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# Cadmium, Lead, and Zinc from Terrestial Plants in the Enyigba-Abakaliki Lead and Zinc Mine: Search for a Monitoring Plant Species in Trace Element Distribution

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Globally, there is a need to combat environmental perturbations in all aspects. It is necessary to monitor the concentrations of elements which are bioaccumulated in wild terrestrial plants. Some plants specifically take up certain trace elements in metal-contaminated soils and have been used in locating ores. In Africa, the basil 'Becium homblei' is associated with copper deposits (Edington & Edington, 1977). The acquisition of data using a well-defined monitoring programme as regards the temporal and spatial concentrations of metal-contaminants in a particular plant species on a local, regional, or national scale is needed in Nigeria as well as the whole West African region with their similar vegetation and soil characteristics. The Enyigba lead-zinc mine transect has contrasting floras and a few plant species in common. For this reason, different terrestrial/wild plant species were collected from the derelict Enyigba-Abakaliki lead and zinc mine, Nigeria, and analysed for their contents of zinc (Zn), lead (Pb), and cadmium (Cd), which are compared to their concentrations in corresponding soils. Alfisols, oxisols and ultisols dominate with overlapping variations of other types as is also obtainable in most of West Africa. The Enyigba-Abakaliki Pb-Zn mine is situated about 17-18 Km on the rural outreach of urban Abakaliki. Traffic in this area is minimal. Mining of the Pb-Zn ore commenced in 1925, but was later abandoned due to low economic returns. Recently, interests are being shown to re-commence mining operations. The mine has so far been converted by some of the inhabitants of the area for agricultural purposes.

The Pb-Zn deposits are found in most of the mineralized zone of Nigeria, the Benue Valley/Trough that stretches for hundreds of kilometres from the south-east (Abakaliki area) and continues northeasterly. The vast majority of tropical West Africa is underlaid with mostly Precambrian crystalline igneous and metamorphic rocks. Nigeria's Cretaceous metallogenic belt, the Benue Trough, is the only known area with lead-zinc deposits. Especially, in the Abakaliki area, the Nigerian tropical rocks are made up of gneisses, granites, anomalous granites, shales, black shales, sphalerite (Benue Valley/Trough), and average crustal rocks; and the tropical soils are background soils made up of crystalline rocks and black shales, and mineralized soils of black shales (Olade, 1987).

## MATERIALS AND METHODS

Seventeen samples of matured/old leaves from fifteen different wild plant species were collected from the Enyigba-Abakaliki Pb-Zn mine on Dec. 29, 1991, during the harmattan season. The samples were kept in brown paper bags without contact with any metallic materials. Most of the samples were already dry at the time of collection due to the harmattan effect. Samples of leaves and soils were obtained at various distances from the position of the drilling rig to approx 100 m. The soil samples were collected to a depth of about 5 cm.

Table 1. Zn (mg/kg) in the soil (S), plant leaves (P); and P/S ratio at various distances (m).

| Distance | Soil - S | Plant leaves - P | P/S ratio |
|---|---|---|---|
| 0-15m | 463.1 | Spondias mombin (53) | 0.11 |
| | | Rauvolfia vomiforia (113.5) | 0.25 |
| | | Nauclea popeguinei (16.8) | 0.04 |
| | | Sida acuta (150.9) | 0.33 |
| | | Eleusine indica (123.3) | 0.27 |
| | | Eupotorium odoratum (120) | 0.26 |
| 15-30m | 837.3 | Mucuna pruriens (100.2) | 0.12 |
| 30-50m | 441.1 | Discorea bulbifera (144.6) | 0.33 |
| | | Nauclea popeguinei (23) | 0.05 |
| | | Ageratum conyzoides (212.3) | 0.48 |
| | | Pentaclethra macrophylla(104.4) | 0.24 |
| 50-70m | 301.02 | Imperata cylindrica (34.53) | 0.11 |
| | | Gmelina arborea (642.3) | 2.13 |
| 70-80m | 330.9 | Imperata cylindrica (10.7) | 0.03 |
| 80-100m | 3204.7 | Discorea bulbifera (592.1) | 0.18 |
| | | Bryophyllum pinnatum (71.6 | 0.02 |
| | | Vernonia species (1949.1) | 0.61 |
| MEANS FOR (P) AND (P/S) | | 262.5 | 0.33 |

The soil samples were homogenized by grinding in a porcelain mortar and an agate pestle, and then sieved through a 2 mm polyethylene screen to exclude any plant debris or larger particles. About 1 g of each soil sample was oven-dried at 105°C. To each soil sample, 20 ml $HNO_3$ (7 mol/l) was added; and heated in an autoclaved vessel for 1/2 hr at 120°C and 200 kPa. Each solution was made up to 100 ml with distilled water, and then filtered with a 110 mm paper (SFS 3044 Certified Standard Soil Analysis of Finland). The preparations with their replicates were analysed for Cd, Pb, and Zn by flame atomic absorption spectrophotometer (Varian Spectr AA-40); Cd preparations were further analysed by graphite furnace AAS (Varian Spectr AA-40 equipped with GTA-96) in those samples which showed low detection levels by flame. The detection limits for Zn, Pb, and Cd were respectively, 1.3 mg/kg (flame), 6.3 mg/kg (flame), and 0.01 mg/kg (graphite).

The leaf samples were left unwashed to ascertain the intake of trace elements via the food chain linkage from animals to humans; moreover, animals do not wash their food before consumption. About 0.5 g of each sample was homogenized, dried at 105°C overnight, and then dissolved in 5 ml conc $HNO_3$. Each preparation was heated at 50°C for 2 hr, 105°C for 4 hr, 180°C for 4 hr, filtered with a 110 mm paper, and made up to 25 ml with distilled water. The elements were analysed by flame AAS; in those Cd and Pb preparations which showed low detection levels, they were further analysed by graphite furnace AAS (Nuorteva, 1990). The detection limits for the elements were Zn, 2.1 mg/kg (flame); Cd, 0.8 mg/kg (flame) and 0.02 mg/kg (graphite); Pb, 25.0 mg/kg (flame) and 0.02 mg/kg (graphite). National Bureau of Standards Certificate of Analysis

Table 2. Pb (mg/kg) in the soil (S), plant leaves (P); and P/S ratio at various distances (m).

| Distance | Soil -S | Plant leaves - P | P/S ratio |
|---|---|---|---|
| 0-15m | 173.3 | Spondias mombin (1.3) | 0.01 |
| | | Rauvolfia vomiforia (14.1) | 0.08 |
| | | Nauclea popeguinei (14.5) | 0.08 |
| | | Sida acuta (24.1) | 0.14 |
| | | Eleusine indica (15.8) | 0.09 |
| | | Eupotorium odoratum (0.2) | 0.001 |
| 15-30m | 131.2 | Mucuna pruriens (9.4) | 0.07 |
| 30-50m | 292.2 | Discorea bulbifera (10.4) | 0.04 |
| | | Nauclea popeguinei (21.2) | 0.07 |
| | | Ageratum conyzoides (11.6) | 0.04 |
| | | Pentaclethra macrophylla (0.6) | 0.002 |
| 50-70m | 202 | Imperata cylindrica (32.3) | 0.16 |
| | | Gmelina arborea (0.9) | 0.004 |
| 70-80m | 108.4 | Imperata cylindrica (1.0) | 0.01 |
| 80-100m | 942 | Discorea bulbifera (10.1) | 0.01 |
| | | Bryophyllum pinnatum (0.1) | 0.0001 |
| | | Vernonia species (12.2) | 0.01 |
| MEANS FOR (P) AND (P/S) | | 10.60 | 0.05 |

Standard Reference Material (SRM) 1575 (Pine Needles) was used for both Pb and Cd as the quality control reference material. The certified values and those obtained in our lab were respectively, Cd < 0.5 μg/g and 0.2±0.02 μg/g; Pb 10.8±0.5 μg/g and 12±1 μg/g. Zn SRM was prepared in our lab from Merck Art 9953 Zn(II)Cl 1000 mg/l Titrisol standard solution. For plant and soil samples below 8 μg/ml, the Zn standards used were 1, 2, 4 , 6, 8 μg/ml; while for those over 8 μg/ml, 4, 10, 20, and 40 μg/ml of Zn standard preparations were used. 14% nitric acid was used as the base solution.

## RESULTS AND DISCUSSION

The concentrations of Zn, Cd, and Pb are expressed in mg/kg (Tables 1-3).
From Table 1, the mean and highest values of Zn content in the plants are respectively, 262.49 mg/Kg and 1,949.14 mg/kg. Zn levels in terrestrial plants are 20-400 mg/kg (Jones, 1972). In old mining areas, Zn levels in plants may be from 65-450 mg/kg (Mathews & Thornton, 1980).

From Table 2, the mean and highest values for Pb are respectively, 10.58 mg/kg and 32.31 mg/kg. Pb concentrations in terrestrial plants are 1-13 mg/kg (Bowen, 1979). Levels of Pb in plants in mining or mineralized areas are from 63-570 mg/kg (Kovalevskiy, 1979).

From Table 3, the mean and highest levels for Cd are respectively, 4.56 mg/kg and 45.63 mg/kg. Cd concentrations in terrestrial plants have been shown to be from 0.1-2.4 mg/kg (Shacklette et al. 1973). Levels of Cd grown in old mining areas are 1.0-22

Table 3. Cd (mg/kg) in soils (S), plant leaves (P); and P/S ratio at various distances (m).

| Distance | Soil -S | Plant leaves - P | P/S ratio |
|---|---|---|---|
| 15m | 0.8 | Spondias mombin (0.3) | 0.40 |
| | | Rauvolfia vomiforia (1.0) | 1.3 |
| | | Nauclea popeguinei (0.6) | 0.7 |
| | | Sida acuta (0.9) | 1.1 |
| | | Eleusine indica (1.6) | 2.01 |
| | | Eupotorium odoratum (0.8) | 1.04 |
| 15-30m | 2.1 | Mucuna pruriens (1.8) | 0.9 |
| 30-50m | 1.5 | Discorea bulbifera (2.0) | 1.4 |
| | | Nauclea popeguinei (0.1) | 0.08 |
| | | Ageratum conyzoides (7.4) | 5.1 |
| | | Pentaclethra macrophylla (2.3) | 1.6 |
| 50-70m | 0.7 | Imperata cylindrica (0.2) | 0.3 |
| | | Gmelina arborea (4.8) | 7.3 |
| 70-80m | 0.9 | Imperata cylindrica (0.1) | 0.1 |
| 80-100m | 11.2 | Discorea bulbifera (6.9) | 0.61 |
| | | Bryophyllum pinnatum (1.3) | 0.12 |
| | | Vernonia species (45.6) | 4.08 |
| MEANS FOR (P) AND (P/S) | | 4.6 | 1.6 |

mg/kg (Mathews & Thornton, 1980).

The bioavailability of heavy metal deposits in the soil including actual inputs from contaminated dusts and precipitation rather than geochemical background influence the analytical concentrations in leaves (Wagner, 1987). Soil dust may not have influenced the concentrations of elements in the unwashed leaves to any appreciable degree, since they approximate those in other mining areas. Moreover, with the absence of any mining or industrial activity, and the non-use of fertilizers or pesticides, Gmelina arborea standing over 4 m tall has the highest plant (P)/soil (S) of Cd than all the other shorter plants in this mine transect. The elemental concentration with respect to height is dependent on the specific site condition, each individual plant, and the respective ratio of directly available elemental forms and those which enter the plant roots (Wagner, 1990). There are also systematic variations in the contents of these elements in the leaves of the plants. Fluctuations may be due to differing levels of the ore (Pb-Zn) or PbS or associations of Cd-Zn and Pb-Cd, or other soil factors. There is accumulation of non-essential chemical elements with ageing of leaves (Ernst, 1990).

Cd concentration in the soil at the 30-50 m site is higher than at the 0-15 m site, but Nauclea popeguinei has a higher uptake at the latter site. At 70-80 m, Cd soil content is greater than at the 50-70 m site, yet Imperata cylindrica uptake is lower at the former site. This supports the observation that plant availability is dependent on elemental forms rather than on its total soil concentrations (Kabata-Pendias & Kabata, 1984). The decreasing order of the elemental concentrations in the leaves of the plants is Zn > Pb > Cd, while the P/S ratio is Cd > Zn > Pb which reflects the concentrations of the elements in the soils.

In order to determine an appropriate monitoring plant species, a means of classification can be proposed that all plants having elemental concentration above the mean may be classified as accumulators, those approximate to the mean as indicators, while those well below the mean as excluders. By taking the mean values of Zn, Pb, and Cd in the plants and plants/soil ratio, a relative classification of the elemental uptake capability of terrestrial plants specific to an environment can be ascertained. The indispensability of multielement data in environmental monitoring programmes cannot be over-emphasised. Interelement relationships to elucidate sources of pollution can be successfully applied in the West African region.

The mean value of the uptake of Zn by the various plant species is 262.50 mg/kg (Table 1); therefore, the principal accumulator is the Vernonia species, indicator is Ageratum conyzoides (goat weed), and the excluder, Imperata cylindrica. As regards P/S ratio of Zn, the mean is 0.33. The major accumulator is Gmelina arborea, indicators are Sida acuta and Discorea bulbifera, and the excluder is Bryophyllum pinnatum.

The mean value of Pb uptake by the plants is 10.60 mg/kg (Table 2); the main accumulator is Imperata cylindrica, the indicator is Discorea bulbifera, and the excluder is Bryophyllum pinnatum. With respect to P/S ratio of Pb, the mean is 0.05. The main accumulator is Imperata cylindrica, indicators are Discorea bulbifera and Ageratum conyzoides, and the excluder is Bryophyllum pinnatum.

The mean value of Cd uptake by plants is 4.56 mg/kg (Table 3); therefore, the main accumulator is the Vernonia species, indicator is Gmelina arborea, and the excluder is Imperata cylindrica. The mean P/S ratio of Cd is 1.64; therefore, the principal accumulator is Gmelina arborea, the indicator is Eleusine indica, and the excluder is Imperata cylindrica.

Broadly, the plant species fall into the categories of accumulators, indicators or excluders using the uptake of Zn, Pb, and Cd by plants and/or P/S ratio. Plants may be classified as accumulators or indicators or excluders with respect to any particular element (Brooks, 1983; Kloke et al., 1984). Accumulators can take up high concentrations of certain heavy metals without the plants having any toxicity effect (Kabata-Pendias & Kabata, 1984). Indicators take up metals to reflect the levels in the soil environment. They are useful as indicators of the source and the intensity. Excluders have a discriminative effect against metal ions (Brooks, 1983), and biopurify regarding the particular elements.

Imperata cylindrica accumulates Pb, but excludes both Zn and Cd. Ageratum conyzoides is either an accumulator or indicator depending on the element or whether it is being classified as regards plant uptake or the plant/soil system. Generally, Gmelina arborea and the Vernonia species may be classified as accumulators, Discorea bulbifera and Ageratum conyzoides as indicators, and Imperata cylindrica and Bryophyllum pinnatum as excluders.

In Western Europe, Thlaspi calaminare, a variety of the mountain pansy 'Viola lutea' can accumulate > 10%, while Equisetum arvense takes up 0.1 to 1% Zn, and other trace elements (Petrunina, 1974; Edington & Edington, 1977). In Australia, the grass 'Eriachne mucronata' is associated with lead uptake (Cannon, 1977). Dandelion, orchard grass, plantain, and lichens seem to be the best indicator plants for Cd concentrations in soils of Poland (Kabata-Pendias & Dudka, 1990).

Monitoring activities for the determination of trace elements are essential on a local, regional, national, or international scale in the whole of West Africa. There are no uniform monitoring data systems with regard to concentrations of contaminants in plants in the West African Region. A monitoring programme needs to be developed for the sampling of the same plant species using standardized sampling and analytical methods for the maximization of the comparability of data. Since the vast area of the region, especially Nigeria, is highly mineralized most of the land area, rivers, ponds, lakes, etc. containing diverse flora and fauna may contain excessive amounts of trace elements which may be inimical to the environment, animal and human health. Since most of the plants incorporated in this study are widely distributed nationally and regionally, they could be sampled regularly with standardized sampling and analytical techniques to monitor the time-trend distribution of trace elements which may constitute environmental and animal and human health problems. For the determination of the food-chain linkage in the bioaccumulation of heavy metals, the goat-weed (Ageratum conyzoides) may serve a better purpose as an indicator of the distribution of Zn, Pb, and Cd. For biopurification purposes, Imperata cylindrica and Bryophyllum pinnatum may suffice. For biological locating of ores, Discorea bulbifera could be useful.

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REFERENCES

Bowen HJM (1979) Environmental chemistry of the elements. Academic Press, London.

Brooks RR (1983) Biological methods of prospecting for minerals. Wiley.

Cannon HL (1971) The use of plant indicators in ground water surveys, geologic mapping, and mineral prospecting. Taxon 20:227-256.

Edington JM & Edington MA (1977) Ecology and environmental planning. Chapman & Hall, London, p 64.

Ernst WHO (1990) Element allocation and (re)translocation in plants and its impact on representative sampling. In: Lieth H, Markert B (eds) Element concentration cadasters in ecosystems - methods of assessment and evaluation. VCH Verlagsgesellschaft mbH, D-6940 Weinheim (F.R.G.), pp 17-40.

Jones JB (1972) Plant tissue analysis for micronutrients. In: Mortvedt JJ, Giordano PM, Lindsay WL (eds) Micronutrients in agriculture. Soil Sci Soc Amer Inc, Madison, Wisc, p. 319.

Kabata-Pendias A & Pendias H (1984) Trace elements in plants and soils, CRC Press, pp 315.

Kabata-Pendias A & Dudka S (1990) Evaluating baseline data for cadmium in soils and plants in Poland. In: Lieth H. Markert B (eds) Element concentration cadasters in ecosystems - methods of assessment and evaluation. VCH Verlagsgesellschaft mbH, D-6940 Weinheim (F.R.G.), pp 265-280.

Kloke A, Sauerbeck DR, & Vetter H (1984) The contamination of plants and soils with heavy metals and the transport of metals in terrestrial food chains. In: Nriagu J O (ed) Changing metal cycles and human health, Dahlem Konferenzen, pp 113-141.

Kovalevskiy AL (1979) Biogeochemical exploration for mineral deposits. Amerind Publ. Co. Pvt, Ltd., New Delhi, p 136.

Mathews H & Thornton I (1980) Agricultural implication of Zn and Cd contaminated land at Shipham, Somerset. In: Trace Subst. Environ. Health, vol. 14, Hemphill D D (Ed), University of Missouri, Columbia, Mo, p 478.

Nuorteva P (1990) Metal distribution patterns and forest decline. Seeking Achilles' heels for metals in Finnish forest bioeconoses. Publication of the Dept. of Environmental Conservation, University of Helsinki, No. 11.

Olade MA (1987) Dispersion of cadmium, lead and zinc in soils and sediments of a humid tropical ecosystem in Nigeria. In: Hutchinson TC, Meema KM (eds) Lead, mercury, cadmium and arsenic in the environment, Scope: 31, pp 303-313.

Petrunina NS (1974) Geochemical ecology of plants from the provinces of high trace element contents. In: Problems of Geochemical Ecology of Organisms, Izd. Nauka,

Moscow, p 57 (Ru).
Shacklette HT, Boerngen JG, Cahill JP, Rahill RL (1973) Lithium in surficial materials of the conterminous United States and partial data on cadmium. U.S. Geol Surv. Circ., 673:7.
Wagner G (1990) Variability of element concentrations in tree leaves depending on sampling parameters. In: Lieth H, Markert B (eds) Element concentration cadasters in ecosystems - Methods of assessment and evaluation. VCH Verlagsgesellschaft mbH, D-6940 Weinheim (F.R.G.), pp. 41-54.
Wagner G (1987) Entwicklung einer Methode zur groBräumigen Uberwachung der Umweltkontamination mittels standardisierter Pappelblattproben von Pyramidenpappeln (Populus nigra 'Italica') am Beispiel von Blei, Cadmium und Zink, Saarbrucken (Dissertation), pp 225.

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