

Heavy trace metals and macronutrients status in herbal plants of Nigeria

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Abstract

The concentration levels (ppm) of selected toxic trace metals (Fe, Mn, Cu, Pb and Zn) and macronutrients (Na, K, Mg and Ca), along with P, were estimated in some of the important herbal plants of the southwest part of Nigeria. The atomic absorption spectrophotometer was employed for the estimation conducted on 10 plant species collected from different locations within Ogbomosho. The plants were *Anacardium occidentale*, *Azadirachta indica*, *Butyrospermum paradoxum*, *Mangifera indica*, *Morinda lucida*, *Ocimum canum*, *Solanum erianthum*, *Solanum torvum*, *Zingiber officinale* and *Hyptis suaveolens*. The metal contents in the samples were found at different levels. The highest mean levels (ppm) of Zn (35.1 ± 0.01) and Cu (24.4 ± 0.01) were found in *Hyptis suaveolens* while those of Mn (685 ± 0.02) and Ca ($51\,340 \pm 21$) were found in *Morinda lucida*. The result also showed that *Ocimum canum* had the highest amounts of K ($36\,600 \pm 350$), P (3700 ± 35) and Fe (241 ± 0.05). *Anacardium occidentale* had the highest concentration of Na (613 ± 0.60) while *Azadirachta indica* had the highest mean concentrations of Pb (0.49 ± 0.03) and Mg (5630 ± 12).

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1. Introduction

The human body requires a number of minerals in order to maintain good health. A number of minerals essential to human nutrition are accumulated in different parts of plants as it accumulates minerals essential for growth from the environment and can also accumulate metals such as Cd, Co and Ag which are of no known direct benefit to the plant (Dushenkov, Kumar, Motto, & Raskin, 1995). It has been reported that traces of Cd and Pb can be detected in all plants and food-stuffs (Piscator, 1985; Sherlock, 1983). Recently, plant species have been identified that contain nutrients displaying new beneficial medicinal or therapeutic properties (Fahey, Zhang, & Talalay, 1997; Mark, Michael, Jianwei, & Christopher, 2000).

Medicinal plants play an important and vital role in traditional medicine and are widely consumed as home remedies. The past decade has seen a significant increase in the use of herbal medicine due to their minimal side effects, availability and acceptability to the majority of the populace of third world countries. Consumption contributes to the intake of minerals (essential and non essential) by infants and elderly people. Numerous medicinal plants and their formulations are used for treating diseases in ethno-medical practices as well as in traditional systems of medicine in Nigeria. Environment, pollution, atmosphere, soil, harvesting and handling are some of the factors, which play an important role in contamination of medicinal plants by metals and microbial growth. Trace elements have both a curative and a preventive role in combatting diseases. It is therefore of major interest to establish the levels of some metallic elements in common herbal plants because, at elevated levels, these metals can also be dangerous and toxic (Schumacher, Bosque, Domingo, & Corbella,

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1991; Somers, 1974). The World Health Organization (WHO, 1992), in a number of resolutions, has also emphasized the need to ensure the quality control of plant products by using modern techniques and applying suitable standards. Thus the analytical control of metals in plants especially medicinal plants, is part of quality control, which should establish their purity, safety and efficacy.

Several attempts have been made at determination of the metal contents of herbal, medicinal, and aromatic plants from other parts of the world (Abou-Arab, Kawther, El Tantawy, Badeaa, & Khayria, 1999; Chizola & Franz, 1996; Kaneez, Shirin, Qadiruddin, Kalhor, & Badar, 2000; Kaneez, Qadiruddin, Kalhor, Shirin, & Badar, 2001; Lavilla, Fulgueiras, & Bendicho, 1999; Majid, Sarmani, Yusoff, Wei, & Hamzah, 1995; Parman, Gupta, Jha, & Verma, 1993; Vartika, Poonam, Sayyada, Rawat, & Shantan, 2001), but reports are scanty with respect to such plants endemic to Nigeria. It was therefore imperative to explore the present status of local herbal plants in terms of selected heavy trace metals (Fe, Mn, Cu, Pb and Zn) and macronutrients (Na, K, Mg and Ca) along with P.

2. Materials and methods

2.1. Grinding

A 3379-k20 Wiley mill (Thomas scientific, USA), equipped with a 0.50 mm diameter sieve and stainless steel container, was used for pulverization of the oven-dried plant materials.

2.2. Microwave oven

An Ausgang (vorsicht Hochspannung, Germany) high performance microwave system that could operate up to the power of 1200 W was used. The system was pressure programmed with the following stages; 0% for 5 s; 10% for 1 min; 0% for 1 min; 30% for 5 min; vent for another 5 min.

2.3. Digestion vessel

The acid digestions of plants were carried out in Teflon PFA vessels. The vessels consists of vessel bodies, vessel caps, safety valves and venting nuts.

2.4. Atomic absorption spectrophotometer

An Analysengerate GmbH model 200A (Buck Scientific, Germany) was used for metal determination, with Cathodeon (England) hollow cathode lamps for Zn, Mn, K, Mg, Ca; Buck Scientific hollow cathode lamps of Cu, Na and Pb, and Fischer Scientific hollow cathode

lamp for Fe, used as radiation sources. The elements were measured under the optimum operating conditions with an air-acetylene flame. Phosphorus levels of the plant samples were determined by colorimeter at 630 nm.

2.5. Ultra pure water machine

An Elga (model—Elgastat UHQ MKII, England) ultra pure water machine was used to generate the ultra pure water for dilution. Distilled water was used to generate the ultra pure water.

2.6. Reagents

The concentrated acids, HClO₄ (BDH Laboratories Supplies, England) and HNO₃ (GFS Chemicals, Inc. Columbus) used were of analytical reagent grade. The ultra pure water, which was generated as stated above, was used during the course of the experiment.

Stock standard solutions of Zn, Cu, Fe, Mn, Na, Pb, K, Mg, Ca, and P containing 1000 ppm of each metal, were used. Calibration standards of each element were obtained by appropriate dilution of the stock solutions.

2.7. Sample treatment

Ten different herbal plant samples were used in this investigation. The samples were harvested at different locations within Ogbomoso town in September 2000. The plants were authenticated by Mr. T.K. Odewo of the Herbarium headquarter, Forestry Research Institute of Nigeria (FRIN), Ibadan, where voucher specimens were kept. The identities, as well as the medicinal properties, of the plant samples under investigation are shown seen in Table 1.

The samples were washed with deionized water and allowed to dry in moisture extraction oven for 48 h at a temperature of 65 °C. The samples were then ground with a Wiley mill for a time between 2 and 5 min and sieved through a 0.5 mm diameter sieve supplied with the mill. The pulverized and powdered plant samples were stocked in paper sample bags inside desiccators before analysis.

2.8. Digestion of the samples

The wet-ashing microwave-assisted method was employed for the digestion procedure described below. From 0.4 to 0.45 g of the powdered plant samples were weighed into the Teflon PFA vessels and treated with 5 ml (2:1) of 69.4% w/w HNO₃ and 70.0% w/w HClO₄. The vessels was covered with a lid and screw cap; the contents of each vessel were arranged in the turntable and put into the microwave oven for digestion in a pre-selected programme (one stage at 0% for 5 s; two stages

of 60 s each at 10% and 0%, one stage at 30% of 300 s; and a final stage, vented for 300 s). 25 ml of ultra pure water were added to each of the samples and the samples were transferred to vials.

2.9. Analytical procedure

Three sub-samples of each material were digested using the above method. All measurements were run in triplicate for the sample and standard solutions.

3. Results and discussion

A total of 10 elements (i.e. Zn, Cu, Fe, Mn, Na, Pb, K, Mg, Ca, and P) were determined in the powdered medicinal plant samples by atomic absorption spectrophotometry (AAS). Table 2 shows the mean concentrations of various metals, in the herbal plants. From the study, it was revealed that all the metals were accumulated to greater or lesser extents by all 10 plant species studied. Elemental studies of the plants showed that they contained large amounts of nutrients and were rich in Mg, Ca, Na and K. The Zn concentrations varied from 3 to 35 ppm, most samples having contents between 16 and 35 ppm. *M. indica* had the lowest Zn concentration and *H. suaveolens* the highest. The con-

centrations of Zn were comparable in *A. occidentale* and *M. indica* with a range of 3.24–3.31 mg/l, the same being true for *M. lucida* and *Z. officinales* at 33.6 and 33.3 ppm. Cu concentrations varied from 1 to 24 ppm, with values frequently in the range 10–24 ppm. *A. indica* had the lowest Cu concentration and *H. suaveolens* had the highest. As Cu and Zn are considered micronutrients, the WHO limits for these metals have not yet been established. According to Bowen (1966) and Allaway (1968), the range of the elements in agricultural products should be between 4 and 15 ppm for Cu and 15–200 ppm for Zn. After comparison of the metal limits in the studied plants with those proposed by these authors, it was found that *M. lucida*, *S. erianthum* and *H. suaveolens* accumulated Cu metal beyond these ranges. However, the Zn concentrations of all the samples were found to be within the range.

The Fe concentrations varied from 36 to 241 ppm, with values frequently 121–188 ppm. *A. occidentale* had the lowest Fe concentration while *O. canum* had the highest. The Mn concentration level ranged from 32 to 685 ppm, most samples having contents from 32 to 90 ppm. *B. paradoxum* had the lowest Mn concentration whereas *M. lucida* had the highest. The Na concentration levels ranged from 44 to 614 ppm, four samples having concentrations ranging from 43 to 79 ppm, three samples in the range 110–175 ppm and the others in the

Table 1
Herbal plants under investigation; name, parts studied and medicinal properties

Plant species	Local name	Part used	Medicinal properties
<i>A. occidentale</i>	Kaju	Stem bark	Astringent, dysentery, antibacterial
<i>A. indica</i>	Dogonyaro	Leaves	Anti-inflammatory
<i>B. paradoxum</i>	Emi	Leaves	Malaria, ulcer
<i>M. indica</i>	Mangoro	Leaves	Astringent, malaria
<i>M. lucida</i>	Oruwo	Stem bark	Yellow-fever, antibacterial
<i>O. canum</i>	Curry	Leaves	Asthma, febrigue
<i>S. erianthum</i>	Ewuro-Ijebu	Leaves	Cancer, malaria
<i>S. torvum</i>	Ewuro elegun	Leaves	Ulcer, malaria
<i>Z. officinales</i>	Atale	Rhizome	Rubefacient, ulcer
<i>H. suaveolens</i>	Ore-eefon	Leaves	Carminative, stomachic.

Table 2
Result of the Metal contents from the analysed samples (ppm)^a

Plants	Zn	Cu	Fe	Mn	Na	Pb	K	Mg	Ca	P
<i>A. occidentale</i>	3.31±0.02	2.96±0.01	35.6±0.02	89.9±0.03	613±0.60	0.44±0.02	6380±25	1540±26	6103±15	100±2
<i>A. indica</i>	15.7±0.01	1.12±0.01	188±0.10	46.5±0.04	138±0.60	0.49±0.03	19220±55	5630±12	3543±15	900±10
<i>B. paradoxum</i>	8.87±0.01	10.3±0.01	96.1±0.05	31.7±0.06	544±0.03	0.21±0.02	8170±16	5380±10	21850±40	300±15
<i>M. indica</i>	3.24±0.01	3.07±0.01	46.6±0.01	133±0.06	43.6±0.03	0.29±0.03	7470±15	1372±9	18810±11	100±4
<i>M. lucida</i>	33.6±0.01	16.5±0.01	122±0.02	685±0.02	176±0.97	0.35±0.01	13100±101	5470±59	51340±21	598±8
<i>O. canum</i>	30.8±0.01	15.1±0.01	241±0.05	51.3±0.04	111±1.18	0.33±0.02	36600±350	3230±14	32420±52	3700±35
<i>S. erianthum</i>	24.2±0.01	21.7±0.01	178±0.05	34.1±0.02	79.6±0.31	0.31±0.02	28750±51	3160±9	7280±30	3400±15
<i>S. torvum</i>	23.4±0.01	13.9±0.02	208±0.03	48.7±0.06	78.7±0.49	0.34±0.02	31550±102	2460±70	11390±20	3101±5
<i>Z. officinales</i>	33.3±0.01	14.4±0.01	144±0.05	413±0.70	322±2.00	0.26±0.04	25280±113	4210±10	2610±10	1803±15
<i>H. suaveolens</i>	35.1±0.01	24.4±0.01	142±0.10	39.4±0.30	72.5±0.05	0.28±0.02	18260±233	4780±100	19780±8	1200±27

^a Average Concentration±Standard deviation ($n=3$) (ppm) (mg/l).

range 322–613 ppm. *M. indica* had the lowest Na concentration whereas *A. occidentale* had the highest. The K concentrations were 6380–36 600 ppm, most samples being in the range 13 000–36 600 ppm. *A. occidentale* had the lowest K concentration whereas *O. canum* had the highest. Mg concentrations varied from 1370 to 5470 ppm, most samples having concentrations between 3200 and 5500 ppm. *M. indica* again, had the lowest Mg concentration whereas *M. lucida*, had the highest. The Ca concentrations varied from 2610 to 51 340 ppm, most samples being in the 11 390–51 350 ppm range. *Z. officinales* had the lowest Ca concentration and *M. lucida* had the highest. Finally, the P concentrations were in the range 100–3700 ppm, five samples having concentrations from 100 to 1000 ppm, and the rest from 1100 to 3800 ppm. *A. occidentale* and *M. indica* had the lowest P concentration whereas *O. canum* had the highest.

The results above indicated that the herbal plants contain large amounts of nutrients and are rich in Fe, Mg, Ca, Na, K and P. The abundance of K, Mg and Ca, in the result of this analysis, was in agreement with previous findings that these three metals represent the most abundant metal constituents of many plants (Chizzola & Franz, 1996; Lavilla et al., 1999).

The Pb concentration levels ranged from 0.2 to 0.5 ppm, most samples having values in the 0.2–0.3 ppm range. *B. paradoxum* had the lowest Pb concentration while *A. indica* had the highest. The concentrations of Pb were comparable in *A. occidentale* and *A. indica* (range 0.44–0.49 ppm) and, similarly, between *B. paradoxum*, *M. indica*, *Z. officinales* and *H. suaveolens* in a range 0.21–0.29 ppm, the same being true for *O. canum*, *M. lucida*, *S. erianthum* and *S. torvum*, in a range of 0.31–0.35 ppm. According to the WHO, the permissible limit for medicinal plants, based on ADI (Acceptable Daily Intake) for Pb, is 10 ppm. The herbal plants under investigation accumulated this metal at a level appreciably below the permissible level.

Differences of metal concentration in plants from different sites are related to the condition from where the samples are collected. Though much is known about the functional role of a number of elements, the best foreseeable benefit for human health, by mineral nutrition, lies in obtaining the correct amount of supplementation in the right form at the right time. Parman et al. (1993) showed that the medicinal values of some plant species used in homoeopathic system may be due to the presence of Ca, Cr, Cu, Fe, Mg, K and Zn. According to Hooker (1987), Cr, Mg and Zn have important roles in the metabolism of cholesterol as well as heart diseases. The presence of Cr and Mn in plants may be correlated with therapeutic properties against diabetic and cardiovascular diseases (Perry, 1972). Deficiency or excess of Cu, Mn, Zn, Cr, Ca, Mg and K may cause a number of disorders (Ahmed, Rahman, Qadiruddin, & Badar, 1994). These elements also take part in neurochemical

transmission and also serve as constituent of biological molecules, as a cofactor for various enzymes and in variety of different metabolic processes (Mayer & Vyklicky, 1989).

In view of the above facts, the medicinal plants studied are a source of biologically important elements, which may play a part in the observed therapeutic properties of these plants. Hence it is expected that plants with high concentrations of the above-mentioned macro and micronutrients, which in most cases are present in permissible levels, might play an important role in maintenance of human health. According to Schwart and Mertz (1952), Curran (1954) and Schroeder (1965), wide applications of the medicinal benefits of these trace elements have been limited, due to insufficient work regarding the detection and estimation of trace elements of the God-gifted flora spread all over the earth. Thus, it is imperative to analyze the plants for their trace element contents, which have healing power for mankind in numerous ailments and disorders. From the present study, it was revealed that the detection of metal accumulation is highly relevant for the assessment of herbal drugs quality. This study has illustrated metal accumulation in various herbal plants used in traditional healing system in southwest Nigeria.

The continuity of such research endeavours, in terms of periodical assessment of these and other metal concentration in all the known herbal plants used in traditional medicine, would go a long way toward predicting the quality assurance and safer use of herbal products. The present work will be useful in this regard.

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References

- Abou-Arab, A. A. K., Kawther, M. S., El Tantawy, M. E., Badaea, R. I., & Khayria, N. (1999). Quantity estimation of some contaminants in commonly used medicinal plants in the Egyptian market. *Food Chemistry*, 67, 357–363.
- Ahmed, S., Rehman, A., Qadiruddin, M., & Badar, Y. (1994). Elemental analysis of a herbal drug Intella, a neuroenergiser. *Journal of Faculty of Pharmacy, Gazi University, Turkey*, 2(1), 83–90.
- Allaway, W. H. (1968). Agronomic controls over environmental cycling of trace elements. *Advance Agronomy*, 20, 235–274.
- Bowen, H. J. M. (1966). *Trace elements in biochemistry*. New York: Academic Press.

- Chizzola, R., & Franz, Ch. (1996). Metallic trace elements in medicinal and aromatic plants from Austria. *Journal of Applied Biology*, 70, 52–56.
- Curran, G. L. (1954). Effect of certain transition group elements on Hepatic synthesis of cholesterol. *Journal of Biological Chemistry*, 210, 765–770.
- Dushenkov, V., Kumar, P. B. A. N., Motto, H., & Raskin, I. (1995). Rhizofiltration: the use of plants to remove heavy metals from aqueous streams. *Environmental Science and Technology*, 29, 1239–1245.
- Fahey, J. W., Zhang, Y., & Talalay, P. (1997). Broccoli sprouts: an exceptionally rich source of inducers of enzymes that protect against chemical carcinogens. *Proceedings of the National Academy of Science, USA*, 94, 10367–10372.
- Hooker, J. D. (1982). *The flora of British India* (Vol. III, p. 640). Reeve and Co.
- Kaneez, F. A., Shirrin, K., Qadiruddin, M., Kalhor, M. A., & Badar, Y. (2000). Essential elements in different parts of Kasni (Cichoriumintybus). *Pakistan Journal of Scientific and Industrial Research*, 43(5), 283–284.
- Kaneez, F. A., Qadiruddin, M., Kalhor, M. A., Shirrin, S., & Badar, Y. (2001). Determination of major and trace elements in Artemisia elegantissima and Rhazya stricta and their relative medicinal uses. *Pakistan Journal of Scientific and Industrial Research*, 44(5), 291–293.
- Lavilla, I., Filgueiras, A. V., & Bendicho, C. (1999). Comparison of digestion methods for determination of trace and minor metals in plant samples. *Journal of Agricultural and Food Chemistry*, 47(12), 5072–5077.
- Majid, A. Ab., Sarmani, S., Yusoff, N. I., Wei, Y. K., & Hamzah, F. (1995). Trace elements in Malaysian Medicinal plants. *Journal of Radionanalytical Nuclear Chemistry Articles*, 195, 173–183.
- Mayer, M. L., & Vyklicky, L. (1989). The action of Zinc on synaptic transmission of mouse neuronal excitability in culture of mouse hippocampus. *Journal of Physiology*, 415, 351–365.
- Mark, P. E., Michael, J. B., Jianwei, W. H., & Christopher, D. G. (2000). Plants as a natural source of concentrated mineral nutritional supplements. *Food Chemistry*, 77, 181–188.
- Parman, V. S., Gupta, A. K., Jha, H. N., & Verma, P. N., et al. (1993). Metal content of the medicinal plants Agave marianum, Sambucus nigra and Silybum marianum. In R. Vartika, K. Poonam, K. Sayyada, A. K. S. Rawat, & M. Shantan (Eds.), *Heavy metal accumulation in some herbal drugs. Pharmaceutical Biology*, 39(5), 384–387.
- Perry, H. M. (1972). *Hypertension and true geochemical environments in relation to health and diseases*. New York: Academic Press.
- Piscator, M. (1985). Dietary exposure to Cd and health effects: Impact of environmental changes. *Environmental Health Perspectives*, 63, 127–132.
- Schroeder, H. (1965). Influence of Cr, Cd and Pb on rat aortic lipids and circulating cholesterol. *American Journal of Physiology*, 209, 433.
- Schumacher, M., Bosque, M. A., Domingo, J. L., & Corbella, J. (1991). Dietary intake of lead and cadmium from foods in Tarragona Province, Spain. *Bulletin of Environmental Contaminant and Toxicology*, 46, 320–328.
- Schwartz, K., & Mertz, W. (1952). Prevention of respiratory decline in neurotic liver degeneration by antioxidant. *Archives of Biochemistry and Biophysics*, 85, 292.
- Sherlock, J., Smart, G. A., & Walters, B. (1983). Dietary surveys on a population at Shipham, Somerset, United Kingdom. *Science Total Environment*, 29, 121–142.
- Somers, E. (1983). The toxic potential of trace metals in foods. A review. *Journal of Food Science*, 39, 215–217.
- Vartika, R., Poonam, K., Sayyada, K., Rawat, A. K. S., & Shantan, M. (2001). Heavy metal accumulation in some herbal drugs. *Pharmaceutical Biology*, 39(5), 384–387.
- WHO. (1992). *Expert committee on specification for pharmaceuticals preparation*. Report Geneva WHO 32 (pp. 44–52, 75–76). WHO technical report series 823.