# Mobilization of trace and toxic metals from tailing to soil and some wild plants near gold mines at South Egypt

**RASHED M.N.** (1) **and SANZOLONE R.** (2)

(1) Chemistry Department, Faculty of Science, 81528 Aswan, Egypt
(2) US Department of the interior, Geological Survey, Box 25046, Federal Center, Denver CO 80225-0046, USA

## Abstract

Toxic elements Hg, Cd, Al, Pb and As resulting from gold extraction process as well as associated trace elements Ba, Cr, Li, Ag, Ni, Au, Mo, Zn, Mn and Cu and major elements Ca, Mg, Na and K may be mobilized by weathering to the adjacent soil and plants. These elements were studied in the gold extraction tailing, soil and wild plants (*Acia raddiena* and *Aerva javanica*) collected from Allaqi Wadi (170 km east of Aswan, Egypt) near gold mines used by incident Egyptian and for 100 year by some companies. Element concentrations were measured using atomic absorption spectrophotometer, ICP-AES, ICP-MS and CVAA. The results reveal that elements K, Cr, Li, Zn, Ni, Ag, Au, Zn, Hg, As, Ag, Au and Pb in soil decreased faraway from tailing, while Al, Ca, Mg, Na, Fe, Ti, Mn and Cu increased as the result of input from surrounding rocks. Wild plants show positive and significant correlation coefficient (r >0.500) with their root soil for the elements Cr, Cu, Ni and K (r; 0.595,0.912, and 0.863) which indicated the high selectivity of the plant for accumulation of those elements. *Acia raddiena* concentrated and accumulated toxic elements As, Cd and Pb in higher levels than *Aerva javanica*. The overall results of this study show that the soil and plants near the gold mine tailing was highly toxic, and the plants and soil must not be used for grazing or agriculture.

**Keywords:** toxic, trace elements, wild plants, Egypt, gold tailing, pollution

## Introduction

Mining of minerals and metals is important in all industrialized and developing countries. In the past century, much of the mining has concentrated on the extraction of metals necessary for the economic or industrial development of societies for example, gold, silver, iron, copper, lead, zinc, chromium, mercury and others. Other metals as As, Cd and Se are often enriched in mineral deposits and recovered as byproducts. Because many of these metals can be toxic to plants, animals and humans their interaction with the environments is a national concern. To address this concern, studies of natural and man-made environmental interaction of metals after mining have become increasingly important to society. After the mine was abandoned environmental studies include analysis of soil and vegetation at the mine site surrounding area was run (Pinochet *et al*., 1999) There are 16 known essential trace elements for man, animals and plant; Fe, Cu, Li, Sn, Ni, V, Mn, Zn, Co, I, Mo, Se, F, Cr, B and Si. Some elements as Al, Hg, Cd, Ge, Sb, V, Si, Rb, Ag, Au, Pb, Bi and Ti are believed to be acquired by the animal body as environments and to reflect the content of the organism with its environment (Valkovic, 1975). Some elements such as As, Pb, Cd, Hg and Al are frequently classified as toxic elements because their biological activity is largely confined to toxic reaction (Underwood, 1973; Bowen, 1979). To evaluate environmental concerns, scientists measure metal concentrations in the ecosystem around the mines (Gray and Sanzolone, 1996; Chlopecka *et al.,* 1996; Beaker and Senft, 1995; Milton and Johnson, 1999; Hrsak *et al*., 2000 ) The aim of this study is target to fellow up the mobilization of major, trace and toxic metals from gold mine and the extraction tailing to soil and some wild plants near this mines which located at Wadi El-Allaqi, south of Egypt in the Eastern Desert (Figure 1).

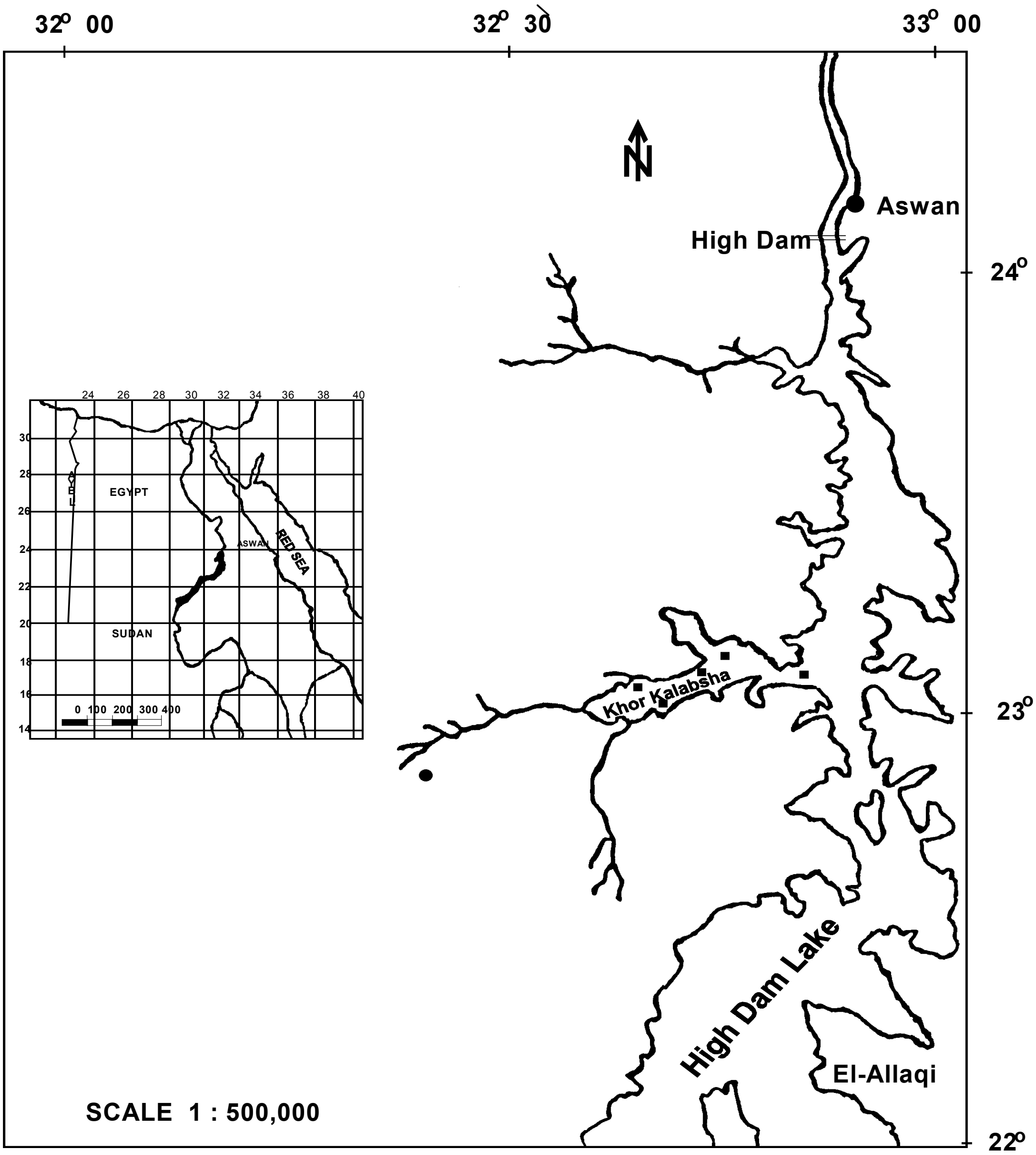


**Figure 1** Map showing the study area

**Study area**

Wadi El-Allaqi located 170 km east of Aswan, Egypt in the Eastern Desert (Figure 1), There are many gold mines in this area, but this gold mine under study was the most one used by incident Egyptian and by some companies since 100 years ago. This mine was closed since 1948, but there is many gold extraction tailing adjacent to the mine. The Eastern Desert composed mainly rocks formation of Pre-Cambrian basement complex including basalt, granite, granodiorit with Nubian sandstone and the Pliocene-Quaternary sediments. Ores of chromite, calcopyrite, barite, serpentine, talc and gold deposits in smoking quartz are found in the area (Hume, 1934) (nearly 6 gold mines used by ancient Egyptian).

Eastern deserts contains different species of wild plants but the mainly wild plants which found are for example, *Glinus lotoides, Aerva javanica*, *Astragalus vogelli* and *Tamarix nilotica,* which has the medicinal uses for mans.

## Materials and Methods

**Sample collections**

Thirty samples of soil (S1-S8) and wild plants P1-P4 (*Acia raddiena* and *Aerva javanica*) were collected from the area near the gold mine and extraction tailing, the soil samples were collected from the site S1 near the tailing and the mine,while S2 to S8 samples from the sites as faraway from the gold mine to S8 (background sample ) . Ten tailing samples were collected from the two tailing sites T1 and T2 adjacent to the mine. Plant samples P1 (*Acia raddiena )* and P2 (*Aerva javanica*) near the tailing sites and P3 (*Acia raddiena )* and P4 (*Aerva javanica* ) far from the tailing sites were collected from the wadi floor . The plants were cleaned to remove the visible soil and then washed with tap and bidistilled waters several times, then oven dried at 100°C for 24 h. They were mixed in stainless steel blender. The representative soil and tailing samples were grounded and powdered with the aid of a mechanical agate mortar to 100 mesh, therefore they were oven dried at 100°C for 5 h. The powdered samples of plants, soils and rocks were stored in clean polyethylene bottles until analysis.

**Contamination control**

Accurate multi-element analysis at trace levels (mg $kg^{-1}$; mg $L^{-1}$ and μg $kg^{-1}$; μg $L^{-1}$) is dependent upon the prevention of element contamination. All stages of sample preparation and analysis were carried out in a clean air from the studied elements. All laboratory equipment used for analysis were made of Pyrex, washed with $HNO_3$, rinsed twice with bidistilled water and placed in a clean environment until dry. All reagents used were of analytical grade (BDH, Merk).

**Analytical accuracy**

Certified standard solutions 1,000 mg $L^{-1}$ (BDH, Ltd) of elements Ag, Au, Ca, Co, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Sr and Zn were used for Atomic Absorption Analysis. Standard reference materials, alfalfa, for plant and GXR-2 for soil samples were used through measurements using ICP-AES and ICP-MS (Table 1).

**Sample preparation and analysis**

**Soil and tailing samples**

0.5 g of the finely ground sample was accurately weighed into Teflon beaker with cover, 40 mL HF and 10 mL conc. HCl acids were added, the covered beaker was heated to 130-140$^o$C to complete attack, the acids were evaporated then 1:1 HCl was added and the solution was diluted to 100 mL with bisdistilled water.

**Plant samples**

Two-gram portions of the plant samples were wet ashed in Teflon beaker using 2:1 $HNO_3$/HCl acid mixture flowed by addition of 3 drops HF acid. It was allowed to settle for 8 h, and then heated to 130-140$^o$C for 1 h and digestion completed at 170$^o$C until a clear solution was obtained. The content was diluted to 50 mL by bidistilled water. Blank samples for rock, soil and plant were prepared. Each preparation of sample was repeated in triplicate.

**Analytical determination**

Major elements Al, Ca, Fe, K, Mg, Na and Ti and trace elements Ag, Au, As, Cd, Co, Cu, Cr, Hg, Mn, Mo, Ni, Li, Zn and Pb were determined in soil, tailing and plant samples.

A Shimadzu ICPV-100 Inductively coupled plasma atomic emission spectrometer ICP-AES was used for measurement of the studied elements in the soil and tailing samples, while ICP-MS Inductively coupled plasma mass spectrometer was used for measurement of the studied elements in the wild plant samples. A SP 190 Atomic Absorption Spectrophotometer, AAS, equipped with air-acetylene burner, was used for measurements of Ag and Au using their hollow cathode lamps at the recommended current and conditions.

**Statistical analysis**

The chemical analysis results were calculated using MINITAB program. Mean, standard deviation and correlation coefficient were obtained.

## Results and Discussion

**Standard reference materials**

Element concentrations Al, Ca, Fe, K, Mg, Na, Ti, Ag, Au, As, Cd, Cu, Co, Cr, Li, Mo, Mn, Ni, Zn, Hg and Pb were determined in soil standard reference material (GXR-2) and plant standard reference material (alfalfa) by ICP-AES and ICP-MS. Each value is expressed as mean for the three replicates. Element concentrations in alfalfa determined by ICP-MS are in agreement with certified values than the measurement by ICP-AES (Table 1). Measurement by ICP-AES for standard reference material (GXR-2) gives good results than the measurement using ICP-MS (Table 1). This give rises to using ICP-MS for the analysis of plant samples and ICP-AES for the soil and tailing samples.

**Metal contents in soil samples**

For the accuracy of the chemical analysis, ICP-AES showed good linearity over a wide concentration range from 20 μg $kg^{-1}$ to 130 mg $kg^{-1}$ for the studied elements Al, Ca, Fe, K, Mg, Na, Ti, Ag, Au, As, Cd, Cu, Co, Cr, Li, Mo, Mn, Ni, Zn, Hg and Pb in soil samples S1, S2, S3, S4, S5, S6, S7 and S8 (Table 2) and tailing samples T1 and T2 (Tables 3 and 4). The results has shown that Al, Ca, Fe, K, Mg, Na, Ti and P present in soil samples as major concentrations (0.04-5.9%), while Ag, As, Au, Cd, Co, Cu, Cr, Li, Mo, Mn, Ni, Zn, Hg and Pb present in trace amounts (μg $kg^{-1}$ and mg $kg^{-1}$). The overall results show that concentration of K, Cr, Li, Zn, Ni, Ag, Au, Zn, Hg, As and Pb in soil decreased as faraway from the mine and tailing sites. This decreasing in element concentration result from the mobilization of these elements by weathering from the tailing sites to the soil floor (Levy *et al*., 1992). The presence of these elements in closed concentrations between soil and tailing reflect their mobilization from tailing to the soil floor. Standard deviation SD of the studied elements in the soil from the 8 sites shows the decrease in the order P (0.0075)<Ti (0.082)<Mg (0.125)<Na (0.141)<K (0.179)<Ca (0.396)<Al (0.530)<Fe (0.702). On the other hand concentrations of Al, Ca, Mg, Na, Fe, Ti, Mn and Cu increased in soil samples increased as faraway from the gold mine and the tailing sites. This increase was as a result of input of these elements from the surrounding rocks by weathering.

**Table 1** Element contents in GXR-2 standard reference material for soil, determined by ICP-AES and in alfalfa standard reference material for plants, determined by ICP-MS.

| Elements | GXR-2 (ICP-AES) | GXR-2 Certified values | Alfalfa (ICP-MS) | Alfalfa Certified values |
|---|---|---|---|---|
| Al (%) | 6.10 | 18.60 | 0.0061 | 0.0062 |
| Ca | 0.84 | 0.88 | 0.71 | 1.12 |
| Fe | 1.80 | 1.86 | 0.0063 | 0.0079 |
| K | 1.30 | 1.63 | 2.50 | 1.70 |
| Mg | 0.83 | 0.88 | 0.257 | 0.261 |
| Na | 0.55 | 0.45 | 0.106 | 0.099 |
| P | 0.07 | 0.068 | 0.280 | 0.193 |
| Ti | 0.27 | 0.290 | 0.005 | 0.0008 |
| Ag (mg $L^{-1}$) | 17 | 18 | <2 | ---- |
| As | 35 | 21 | 0.10 | 0.06 |
| Au | ND | ND | <8 | ---- |
| Cd | 3 | 4.1 | 0.0003 | 0.0004 |
| Co | 9 | 9 | 0.16 | 0.31 |
| Cu | 78 | 70 | 6.40 | 5.90 |
| Cr | 35 | 34 | 0.13 | 0.23 |
| Hg | ND | ND | ND | ND |
| Mn | 1000 | 2.7 | 19.3 | 23 |
| Mo | 12 | 980 | 2.10 | 2.30 |
| Ni | 54 | 9 | 1.2 | 1.40 |
| Zn | 540 | 460 | 11.10 | 19.70 |
| Pb | 690 | 670 | 0.55 | 0.57 |

*ND not determined by these methods. Au and Ag were determined by AAS, while Hg were determined by CVAA.

**Table 2** Element concentrations in soil samples as determined by ICP-AES.

| Elements | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | Mean | SD |
|---|---|---|---|---|---|---|---|---|---|---|
| Al (%) | 5.3 | 4.6 | 4.9 | 4.7 | 5.7 | 4.8 | 5.8 | 5.9 | 5.21 | 0.530 |
| Ca | 2.5 | 2.8 | 3.5 | 2.5 | 3.1 | 2.8 | 2.8 | 3.5 | 2.93 | 0.396 |
| Fe | 3.5 | 2.5 | 2.5 | 2.2 | 3.7 | 2.5 | 3.6 | 4 | 3.06 | 0.702 |
| K | 1.2 | 1.1 | 1.1 | 1.0 | 0.68 | 0.93 | 0.90 | 0.75 | 0.957 | 0.179 |
| Mg | 0.95 | 0.92 | 1.0 | 0.89 | 1.0 | 0.90 | 1.2 | 1.2 | 1.0 | 0.125 |
| Na | 1.0 | 1.2 | 1.1 | 1.3 | 1.4 | 1.3 | 1.2 | 1.4 | 1.237 | 0.141 |
| Ti | 0.31 | 0.38 | 0.37 | 0.30 | 0.30 | 0.28 | 0.53 | 0.40 | 0.358 | 0.082 |
| P | 0.06 | 0.06 | 0.06 | 0.05 | 0.04 | 0.05 | 0.06 | 0.06 | 0.055 | 0.007 |
| Ag (mg $kg^{-1}$) | 0.11 | 0.11 | 0.07 | 0.06 | 0.04 | 0.06 | 0.10 | 0.07 | 0.077 | 0.026 |
| As | 700 | 24 | 4 | 5.6 | 5.3 | 6.3 | 7.4 | 7.4 | 96.3 | 244 |
| Au | 6 | 2.5 | 4 | 0.50 | 1.0 | 1.5 | 1.5 | 2.5 | 3.18 | 2.10 |
| Cd | 0.20 | 0.20 | 0.1 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.125 | 0.046 |
| Co | 22 | 13 | 14 | 12 | 20 | 13 | 19 | 21 | 16.75 | 4.13 |
| Cu | 57 | 25 | 21 | 20 | 52 | 24 | 39 | 60 | 37.25 | 16.9 |
| Cr | 530 | 190 | 140 | 170 | 290 | 200 | 280 | 260 | 257 | 122 |
| Hg | 2.7 | 0.18 | 0.07 | 0.10 | 0.03 | 0.03 | 0.15 | 0.07 | 0.41 | 0.924 |
| Mn | 700 | 510 | 470 | 420 | 730 | 480 | 680 | 790 | 597 | 142 |
| Mo | 60 | 9 | 11 | 24 | 38 | 25 | 39 | 37 | 30.37 | 16.7 |
| Ni | 260 | 93 | 68 | 76 | 130 | 100 | 120 | 110 | 119 | 60.4 |
| Zn | 92 | 52 | 55 | 48 | 55 | 47 | 67 | 62 | 59.75 | 14.66 |
| Pb | 29 | 7 | 7 | 5 | 5 | 4 | 5 | 7 | 8.62 | 8.31 |

Studies of trace elements in ecosystems have indicated that many areas near metalliferous mines, urban complexes or major road systems contain anomalously high concentration of these elements (Chlopecka *et al*., 1996). Trace metals Cd, Cu, Pb and Zn were determined in contaminated soils through the deposition of hydraulically transported mine tailings in the early 1900s, Colorado, USA. The greatest concentrations of total metals were found in the surface horizon, total soil metals ranged from Cu 14-1,200, Cd 3-110, Pb 46-49,000 and Zn 44-1,200 mg $kg^{-1}$ (Levy *et al*., 1992). Soil contamination by Pb, Zn and Cd from Lead smelter in Croatia had been studied (Hrsak *et al*., 2000); also, trace elements pollution of soil collected near a municipal solid waste incinerator in Spain was studied (Schuhmacher *et al*., 1997).

**Metal contents in tailing samples**

Tailing contains Ag, Au, As, Cd, Mn, Hg and Pb in higher concentration than in soil (Tables 3 and 4). Mercury present in the tailing as the result of using liquid mercury for the extraction of gold (amalgamation of gold) from the rocks containing gold deposits, some liquid mercury may remain in the floor near old operation because it was sometimes spilled, lost, or discarded. Heavy metals such as As, Cu, Pb, Zn and Cd are associated with many of the gold deposits. High concentrations of Hg (0.005 -0.48 μg $kg^{-1}$) and the other heavy metals were found in marine waters near the Nome placer deposits, USA (Gray and Sanzolone, 1996).

**Table 3** Major element concentrations in tailing samples as determined by ICP-AES.

| Sample (%)Al | Ca | Fe | K | Mg | Na | Ti | P | |
|---|---|---|---|---|---|---|---|---|
| T1 | 2.6 | 1.4 | 1.6 | 0.73 | 0.33 | 0.50 | 0.11 | 0.02 |
| T2 | 2.2 | 1.2 | 1.3 | 0.67 | 0.29 | 0.45 | 0.10 | 0.02 |

**Table 4** Trace element concentrations in tailing samples as determined by ICP-AES.

| Sample (mg kg$^{-1}$) | Ag | As | Au | Cd | Co | Cu | Cr | Mo | Mn | Ni | Zn | Hg | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T1 | 1.0 | 8.0 | 1100 | 0.30 | 9.0 | 57 | 220 | 3.0 | 45 | 320 | 55 | 4.6 | 16 |
| T2 | 1.8 | 8.0 | 1300 | 0.30 | 6.0 | 56 | 110 | 2.0 | 12 | 250 | 54 | 3.8 | 12 |

**Metal contents in wild plant samples**

ICP-MS showed good linearity over a wide concentration range from 5 µg kg$^{-1}$ to 22 mg kg$^{-1}$ for the studied elements Al, Ca, Fe, K, Mg, Na, Ti, Ag, Au, As, Cd, Cu, Co, Cr, Li, Mo, Mn, Ni, Zn, Hg and Pb in the plant samples (Table 5). Plant samples contain lower element concentrations than in the soil and tailing samples except potassium,

**Table 5** Element concentrations in plant samples as determined by ICP-MS.

| Elements | Near mine and tailing | | Far from mine and tailing | |
|---|---|---|---|---|
| | P1 | P2 | P3 | P3 |
| Al (%) | 0.016 | 0.022 | 0.006 | 0.01 |
| Ca | 0.64 | 0.71 | 0.71 | 1.54 |
| Fe | 0.016 | 0.027 | 0.01 | 0.005 |
| K | 0.81 | 1.23 | 1.09 | 0.46 |
| Mg | 0.30 | 0.18 | 0.23 | 0.08 |
| Na | 0.24 | 0.05 | 0.03 | 0.01 |
| Ti | 0.005 | 0.005 | 0.005 | 0.005 |
| P | 0.28 | 0.46 | 0.11 | 0.26 |
| Ag (mg kg$^{-1}$) | 0.10 | 0.04 | 0.07 | 0.06 |
| As | 0.40 | 0.02 | 0.15 | 0.01 |
| Au | 1.5 | 1.0 | 0.25 | 0.50 |
| Cd | 0.30 | 0.08 | 0.18 | 0.03 |
| Co | 0.24 | 0.35 | 0.15 | 0.10 |
| Cu | 4.1 | 4.9 | 3.2 | 3.1 |
| Cr | 10.1 | 18.1 | 2.0 | 0.04 |
| Hg | 0.01 | 0.02 | 0.02 | 0.02 |
| Mn | 18.7 | 21.1 | 10.5 | 17.2 |
| Mo | 2.0 | 1.9 | 2.0 | 1.3 |
| Ni | 6.0 | 15.2 | 1.10 | 2.0 |
| Zn | 7.8 | 7.1 | 3.0 | 18.8 |
| Pb | 0.23 | 0.13 | 0.03 | 0.18 |

P1 and P3 *Aerva javanica*
P2 and P4 *Acia raddiena*

which present in higher concentration in the plant than in the soil and tailing. Potassium is very essential elements for plant metabolism (Bowen, 1979). Plant samples (P1 and P2) near the tailing sites contain the higher element concentrations than those from the other sites (P3 and P4) far from the tailing and the mine. *Acia raddiena* and *Aerva javanica* plants have the ability to concentrate definite elements from the soil especially Mn, Cr, Cu and Zn (Rashed, 2000). *Acia raddiena* concentrated and accumulated toxic elements As, Cd and Pb in higher levels than *Aerva javanica* This indicate the selectivity of the plant for definite element, and the concentration of elements by plant from the soil depend upon the selectivity of plant to the elements and the abundance of the elements in the soil (Yagodin, 1982). The element concentrations in *Acia raddiena* and *Aerva javanica* plants located at far from the tailing and gold mine were present in safety baseline levels for human uses (EOSC, 1993).

A significant pathway for the pollution terrestrial by toxic elements goes through the atmosphere, according to the meteorological conditions they can be transported over varying distances before deposition in different ecosystem (Beaker and Senft, 1995). Lead, zinc and cadmium were determined in the tissues of bank vole *(Clethrionomys glareolus)* to determine the potential toxicological effects produced from a revegetated surface at a modern metalliferous mine tailing in the Republic of Ireland (Milton and Johnson, 1999). Wild plants show positive and significant correlation coefficient ($r > 0.500$) with their roots soil for the elements Cr, Cu, Ni and K (r; 0.595, 0.912, and 0.863) which indicated the high selectivity of the plant for accumulation of those elements.

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