

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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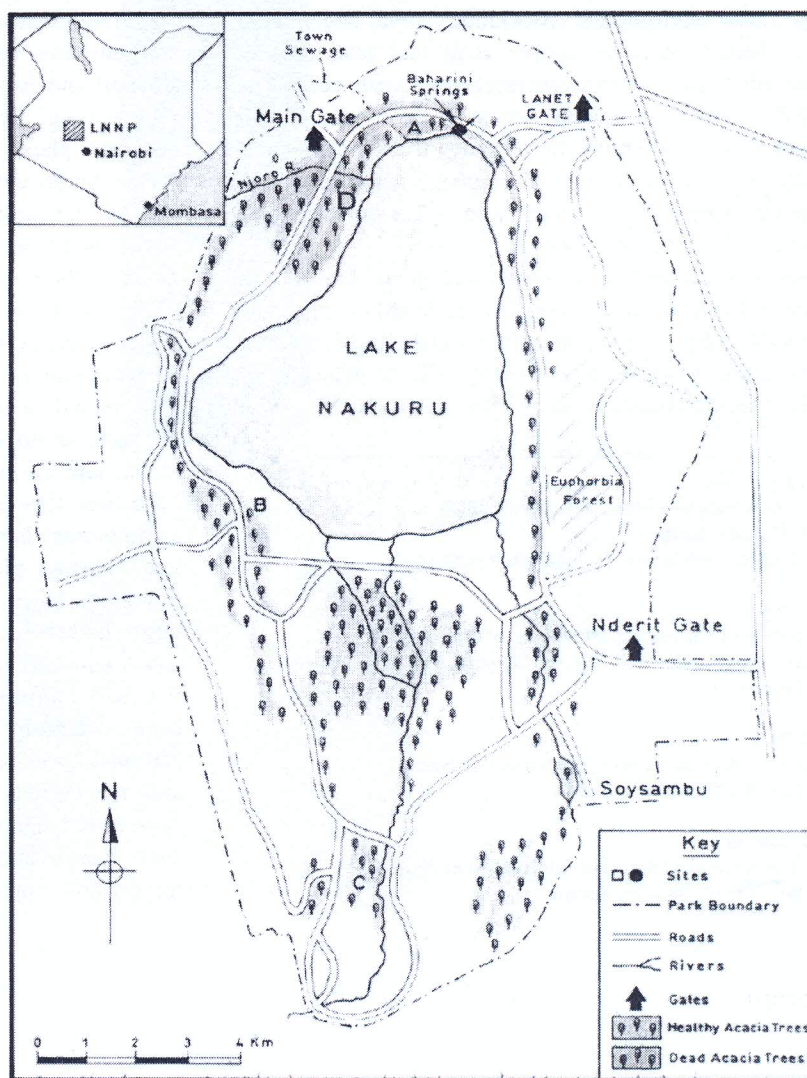
Materials and Methods

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 km² at its lowest point in a wider catchment basin of approximately 1800 km². 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 (HClO₄) 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

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

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.

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 xanthophloe* 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. xanthophloe* 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

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
<i>Acacia xanthophloea</i>		
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

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 ± 6.5 mg/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,

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

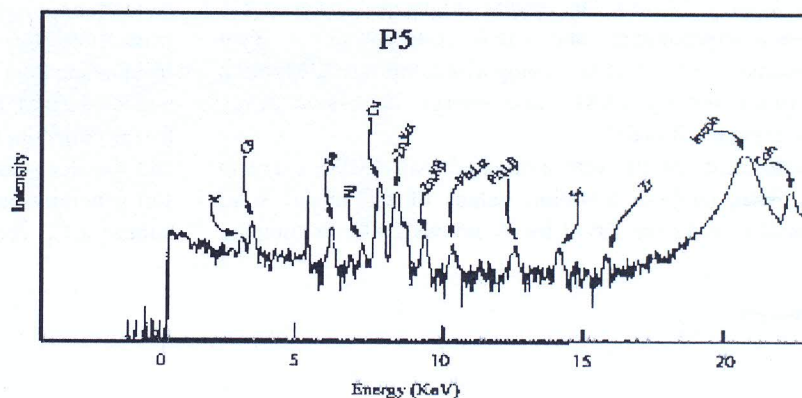


Fig. 3 Concentration (mean \pm SD) of copper in soil samples collected from sites A, B, C and D during the rainy season and the dry seasons

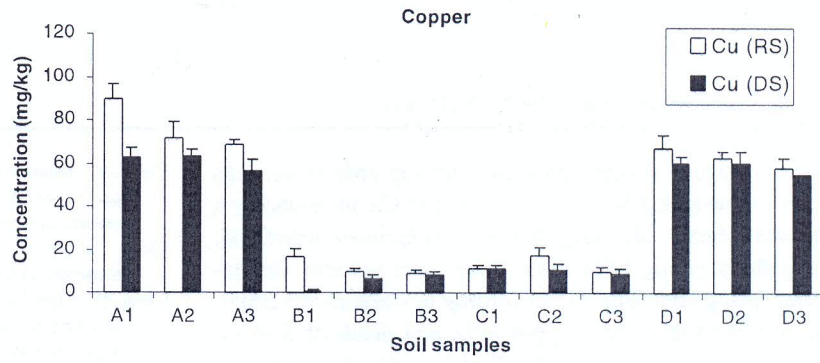


Fig. 4 Concentration (mean \pm SD) of lead in soil samples collected from sites A to D during the rainy season and the dry seasons

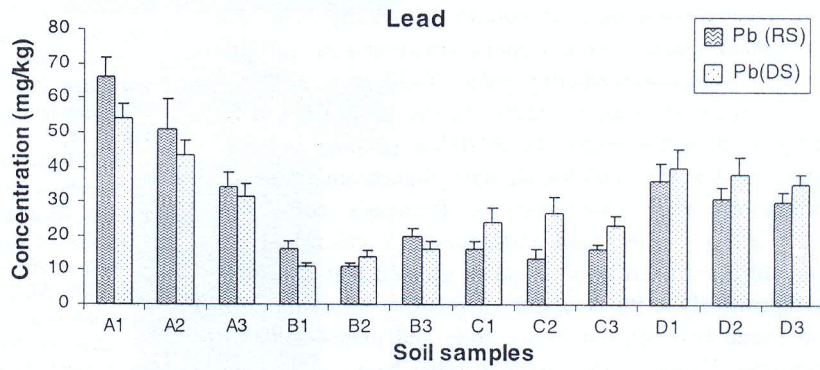


Fig. 5 Concentration (mean \pm SD) of copper in *Acacia xanthophloea* samples

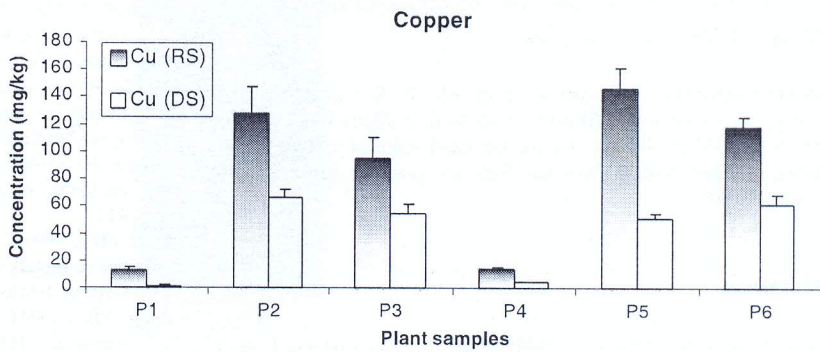
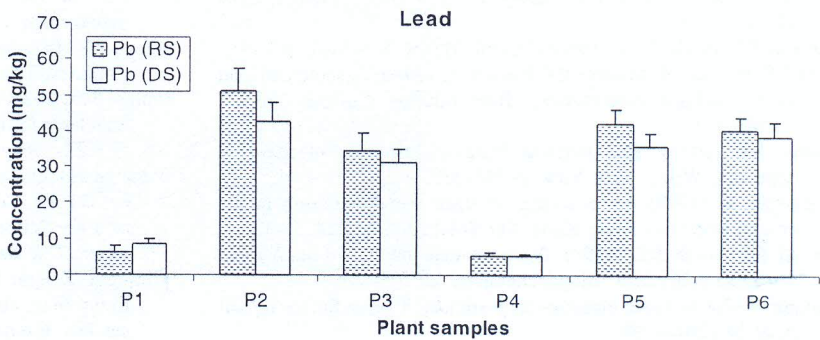


Fig. 6 Concentration (mean \pm SD) of lead in *Acacia xanthophloea* samples



storm/sewage drainage, and seed company operations. This study suggests that heavy metals such as Cu are probably a causative factor affecting the *A. xanthophloea* 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 *Robinia 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. xanthophloea* trees, and for recommendations of an appropriate management plan.

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