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ASSESSMENT OF METALS IN SOIL EXTRACTS AND THEIR UPTAKE AND MOVEMENT WITHIN TAMARIX NILOTICA AT LAKE NASSER BANKS, EGYPT

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This study aims to determine heavy-metal levels in soil from the banks of Lake Nasser, the ability of Tamarix nilotica to accumulate such metals from soil and hence its potential for phytoextraction. Soil and Tamarix samples were collected from the banks of four bights around Lake Nasser and analysed for Fe, Mn, Ca, Mg, Cr, Cu, Ni, Zn, Cd and Pb by atomic absorption spectrometry, whereas Na and K were measured by atomic emission spectrophotometry. Three different methods of extraction were used for the soil samples. Lead, copper and zinc were equally distributed between the exchangeable phase and Fe/Mn oxide-bound form, while other measured metals were mainly present in the Fe/Mn oxide fraction. With the exception of iron, all metals studied showed total concentrations within the geochemical background values. T. nilotica exhibited elevated concentrations of total concentrations within the geochemical background tines. It interest clinical concentrations of Pb, Cd and Co $(0.39-1.03 \ \mu g \ g^{-1})$ and K $(2.74-4.33 \ m g \ g^{-1})$ instems, and relatively high concentrations of Pb, Cd and Co $(0.39-1.03 \ \mu g \ g^{-1}, 0.24-1.3 \ \mu g \ g^{-1}$ and $1.94-5.3 \ \mu g \ g^{-1}$, respectively) are found in plant leaves. Bioaccumulation of factors of Na and K (9.3 and 12.63, respectively) were high in T. nilotica stems. While the bioaccumulation of Pb, Cd, Co and Ni (2870.1, 2035.4, 10.5 and 5313.2, respectively) was high in plant leaves, Fe, Mn, Ca and Mg were accumulated relatively equally in plant stems and leaves. T. nilotica was found to secrete high amounts of Na, Ca and K, in addition to small amounts of all accumulated metals except Cd and Cu. These secreted metals appeared as salt crystals (67.5% Na; 25.8% Ca; 5% Mg; 1.5% K and 0.16% trace and minor elements) on the plant surface. The concentrations of all the metals studied in T. nilotica were higher than in the salt crystals. Statistical analysis of the database suggests bioaccumulation of these metals from soil to T. nilotica. This reflects the importance of using T. nilotica as a model in the phytoremediation process as an established environmental clean-up technology.

Keywords: Soil; Tamarix nilotica; Metal accumulation; Phytoremediation; Lake Nasser; Egypt

1 INTRODUCTION

Soil serves many vital functions in society, particularly in agriculture, so it is of extreme importance to protect this resource and ensure its sustainability (Wong *et al.*, 2002). In the last few decades, the assessment of heavy-metal-contaminated soil has received much attention: elevated concentrations of heavy metals in soil potentially have long-term damaging environmental implications, and there are health concerns with respect to their persistence

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and cumulative tendency in the environment, and their associated toxicity to biological organisms (Wong and Li, 2003).

Deteriorating environmental conditions and increasing reliance on agrochemicals have led to growing public concern over the potential accumulation of heavy metals and other contaminants in agricultural soils (Wong *et al.*, 2002). Fialkowski *et al.* (2003) used larvae of two species to investigate spatial and temporal variability in the bioavailabilities of trace metals in the river Biala Przemsza, Poland, and concluded that emphasis in studies of pathways and fates of metals in the environment has shifted towards their accumulation in biota: not all of each metal present may be available for uptake by fauna and flora, and it is the bioavailable fraction that is of direct ecotoxicological relevance and concern. Trace metals, even essential metals, are toxic when present above threshold availabilities and may pose a significant threat to the biota.

Wolterbeek and Van der Meer (2002) studied the accumulation of sediment As, Cd, Cu and Zn in the submerged water plants and concluded the following from upscaling calculations, assuming plant steady-state behaviour: the accumulation in the plants may constitute up to 1% of the sediment metal occurrence; the major part of an accumulated metal is retained in the plant roots; and plant-mediated metal flow into water phase (<0.01% for Cd, Cu and Zn, <0.1% for As, within a growing season) may be regarded as an insignificant contribution to the overall process of metal mobilization. Wong *et al.* (2002) studied the concentrations of heavy metals in crops, paddies and natural soils in the Pearl River Delta, and concluded that the chemical partitioning patterns of Pb, Zn and Cu indicated that Pb was largely associated with the Fe-Mn oxide and residual fractions, while Zn was predominantly found in the residual phase, and a significant fraction of Cu was bound to the organic sulphide and residual phases.

Some chemical techniques for immobilizing metals in soils involve the addition of dolomite, phosphates, or organic matter residues to the polluted soils to reduce the soluble concentration of heavy metals in soils by precipitation, adsorption or complexation (Chen and Lee, 1997). Application of calcium carbonate materials significantly reduces the solubility of heavy metals in contaminated soils (Liu *et al.*, 1998). Many reports also indicate that the addition of hydrous iron oxides or manganese oxides to contaminated soils could reduce the concentration of soluble Cd or Pb in soils (Chen *et al.*, 2000).

A small number of wild plants that grow on metal-contaminated soil accumulate large amounts of heavy metals in their roots and shoots, and this property may be exploited for soil reclamation by phytoextraction. Phytoextraction generally requires the translocation of heavy metals to the easily harvestable shoots. Kumar *et al.* (1995) used several cultivars of Indian mustard (*Brassica juncea*), a high-biomass crop plant, to remove heavy metals from soil and reported that the elemental composition of plants is very different from that of the soil in which they grow. Most of the differences can be attributed to a plant's ability to fix carbon from the air and to absorb essential macro- and micronutrients from the soil, including heavy metals.

The Aswan High Dam has solved the problem of Egypt's power supply and has also provided water reserves covering the needs of water for 2 yr. in the case of low flood seasons. By artificially flooding the fertile soil of Egypt, it has been possible to increase the production of crop and the cultivable area by 30% (Sherif *et al.*, 1981). A vertical change of 1 m in the height of the Lake Nasser can cause the shoreline to move by up to 1500 m. Consequently, some of the *T. nilotica* are periodically inundated but will survive if the inundation period is not too long. However, such inundation events may cause changes in the soil conditions under the *T. nilotica* bushes. The young shoot tips of *T. nilotica* provide browsing for grazing animals all year round and are used as a reserve fodder fed to stock at times of drought or when other food is very scarce, especially for the Bedouin who have settled in

many wadis at the shores of Lake Nasser (Ali *et al.*, 2001). Distribution of the plants around the Lake Nasser depends on the water regime. Thus, at the lake shores, which are frequently flooded by the lake water, *T. nilotica* forms dense thickets. *T. nilotica* forms the major source of livestock grazing due to its dominance around the lake, has high protein and carbohydrate content and is also a salt accumulator (Badri and Hamed, 2000).

T. nilotica is known to concentrate high amounts of sodium chloride in specialized glands in its leaves (Bosabalidis, 1992). The shedding of the leaves with their high salt content is an important mechanism for concentrating salt in the surface layers of the soil, and there is a strong relationship between the amount of *T. nilotica* litter and the conductivity of the soil (Briggs *et al.*, 1993).

Ali *et al.* (2001) measured concentrations of Ca, Mg, K, Na, Cu, Zn, Al, Fe, and Mn in soils and in *T. nilotica* from Wadi Allaqi on the shore of Lake Nasser in the eastern desert of Egypt, and proved that all of the elements were concentrated in the leaves of *T. nilotica* relative to the stems and roots. They also reported leaf/soil concentration ratios, used as an indicator of metal accumulation in the plant.

There are many advantages in using metal-accumulating plants for the removal of metals from contaminated soils/lower costs, generation of recyclable metal-rich plant residues, applicability to a large range of toxic metals and radionuclides, minimal environmental disturbance, elimination of secondary air- or water-borne wastes and public acceptance (Kumar *et al.*, 1995).

This study was specifically conducted to address the following points:

- To study heavy-metal speciation in different extraction phases of the soil samples and its possible relationship to heavy-metal accumulation in *T. nilotica*.
- To collect information on metal bioaccumulation in *T. nilotica* used for animal grazing in this region.
- To assess the potential of using *T. nilotica* in phytoextraction to improve the properties of the Lake Nasser beach soil.
- To measure the composition of the salt crystals, which coat *T. nilotica* branches and its relationship with soil and plant contents.

2 MATERIAL AND METHODS

2.1 Study Area

Lake Nasser is considered the largest man-made lake in the world. It was formed after the construction of the Aswan High Dam in the southern part of Egypt. About 76% of its total area is made up of 100 bights. These are located at the banks of the lake and are considered natural fish farms. The banks of these bights are used as agricultural farms, using the reduction and expansion of the lake water for irrigation.

2.2 Sampling

Plant material and soil samples were collected from four lake bights banks, namely El-Ramel and Dehamite (8 and 15 km south of the High Dam wall, respectively) on the eastern side, and Abdeen and Dehamite (8 and 15 km south of the High Dam wall, respectively) on the western side of lake Nasser during the summer months, 2002 (Fig. 1). These bights were selected near the High Dam as they are close to each other.



FIGURE 1 Sampling sites in Lake Nasser.

2.2.1 Lake Soil

Soil samples were collected from the beginning and end of each bight (five samples from different sites at each station). The samples were then dried at $105 \,^{\circ}$ C in an electric oven for 48 h and sieved through a 2-mm sieve to remove large debris and stones.

2.2.2 Plant Samples

T. nilotica samples were collected from the same sites as the soil samples. Each plant sample (known weight) was washed with 500 ml of bidistilled water to extract the salt crystals which

coat the surface of *T. nilotica* branches (crystal salts solution). This solution was kept for analysis. The plant samples were washed with tap water and then with deionized water. All plant samples were divided into leaves and stems, and dried at $110 \,^{\circ}$ C in an electric oven for 48 h. Dried plant samples were crushed and powdered in an agate mortar prior to digestion.

2.3 Measurements and Analysis

Chemical parameters in soil samples were determined using methods from a textbook of soil analysis (Baruah and Barthakur, 1997). Plant samples were digested according to Allen (1989). The chemical and physical parameters of crystal salt solution were determined using standard procedures (APHA, 1992).

2.3.1 Soil Samples

Single-step leaching techniques were used to partition the heavy metals in the soil samples (1 g dry wt.) into different fractions (Salomons and Förstner, 1980; Saeki *et al.*, 1993; Moalla *et al.*, 1998):

- (1) 1 M ammonium acetate pH 7: 1 g of each soil sample was shaken with 10 ml of ammonium acetate for 3 h (exchangeable phase).
- (2) 0.04 M hydroxylamine HCl: 1 g of each soil sample was extracted for 6 h with 25 ml of 0.04 M HONH₃Cl in 4 M CH₃COOH (fraction bound to iron-manganese oxides).
- (3) Total metal concentrations: 1 g of each soil sample was digested with a mixture of conc. HF, HNO₃ and HCl acids (1/1/1) in a Teflon beaker. Digestion was repeated three times to ensure complete dissolution; then, the residue was dissolved in 5 ml of 2 M HNO₃ and rewarmed at 80 °C for 20 min (residual phase). In all cases, the soil suspensions were filtered through Whatman No. 42 filter paper and then analysed. Organic matter in the soil samples was determined according to Allen (1989), and carbonates determined titrimetrically in the presence of phenolphthalein as indicator. The pH values of the soil samples were measured in 1/2.5 soil/bidistilled water using a pH meter (Orion Research, Model SA 520, USA), and electrical conductivity was measured in the soil suspension obtained in the pH determination using a conductivity meter (Conductivity Meter, HANNA Instruments, HI 8033, Italy).

2.3.2 Plant Samples

One-gram portions of plant (leaves and stems) were digested with 10 ml of a conc. HNO₃/HClO₄ mixture (3/1) in a Teflon reactor under pressure (Allen, 1989) to prevent any atmospheric contamination or loss of volatile elements that might have occurred during dry ashing. After complete digestion and cooling, the solution was diluted with 2% nitric acid solution and then with bidistilled water to a final volume of 25 ml.

2.3.3 Crystal Salt Solution

The whole plant sample collected from each site was first washed with 500 ml of bidistilled water. Various physical parameters were determined in the resulting solution. The pH values of crystal salt samples were measured using a pH meter (Orion Research, Model SA 520,

USA). HCO_3^- (titrimetrically), Cl^- (Mohr's method) and organic matter were determined in crystal salt samples according to standard methods (HPHA, 1992).

2.4 Instrumental Techniques

Metal concentrations (Fe, Mn, Ca, Mg, Zn, Cr, Cu, Co, Ni, Pb and Cd) in the different leachates (soil, different parts of plants, crystal salt of *T. nilotica*) and reference materials were determined by atomic absorption spectrophotometry (Model Solaar 969, ATI Unicam Comp.) equipped with a digital direct concentration read out and an air-acetylene burner. Single-element hollow-cathode lamps (ATI Unicam Comp.) and standard instrumental conditions were used for each element. K and Na were measured using flame emission spectrometry (Jenway Flam Photometer, Model PFP7).

To validate the method for accuracy and precision, certified reference materials were analysed for each element. Suitable precautions were taken to minimize interferences when necessary. Background absorption can be troublesome, so the traditional and simplest method is to monitor absorbance of the continuum output of a deuterium lamp beam and to correct the analysed signal for any absorption detected.

2.5 Statistical Analysis

In order to investigate elemental associations among the heavy metals and major elements in sediments, the Pearson correlation, mean, minimum and maximum were calculated using the SPSS package programs (No. 9.0).

2.6 Quality Control

Accurate analysis of heavy and toxic elements is dependent upon the prevention of element contamination. Quality control was achieved by analysing reference materials independently prepared from the standards. All chemicals used were purchased from BDH, Sigma, Aldrich and E. Merck (A.R., 99.9%). All vessels were made of Pyrex and high-density polyethylene, washed with 30% HNO₃, then rinsed three times with bidistilled water and dried in an oven.

The accuracy of the methods was verified by subjecting standard reference material to the overall analytical procedures. Analysis of reference material yielded metal concentrations within acceptable limits. The mean coefficient of variation of the metal concentrations was calculated from a triplicate analysis of individually digested subsamples of plant or soil.

Atomic absorption spectroscopic standard solutions (1 mg ml^{-1}) for the elements Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn (BDH, UK) were prepared by diluting stock solutions using deionized water. The standard curves were verified after 10 successive runs by analysis of one standard solution within the linear range for each sample.

All stages of samples preparation, analysing and measuring were carried out in a clean environment.

3 RESULTS AND DISCUSSION

3.1 Chemical Partitioning of Trace, Minor and Major Metals in Soil Samples

The element distributions in the soil samples at Lake Nasser banks around the bights under study for the three extraction systems are shown in Figure 2. The maximum, minimum and mean extractable concentrations ($\mu g g^{-1}$ dry wt.) as well as the extractability (%E) as



FIGURE 2 Distribution of several metals $(\mu g g^{-1})$ in the Lake Nasser bank soil.

percentages of total metal concentration for the elements studied (using both hydroxylamine hydrochloride and ammonium acetate extractants) are listed in Table I.

The metals usually associated with Fe-bearing minerals, such as Mn, Co, Cr, Cu, Ni and Zn, show high concentrations in the eastern bank of the lake. A high iron concentration may be ascribed to Fe abundance in soil where the iron (III)-iron (II), coupled with natural organic substances, is able to act as an electron-transfer catalyst for oxidation of natural organic substances such as fulvic acid by oxygen (Awadallah and Soltan, 1996) leading to an increase in iron concentration in beach soil.

Elem.	NH ₂ OH · HCl					Ammonium acetate				
	Min.	Max.	Mean	%E	S.E.	Min.	Max.	Mean	%E	S.E.
Fe	93.5	200.3	146.9	0.47	26.4	4.3	6.3	5.3	0.016	0.433
Mn	262.5	500.0	381.3	74.0	61.0	5.0	6.0	5.5	1.1	0.217
Pb	0.00018	0.00049	0.0034	3.1×10^{-3}	0.00009	0.00017	0.00049	0.00033	$2.8 imes 10^{-3}$	0.00008
Cd	0.0004	0.0008	0.0006	80.0	0.00009	0.0002	0.0006	0.0004	53.3	0.00008
Cu	0.975	1.3	1.1	12.5	0.0687	0.89	1.3	1.1	11.7	0.0876
Со	2.1	4.6	3.4	68.2	0.573	0.24	0.5	0.4	7.3	0.0634
Ni	1.0	2.0	1.5	6.3	0.261	0.0001	0.0009	0.0005	$1.7 imes 10^{-3}$	0.00018
Zn	8.3	11.0	9.7	12.4	0.555	7.75	13.0	10.4	12.0	1.2
Cr	6.0	8.3	7.1	11.4	0.525	4.3	4.8	4.6	7.4	0.1
Ca	10.8	11.0	10.9	97.9	45.0	5.0	7.9	6.5	58.5	634.0
Mg	2.0	2.6	2.3	66.1	135.0	0.2	0.5	0.4	8.9	71.5
Na	4.8	5.6	5.2	78.0	126.0	3.8	4.9	4.3	70.3	255.0
K	165	176	170.5	37.7	15.9	216	295	255.5	24.6	1.7

TABLE I Extractable concentration of metals ($\mu g g^{-1}$ except for Na, Ca, Mg mg g^{-1} dry weight) and extractability (E) as a percentage of total concentrations and standard error (S.E.) of the elements studied in the Nasser Lake banks soil.

Iron (III), Mn (V) and (VII) are present as oxides with very strong capacities to adsorb heavy metals. Therefore, the changes in chemical phases of Fe and Mn would be expected to have a considerable effect on the behaviour of other trace metal elements (Saeki *et al.*, 1993).

Soil Zn in the Fe/Mn fraction accounted for 12.4% of total soil Zn, reflecting the strong association with amorphous Fe/Mn oxides. These findings are in agreement with the known ability of amorphous Fe/Mn oxide to scavenge Zn from solution (Jenne, 1968; Fawzy, 2000). The results show irregular distribution of metals in the extractants of the samples at banks of the bights under study with considerable increase in the east bank samples (Fig. 2).

The mean exchangeable Pb values $(3.3 \times 10^{-4} \,\mu g \, g^{-1})$ in the soil samples were generally low, accounting for 2.8×10^{-3} % total soil Pb. In comparison, the proportion of Pb in the Fe/Mn oxide fraction $(3.4 \times 10^{-3} \,\mu g \, g^{-1})$ of the soils is relatively greater than in the exchangeable phase (Tab. I), indicating that the greater fraction of Pb in soils might be bound to the Fe/Mn fraction. The data represented in Figure 2 show spatial variation along the study area with a remarkable increase in Pb on the bank of the east bights. This can be attributed to the pollution from diesel and gasoline exhaust emissions and oil spills from cruise liners.

Although the concentrations of Cd in soil samples are lower than those of the other heavy metals, the effect of Cd on environments and human beings is important even at low concentrations (Saeki *et al.*, 1993). The data (Fig. 2) reflect relatively higher Cd concentrations in west bank bights than in east bank bights. Cadmium is associated with the natural occurrence of zinc and is found in trace amounts in pyrites (Nriagu, 1980).

The strong association of soil Co with Fe/Mn oxide phase (68.2% of the total soil Co) was anticipated since Co is usually strongly associated with Mn oxides (Wong *et al.*, 2002). The results illustrated in Figure 2 show an increase in the cobalt concentration in soil samples in the east bank bights. Because of the strong association between Mn and Co, the loss of Mn oxides in the soils could indirectly enhance the solubility and leaching of Co, thus resulting in a low Co concentration in the soil (Wong *et al.*, 2002).

Wong *et al.* (2002) reported that a significant fraction of Co (>70% of total soil Co) was associated with Mn oxide minerals. A good correlation is observed between Co and Mg (r=0.903) extracted with ammonium acetate. This is consistent with the fact that some metals such as Co, Ni and Cu are strongly enriched with Mg in ultramafic rocks, *e.g.* pyroxene and olivine (Moalla, 1990). In soils, the hydrous Fe and Mn oxides may hold significant proportions of certain heavy metal ions. These oxides are known to exist as separate phases, and there is evidence from electron microprobe analyses of surface soil that Pb and Ca are concentrated in the Mn oxides, whereas Ni, Cu and Zn are concentrated and distributed almost equally between the Fe and Mn oxides (da Silva *et al.*, 2002). Kheboian and Bauer (1987) studied different extraction solutions using the synthetic sediment model and reported that the selective extraction used for Cu and Pb in exchangeable or reducible fractions did not exactly reflect the chemical phase distributions set up beforehand. They assumed that although an element was in a certain fraction, the element would be reabsorbed on other residual fractions during the process of extraction.

In comparing the results, it appears that high percentages of the total concentrations of Ca (97.8%), Cd (80%), Na (78%), Mn (74%) and Co (68.2%) were extracted by $NH_2OH \cdot HCl$ (Tab. II). The high $NH_2OH \cdot HCl$ -extractable amounts of these metals' concentrations may indicate their association with Fe/Mn oxides. The hydroxylamine hydrochloride extractable concentrations of Na, Co and Cd were generally higher than the corresponding amounts extracted by ammonium acetate. This is possibly attributable to the enrichment of these metals in ferromagnesium minerals (Balkis and Cagatay, 2001).

Distribution of Cr revealed that its occurrence in residual fractions is much higher than in the two other fractions (Fig. 2). This may indicate that most soil Cr occurs in highly resistant minerals. However, the eastern bank bight samples showed a higher Cr content than the

Item pH		Cond. (µ mhos)	$CO_3 (mg g^{-1})$	$O.M. \ (mg \ g^{-1})$	$Cl^{-} (mgg^{-1})$	
Location						
El-Ramel	7.4	1643	105	0.39	0.026	
West-Dehamite	7.4	18,500	175.1	0.43	0.027	
East-Dehamite	8.25	3450	107.6	0.40	0.110	
Abdeen	8.1	5025	112.7	1.90	2.350	

TABLE II Physical and chemical properties of the Lake Nasser banks soil.

western bank samples. The highest average Cr content in the soil samples studied may be due to Cr association with organic matter content (Tab. II) or Cr coprecipitation with iron oxides (Gindy, 2001).

The most striking feature of the Cu distribution is the high percentage in the residual fraction (Fig. 2). This is supported by the positive correlation coefficient of ammonium acetate extractable iron and copper in the residual fraction (r = 0.942). Concerning the distribution of Cu content for the different samples from the bight banks, it is obvious that relatively higher Cu concentrations are found in the eastern bank samples. This is most likely due to Cu association with organic matter content which was encountered in relatively higher amounts at such bights (Tab. II) and/or to the weathering of the basement rocks surrounding such bights (Gindy, 2001).

However, a good correlation was observed for ammonium acetate extracts between Cu and Cd (r=0.955) and between Cu and Cr (r=0.921). This suggests that these metals are removed from extraction solution in a similar form (exchangeable) in soil (Moalla, 1990). A significant positive correlation was observed between Cu in the residual fraction and ammonium acetate extractable Fe, suggesting the effective coprecipitation of copper with amorphous Fe oxide (Shuman, 1985). Copper and lead were found to have stronger adsorptive affinities to oxides and humic substances in soils than Cd, in agreement with Okazaki's (1987) results.

Nickel was present in relatively high concentrations in the east bank samples. The metal is known to be present in a high concentration in ferromanganese nodules (Moalla, 1990). This is supported by the good correlation between exchangeable Ni and Mn in the Fe/Mn fraction (r=0.904). An excellent correlation is found between Ni and Mg (r=0.985). This may be attributed to its incorporation within Mg-bearing minerals, especially olivine and ferromagnesium minerals, or may be due to the similar ionic sizes of Ni²⁺ and Mg²⁺ (Moalla, 1990). Total Ca and Mg concentrations increased in the west bank bights. Considerable amounts of Ca and Mg (97.7% and 66.1% of total soil Ca and Mg) were extracted with NH₂OH · HCl. Good correlations were found between Mg and Mn (r=0.953), between Mg and Pb (r=0.914), between Ca and Cu (r=0.909) and between K (r=0.942) and Na (r=0.961) in different extractants, which indicates that these metals have a similar transport mechanism.

From the results shown in Figure 2, it seems that the variations in the K and Na contents in the soil of the Lake Nasser banks may be due to the geomorphology of these regions. The dominant rocks of the western side are Nubian sandstone, limestone, dolomite and kaolin, while the main rock types on the eastern side are granite, basalt, marble and Nubian sandstone (Soltan and Rashed, 2003). Alternatively, the variations may be related to variations in intensity of chemical weathering of K- and Na-bearing silicates, *e.g.* alkali feldspar (Fawzy, 2000). Relatively higher Na and K concentrations are observed in the west bank samples. According to Elewa (1985), some silicate minerals, *e.g.* alkali-feldspar, can be completely dissolved by weathering, thereby releasing sodium and potassium into solution (Fig. 2), and thus explaining the relatively higher concentrations of Na and K in the NH₂OH \cdot HCI

extractant. This may be related to the enrichment of such soil with ferromagnesium minerals (Gindy, 2001).

Negative correlations are observed in the different extracts among the extractable Na and the corresponding metals such as Co, Cu and Zn (r = 0.970, 0.997 and 0.922, respectively). These findings may be related to the presence of Na-bearing silicate minerals with low metal contents. Results show that all measured metals in the soil are lower than normal background levels (Bowen, 1979).

3.2 Characterization of T. nilotica and its Metal Bioaccumulation

The accumulations of metals (concentration of the metal in the plant/its concentration in soil sample) in different parts (leaves and stems) of *T. nilotica* of Lake Nasser banks are represented graphically in Figure 3 and listed in Table III. All parts of *T. nilotica* showed high metal values. Thus, this plant can be used in phytoextraction. Figure 3 shows that the concentrations of Pb, Cd, Co, Zn, Ca and Mg are higher in the leaves than in the stems, indicating that high amounts of these elements may be recycled back into the soil when these leaves are shed. Relatively high Pb, Cd, Cr, Ni, Cu and Co concentrations in the leaves and stems of *T. nilotica* (Fig. 3) indicate that these metals may use the same uptake mechanisms as the essential metallic elements (Raskin *et al.*, 1994).

Lead and cadmium concentrations in *T. nilotica* samples varied between 0.55 and $0.5 \,\mu g \, g^{-1}$ in leaves and between 0.35 and $0.37 \,\mu g \, g^{-1}$ in stems, respectively. Cd has a higher solubility than other heavy metals (Lewander *et al.*, 1996), and in addition to Pb, such heavy metals as Cr, Ni, Zn and Cu are also major soil contaminants (Kumar *et al.*, 1995). Wenzel and Jockwer (1999) studied the accumulation of heavy metals in plants grown on mineralized soils of the Austrian Alps. They found that the Cd concentrations were typically higher in shoots than in roots and that the soils at these sites have Cd pools (extracted using 1 M NH₄NO₃) that are about seven times larger than any other soil in this study. This indicates that the high concentration of Cd in plant tissues may be restricted to soils that contain considerable amounts of easily extractable Cd.

Based on data obtained by Baker *et al.* (1994) and Wenzel and Jockwer (1999), it seems reasonable to classify plants accumulating >50 mg kg⁻¹ Cd and >10,000 mg kg⁻¹ Zn in shoots as Cd and Zn hyperaccumulators, respectively. Figure 4 shows relatively higher bioaccumulation factors for Cr (1.4), Cu (11), Fe (47.6), Na (9.3) and K (12.6) in the stems of *Tamarix* than in the leaves. Accumulation and tolerance of exceptionally high levels of heavy metals in stems are possibly related to other physiological processes (Wenzel and Jockwer, 1999). A high organic content minimizes the mobility of metals (Kuntze, 1985; Lewander *et al.*, 1996) and is correlated with a low plant availability of heavy metals in soils (Greger and Kautsky, 1990). Stems of *T. nilotica* accumulate high concentrations of Cr (6.15 µg g⁻¹), Cu (12 µg g⁻¹), Fe (237.4 µg g⁻¹), Na (42.07 mg g⁻¹) and K (3.17 mg g⁻¹; Fig. 3). This is in agreement with results reported by Lewander *et al.* (1996), that the metals released from the soil are likely to be accumulated by the plant shoots.

Plant stems show higher concentrations of Na (42.07 mg g⁻¹) and K (3.17 mg g⁻¹) than the other metals analysed (Fig. 3). The potassium concentration decreases with increasing Zn, Mn and Co concentrations. This is consistent with results reported by Reeves and Baker (1984) and Wenzel and Jockwer (1999). They found that reduced K concentrations in regions containing elevated Co and Mn also in higher levels of add Zn in soil. A previous study on heavy metal concentrations in *T. nilotica* growing at the banks of Lake Nasser showed that *T. nilotica* has a great ability to accumulate large amounts of Na, K, Ca and Mg. Badri and Hamed (2000) investigated the accumulating ability of *T. nilotica* and reported that *Tamarix* had 1.68% of Na, thus categorizing it as a high sodium accumulator. Also, Ali *et al.* (2001)



FIGURE 3 Distribution of mean concentration of several metals ($\mu g g^{-1}$) in the Lake Nasser bank soil, *Tamarix nilotica* (leaves and stems) and crystal salt ($\mu g g^{-1}$ dry weight of plant).

	Pb Cd Co	0.064 U.D. 0.19	
Downl	Item	Α	
oaded			El-
At:			1
13:27			
15			
Jar			

		El-Ramel			West Dehamite		East Dehamite			Abdeen		
Item	A	В	С	A	В	С	A	В	С	A	В	С
Pb	0.064	0.39	0.12	0.12	0.63	0.25	0.065	1.03	0.9	0.4	0.13	0.13
Cd	U.D.	0.24	0.36	U.D.	0.25	0.37	U.D.	1.3	0.375	U.D.	0.25	0.375
Со	0.19	1.94	2.14	0.28	1.95	2.15	0.2	5.3	4.65	0.25	2.5	2.25
Ni	0.22	0.24	0.59	0.34	1.57	0.61	0.23	1.63	0.625	0.25	0.25	2.5
Cr	0.62	3.8	5.0	0.643	3.9	5.2	0.62	5.03	8.15	0.63	5.15	6.25
Cu	U.D.	2.12	10.5	U.D.	2.5	10.7	U.D.	5.75	13.15	U.D.	2.13	13.75
Zn	0.51	94.14	34	0.52	103	73	5.5	112.9	34.25	0.61	94.15	116.5
Fe	3.54	118	139	3.58	131.75	139.5	3.55	118.3	144.3	4.65	466.65	526.75
Mn	13.2	79	100	14.2	109.75	100.75	13.3	79.5	128.65	21.85	112.5	106.15
Na	6262	13,937	36,214	6264.3	13,986.7	48,541.6	10,602.2	35,104.2	36,216	4701.6	13,939.4	47,291.67
K	145	1254	2736	156.4	3121.2	2866.7	245.4	1255	4330.35	167.4	1782.5	2738.6
Ca	2418	26,711	19,611	5801.62	31,937.5	33,425	2614.62	30,500	32,000	2418.65	26,712.5	19,612.5
Mg	596	3158	3158	748.1	3330	3160	679.5	16,862.5	16,810	596.21	3710	3785

TABLE III Metal Concentrations ($\mu g g^{-1}$) of *Tamarix nilotica* (leaves and stems) and crystal salts ($\mu g g^{-1}$ dry weight of plant).

Note: A, Concentration of metals on surface of T. nilotica (crystal salt); B, concentration of metals of T. nilotica leaves; C, concentration of metals of T. nilotica stems; U.D.: under detection limit.



FIGURE 4 Bioaccumulation factors of several metals of leaves and stems of Tamarix nilotica.

reported that the high concentration of sodium in the leaves makes them salty, especially with high amounts of K, Mg and Ca, and possibly unpalatable to animals, thus reducing their value as fodder except for the youngest leaves. The mean concentrations were Na 19.2 mg g^{-1} and 42.07 mg g^{-1} , Ca 29 mg g^{-1} and 26 mg g^{-1} and Mg 6.8 and 6.7 mg g^{-1} in the leaves and stems of *T. nilotica*. For adequate animal health, feedings must contain the dietary levels of Na (0.09–0.22%), Ca (0.4%) and Mg (0.2%) (Commonwealth Agricultural Bureau, 1980; Little, 1982). Also, high K, Ca and Mg concentrations indicate that *T. nilotica* can be used as soil fertilizer after treatment to remove toxic metals such as Pb and Cd.

Figure 4 shows that Co (10.5), Ni (5313.2), Pb (2870.1) and Cd (2035.4) show high bioaccumulation factors in *T. nilotica* leaves, while Na (9.3), K (12.6), Cu (12), Cr (6.15) show high bioaccumulation factors in plant stems. Fe, Mn, Ca and Mg are equally accumulated in *T. nilotica* stems and leaves. These data suggest that *T. nilotica* can be useful as a model system to study the mechanisms of metal accumulation and metal tolerance.

It appears that there are no correlations between the concentrations of metals in soil samples and different parts of *T. nilotica*. This suggests that there are bioaccumulations of metals from the soil to *T. nilotica* tissues. This is in agreement with previous results from Badri *et al.* (1996) and Ali *et al.* (2001) for the eastern desert of Egypt, and from Al-Homaid *et al.* (1990) for desert plants of Saudi Arabia.

Our results demonstrate that *T. nilotica* has an unusual ability to take up heavy metals from the soil and concentrate these metals in their leaves and stems (Fig. 4). Therefore, *T. nilotica* could be used in the phytoextraction process to improve the properties of Lake Nasser bank soil.

3.3 Chemical Composition of the Crystal Salt

Crystal salt samples are characterized by high pH (7.3–8.3) values. This may be related to the high concentrations of Cl (104.4–156.6 mg g⁻¹), Ca (96.2–184.4 mg g⁻¹) and HCO₃ (186.6–500.4 mg g⁻¹), and very high Na concentration (512.9–812.5 mg g⁻¹). The data reflect high concentrations of organic matter in the crystal salt samples (14.1–39.2 mg g⁻¹).

Na⁺ is considered the major cation in the crystal salt samples (512.9–812.5 mg g⁻¹). This value represents 67.5% of the total metal concentration (Fig. 5). A high percentage sodium demonstrates the great ability of *T. nilotica* to accumulate Na from its soil. The above data are consistent with results reported by Badri and Hamid (2000) for the same plant. Because of this property crystal salts on the plant's surface, and it is suggested that such a cation can be recycled back into the soil. Potassium concentrations (12.98–18.99 mg g⁻¹) in crystal salt are relatively high and represent about 1.5% of the total metal concentrations. Although potassium is an essential element for plant growth, Na is non-essential, but the high Na content may be related to the high ability of *T. nilotica* to accumulate Na. Elevated Na⁺ and K⁺ concentrations can have a great influence on a soil's properties. The crystal salt samples contain relatively small amounts of Pb, Co, Ni and Zn, representing 0.0013%, 0.00174%, 0.00184% and 0.0069%, respectively, of the total metal concentrations. The abundance of these trace metals in crystal salt is due to the ability of the plant to accumulate these metals from the soil (Soltan and Rashed, 2000).

Relatively high pH values and organic matter content reduce the mobility of metals and their availability to the plant (Driel and Nijssen, 1988). Fe and Mn concentrations represented about 0.03% and 0.11%, respectively, of total metal concentrations. Iron is a major element in various primary minerals, but plant crystal salt samples show a high Mn percentage because manganese is an essential minor nutrient element for plant. The concentration ranges of Fe and Mn normally encountered in plants are 40–500 and 50–1000 μ g g⁻¹, respectively. These



FIGURE 5 Distribution of major, minor and trace metals (%) in crystal salt.

elements are essential to plant life, but non-essential elements such as Pb can also be accumulated and can interact with the essential elements in their biochemical functioning (Langmuir, 1997).

Cobalt is part of the structure of vitamin B_{12} and is involved with certain enzymes. Co represents 0.00174% of total metal concentrations. The concentration range of cobalt is normally 0.1–0.6 µg g⁻¹ for plant materials. Calcium and magnesium are macronutrients for plants; Ca levels vary greatly between species, and Mg has distinctive functions in plants. The variation of Ca in crystal salts samples showed a similar pattern to that of magnesium. The contents of Ca and Mg represent about 25.83% and 5%, respectively, of total metal concentrations.

4 CONCLUSION

The measured heavy metals are in different extraction phases and form in soil samples. Most of them are adsorbed or co-precipitated with amorphous iron-manganese oxide. It appears that Pb, Cu and Zn are equally distributed between the exchangeable form and the iron/manganese oxide fraction, while other metals are present in high density in Fe/Mn oxide form.

The appearance of toxic trace metals such as Pb, Cd, Cr, Co and Ni may be a result of increasing tourism in recent years in Lake Nasser or the effects of fish farms and their discharges. With the exception of iron, the total concentrations of all elements studied in the soil samples are still lower than normal background levels.

T. nilotica has good ability to absorb and accumulate essential and non-essential elements including toxic metals. *T. nilotica* stems accumulate high concentrations of Cr, Cu, Fe, Mn,

Na and K in the order Fe > Mn > K > Cu > Na > Cr, while *T. nilotica* leaves concentrate high amounts of Pb, Cd, Co, Ni, Zn, Ca and Mg arranged in the order Pb > Ni > Cd > Mg > Zn > Co > Ca. The high bioaccumulation factors in *T. nilotica* (leaves and stems) suggest that, *T. nilotica* can be useful as a model system to study the mechanisms of metal accumulation and metal tolerance.

Comparisons of the composition of crystal salt samples with that of *T. nilotica* (leaves and stems) show that *T. nilotica* is able to secrete many accumulated metals onto its surface. Cadmium and copper concentrations in crystal salt samples are below detection limits, which means that *T. nilotica* accumulates small amounts of these metals and cannot secrete them on its surface, suggesting that this plant could be safely used for animal grazing. All measured metals show higher concentration in different *T. nilotica* parts than in crystal salts. There are no correlations between the metal concentrations in the soil and those found in the different *T. nilotica* parts.

All the above results suggest that the bioaccumulation of heavy metals by *T. nilotica* from the soil can have very important commercial implications. For example, the plant could be used in phytoremediation processes as part of an established environmental clean-up technology; it can be grown and harvested economically and can accumulate toxic metals, thus greatly reducing the concentrations of toxic metals in the soil.

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