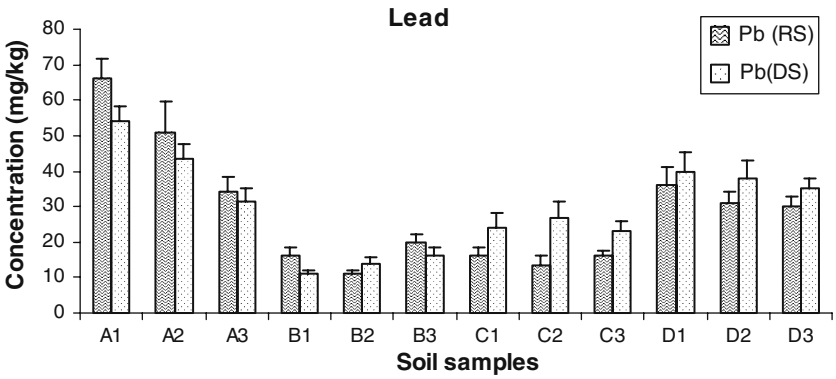

Fig. 4 Concentration (mean ± SD) of lead in soil samples collected from sites A to D during the rainy season and the dry seasons

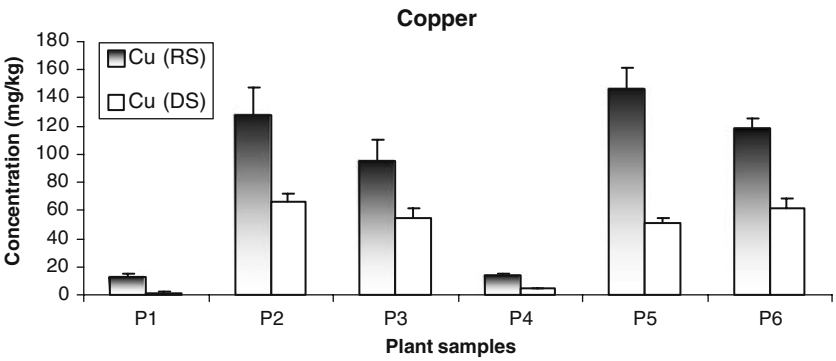

Fig. 5 Concentration (mean ± SD) of copper in *Acacia xanthophloea* samples

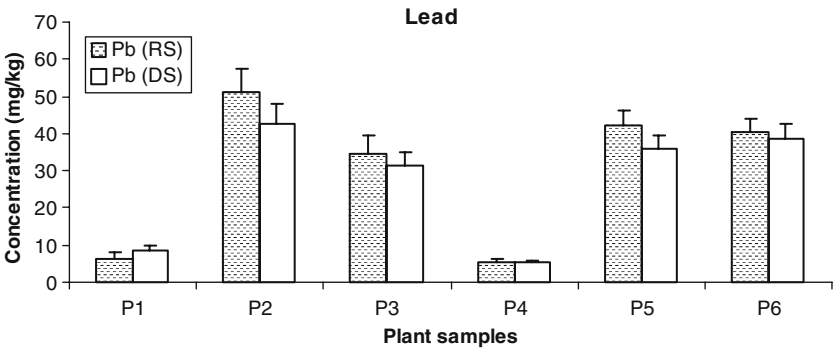

Fig. 6 Concentration (mean ± SD) of lead in *Acacia xanthophloea* samples

storm/sewage drainage, and seed company operations. This study suggests that heavy metals such as Cu are probably a causative factor affecting the *A. xanthphloea* woodland, particularly young trees from Njoro river towards the Baharini spring area (Fig. 5). According to Celik et al. (2005), the threshold level of 43 ppm indicated death of *Robinio pseudo-acacia* L. in Denizli, Turkey, and the high concentrations of heavy metals in the plants 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).

Significant seasonal variations in the mean Cu and Pb values were demonstrated by ANOVA (F test) and Student's t test at $P < 0.05$ for all sites. Significant elemental correlations were calculated by Pearson's correlation coefficient (r). Elemental concentrations calculated for soils collected from sites A and D showed that Cu correlated positively to Pb. A significant positive correlation was also found between Cu in the soils and plants collected from sites A and D. The levels of other heavy metals and pollutants should be investigated to provide further understanding of the detrimental affects on the growth of *A. xanthophlea* trees, and for recommendations of an appropriate management plan.

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References

Aksoy A, Sahin U, Duman F (2000a) *Robinia pseudo-acacia* L. as a possible biomonitor of heavy metal pollution in Kayseri. Tr J Bot 24(5):279–284

Aksoy A, Celik A, Öztürk M (2000b) Plants as possible indicators of heavy metal pollution in Turkey. Chemia Inzneria Ekologiczna 11:1152–1161

Alloway PJ (1990) Heavy metals in soil. Wiley, NewYork, p 339

Aten CF, Bourke JB, Martini JH, Walton JC (1980) Arsenic and lead in an orchard environment. Bull Environ Contam Toxicol 24:108–115

Barber SA (1995) Soil nutrient bioavailability: a mechanistic approach. Wiley, New York, p 202–337

Blackmore G (1998) An overview of trace metal pollution in the coastal waters of Hong Kong. Sci Total Environ 214:21–48

Bowell RJ, Ansah RK (1994) Trace element budget in an African savannah ecosystem. Biogeochemistry 20:103–126

Campos V (2003) Trace elements in pesticides. Comm Soil Sci Plant Anal 34:1261–1268

Celik A, Ashan AK, Abdullah A, Yakup K (2005) Determining the heavy metal pollution in Denizli (Turkey) by using *Robinio pseudo-acacia* L. Environ Int 31:105–112

Chen J, Wei T, Zheng C (1991) Background concentrations of elements in soils of China. Water Air Soil Pollut 57/58:699–712

Chen ZS, Chiu WTF, Peterson JB (2001) Micronutrients deficiencies of crops in Asia. Food and fertilizer technology center for the Asian and Pacific region (FFTC), Taiwan, pp 1–66

Dharmanda D (2002) Heavy metal pollution by lead in the soil and plants. Environ Pollut 50:150–166

Francek MA (1997) Soil Pb levels in orchards and roadsides of mission peninsula Michigan. Water Air Soil Pollut 94:373–384

Frank R, Ishida K, Suda R (1976) Metals in agricultural soils of Ontario. Can J Soil Sci 56:181–196

Franklin RE, Duis L, Smith BR, Brown R, Toler JE (2003) Elemental concentrations in soils of South Carolina. Soil Sci 168:280–291

Kamugi NPV (1990) Investigating into the effect of pH on the availability of trace elements in soil. Dissertation, University of Nairobi, p 20

Khuder A, Khalifa K, Abbas M (1998) Distribution of some elements in soils of Barada River Bank in Syria. Commu Soil Sci Plant Anal 29:2631–2645

Khuhad MS, Malik RS, Singh A (1989) Background levels of heavy metals in agricultural soils of Indo-Gangetic plains of Haryana. J Indian Soc Soil Sci 37:700–705

Ma LQ, Tan F, Harris WG (1997) Concentrations and distributions of eleven metals in Florida soils. J Environ Qual 26:769–775

Marschner H (1997) Mineral nutrition of higher plants, 2nd edn. Academic Press, New York

Maskall J, Thornton I (1996) The distribution of trace and major elements in Kenyan soil profiles and implications for wildlife nutrition. Environ Geochem Health 113:47–62

Muohi AW, Onyari J.M, Omondi JG, Mavuti KM (2003) Heavy metals in sediment from Mkupa and Port – Reitz Creeks systems: Kenyan coast. Environ Int 28:639–647

Nriagu JO (1990) Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature 279:409–411

Pyatt FB (1999) Comparison of foliar and stem bioaccumulation of heavy metals by Corsican pines in the Mount Olympus area of Cyprus. Ecotoxicol Environ Saf 42:57–61

Pyatt FB (2001) Copper and lead bioaccumulation by *Acacia retinoides* and *Eucalyptus torquatain* sites contaminated as a consequence of extensive ancient mining activities in Cyprus. Ecotoxicol Environ Saf 50:60–64

Raini JA (1995) Water quality monitoring in Lake Nakuru. Proceedings of the workshop on use of research findings in the management and conservation of biodiversity 1:58–62

Senwo ZN, Tazisong IA (2004) Metal contents in soils of Alabama. Comm Soil Sci Plant Anal 35:2837–2848

United States Environmental Protection Agency (USEPA) (1995). Standards for the use or disposal of sewage sludge, parts 403 and 503. US Government, Washington, DC

Wandiga SO, Onyari JM (1987) Concentration of heavy metals: Mn, Fe, Cu, Zn, Cd, and Pb in sediments and fish from Winam Gulf of Lake Vitoria and fish bought in Mombasa town markets. Kenya J Sc Ser A 8:89

Yilmaz S, Zengin M (2004) Monitoring environmental pollution in Erzurum by chemical analysis of Scots pine (*Pinus sylvestris* L.) needles. Environ Int 29:1041–1047