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Estimation of Some Heavy Metals and Physico-Chemical Parameters in Selected Herbs Sold in Old Market Area, Sokoto-Nigeria

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Abstract
The emerging global significance and faster rate of increase in interest on herbal drugs for treating various illnesses cannot be underestimated. This coupled with the associated health risk posed by these drugs due to hazardous metal contamination, gives credence to concerns raised by health conscious people. This study was aimed at determining the levels of heavy metals (Cr, Cd, Mn, Cu, Fe, Pb, Zn and Ni) concentration in selected crude medicinal plants sold in old market, Sokoto-Nigeria. The physico-chemical parameters were determined using standard analytical methods and the heavy metals were determined using Atomic Absorption Spectrophotometry (AAS) after wet digestion. The results show that moisture, total ash and acid insoluble ash were in the range of 3.33 – 5.67 %, 9.5 – 17.3 % and 1.4-7.2 % respectively. Also, the samples revealed maximum concentrations (mg/Kg) of the heavy metals in the samples as: 0.112±0.002, 0.038±0.001, 18.136±0.001, 0.218±0.001, 15.138±0.001, 0.943±0.001, 0.577±0.001 and 0.237±0.001 for Cr, Cd, Mn, Cu, Fe, Pb, Zn and Ni respectively. The herbs demonstrated good preservative condition but with relative silica contamination, while the levels of all the metals were found to be within the World Health Organization (WHO) limits for heavy metals in plant samples. The exception was for chromium (Cr) in *Guiera senegalensis,* leaves; as well as for manganese (Mn) in *Cassia singueana, Guiera senegalensis, Combretum micranthum, Anogeissus leiocarpus* and *Detarium microcarpum*; *D Senegalense.* It is therefore, suggested that the quality, safety and efficacy of these medicinal plants be improved through pharmacovigilance.
Keywords: Heavy Metals, Herbal Plants, Physico-chemical and Old market

1. Introduction

Herbs or Herbal drugs play a very important role in the health care delivery systems of many countries. The World Health Organ

ization (WHO) estimates that eighty percent (80%) of the world's population depends on non-conventional medicines mainly of herbal origin for their primary health care needs (Chan, 2003). Herbal medicine enjoys a wider acceptability among people probably because it blends readily and is deeply rooted into the socio-cultural life of the people. It's relatively low cost when compared to allopathic drugs, coupled with the usual difficulty in accessing health care facilities could be the driving forces behind the heavy reliance on herbal drugs by many people for treatment of their sicknesses. Also herbal medicine was the only form of health care available before the advent of modern medicine. Presently, even people close to hospitals consult traditional healers employing herbal drugs as a first choice (Maclean, 1971). Drew and Myers (1997) noted that there has been an increasing growth in popularity of herbal drugs usage in many countries. A reflection of this in local context such as in Nigeria is the upsurge in the advertisement and sale of herbal drugs in both electronic and print media. The advertisers claim and stress that herbal drugs are 'natural', safe with no toxic effects.

These herbal drugs may likely be contaminated with various substances including banned pesticides, microbes, unknown concentrations of heavy metals and chemical toxins. Heavy metals contamination of herbal drugs could result from employing medicinal plants grown or collected from sites where pesticides, herbicides and other harmful agrochemicals were applied to the soil (Chan, 2003). The plants may also absorb these harmful substances from the environment and store them in their tissues. Other sources of herbal drugs contaminations include water contaminated with heavy metals used in preparation of the drugs, and the use of utensils containing metals such as lead, copper and aluminum during manufacture: holding, cooking and storage of the herbal drugs. According to Gaur and Adholeya (2004), some heavy metals are micronutrients necessary for plant growth while others have unknown biological functions.

Heavy metals are defined as those groups of elements that have specific weights higher than 5 g/cm^3. A number of them (Co, Fe, Mn, Mo, Ni, Zn and Cu) are essential micronutrients and are required for normal growth and other important metabolic processes in plants. Metals which are considered non essential (Pb, Cd, Cr, Hg, etc.) are potentially highly toxic (Sebastiani and Scebbaf, 2004; Rama and Prasad, 1998; Rai et al., 2004).

The aim of this research was to estimate the physico-chemical parameters and level of some heavy metals in the selected herbal plants sold in old market, Sokoto-Nigeria and to assess the compliance or other wise of these heavy metals with standard limits.

2. Materials and Methods

2.1Chemicals and equipment

Chemicals of analytical grade were used; nitric acid (HNO_3), sulphuric acid (H_2SO_4) from M&B and perchloric acid ($HClO_4$), hydrochloric acid (HCl) from BDH. Standard solutions of the metals under investigation were from the Manufacturers Atomic Absorption spectrometer (AAS) machine used. Major instruments used were the AAS (240FS model, GCB Scientific Ltd.) and Muffle furnace (Lenton furnace 91E from Eurotherm, U.K)

2.1 Sampling and sample Preparation

The sampling was carried out in the month of May, 2015. The samples were collected at the old Market area within the Sokoto metropolis. The position of the market in the metropolice is shown in Figure 1.

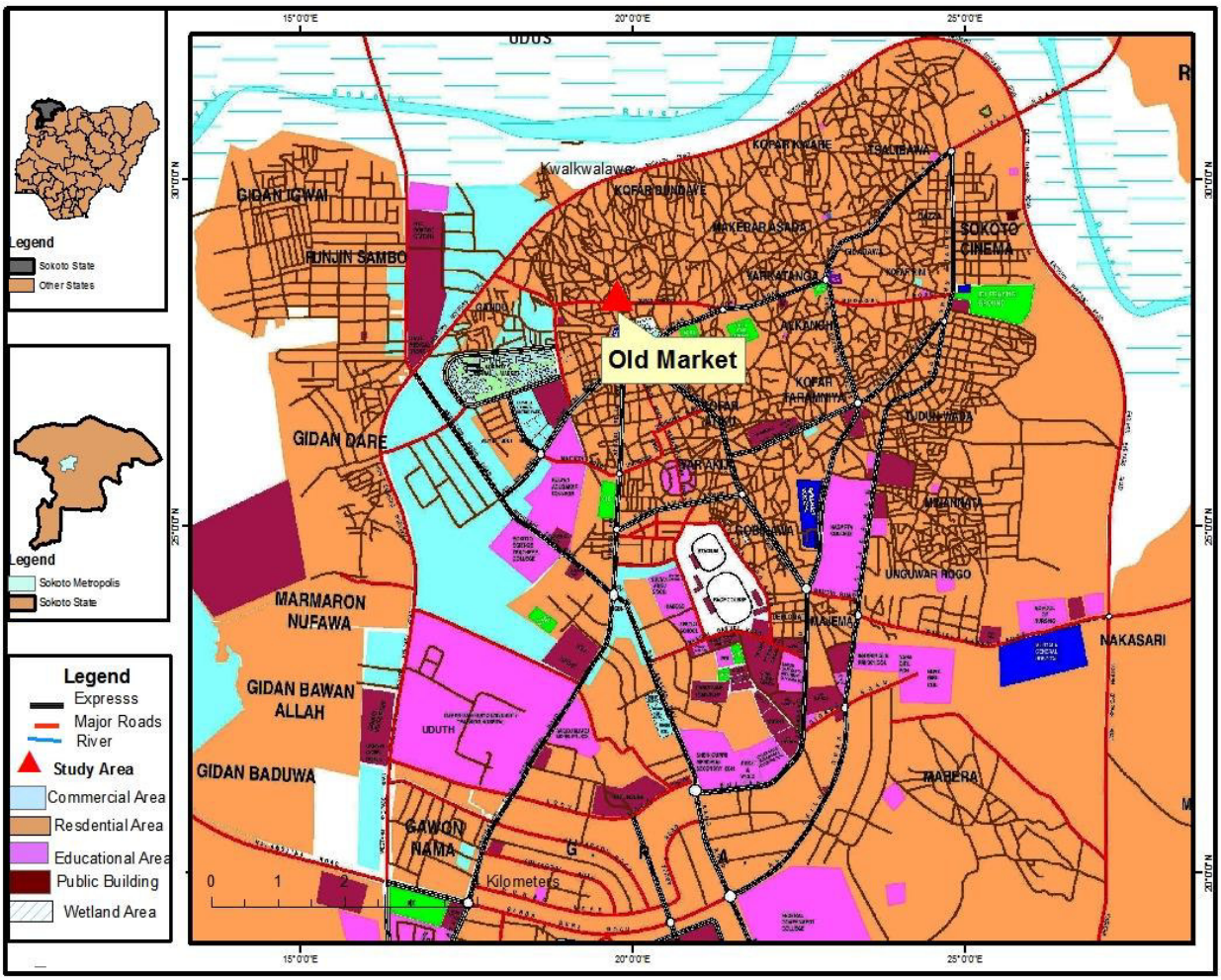

Figure 1: Study Area (Source: Geography Dept., UDUS)

The Figure above (Map of the study area) shows the relative position of the Sokoto province city or State within Nigeria; and the expanded part of the state indicated the position of the sampling area. The old market is a commercial centre in the metropolis where marketing of various traditional materials including medicinal plants relating to the culture of Sokoto people from near and far takes place. Ten (10) samples (5 leaves and 5 barks) were collected in polyethylene bags from this market. The plant parts (leaves, flowers and fruits) were also collected for identification purpose.

Table 1: Medicinal plants, parts used and their Identity

S/N	Scientific Name	local Name	Code	Plant Part used	Voucher No.
01	*Cassia singueana*	Runhu	RH	Leaves	PCG/UDUS/Legu/0001
02	*Guiera senegalensis*	Sabara	SB	Leaves	PCG/UDUS/Comb/0002
03	*Combretum micranthum*	Geza	GZ	Leaves	PCG/UDUS/Legu/0002
04	*Senna italic*	Fulasko	FK	Leaves	PCG/UDUS/Caes/0002
05	*Anogeissus leiocarpus*	Marke	MK-L	Leaves	PCG/UDUS/Comb/0001
06	*Boswellia dalzielli*	Hanu	HN	Bark	PCG/UDUS/Burs/0001
07	*Cassia arereh*	Malga	MG	Bark	PCG/UDUS/Caes/0001
08	*Prosopis africana*	Ƙirya	ƘY	Bark	PCG/UDUS/Legu/0003
09	*Anogeissus leiocarpus*	Marke	MK-B	Bark	PCG/UDUS/Comb/0001
10	*Detarium microcarpum*; *D. Senegalense*	Taura	TR	Bark	PCG/UDUS/Legu/0004

The plant herbs were identified as shown in Table 1 by a Consultant Taxonomist in the Department of Pharmacognosy and Ethnopharmacy, Faculty of Pharmaceutical Sciences, Usmanu Danfodiyo University, Sokoto. Voucher specimens of the plant samples were prepared and voucher numbers were assigned and deposited at the Herbarium of the Department for future reference. The Table also, indicated the plant's scientific names, the local names, codes used for easy identification and the specific part of each plant sample used in this study. The choice of these set of plant samples and parts was purely based on frequent traditional use of the plant parts in the area for various medicaments. All the samples were collected in coarse and powdered forms and were all grounded and sieved separately to very fine particles from which representative samples were quantitatively taken for different determinatons.

2.3 Determination of Moisture Content

The sample (3g) was weighed into a pre-weighed crucible and placed into hot drying oven at 105^0C for 24 hours. The sample was later removed, cooled and placed in desiccators for some time and weighed again to constant weight (James, 1995). The weight lost due to moisture was obtained using this equation

$$\% \text{ Moisture Content} = \frac{W_1 - W_2}{W_1 - W_0} \times 100 \quad \ldots\ldots(1)$$

Where W_0 = Weight of empty crucible
W_1 = Weight of fresh sample
W_2 = Weight of dried sample

2.4 Determination of Total Ash Value

The sample (3g) was weight into pre-weighed crucible and placed in Lenton Furnace at 600^0C for three hours. The sample was cooled in desiccators and weighed. The weight of the ash was determined by the difference between the dried sample, pre-weighed crucible and the ash sample in the crucible. This is obtained as percentage of the initial dry weight of the sample. The percentage ash was calculated using this equation

$$\% \text{ Ash Value} = \frac{W_2 - W_0}{W_1 - W_0} \times 100 \quad \ldots\ldots(2)$$

Where W_0 = Weight of empty crucible
W_1 = Weight of crucible + dry sample
W_2 = Weight of crucible + ash sample

2.5 Determination of Acid Insoluble Ash

The ash obtained from total ash determination was boiled for 5 min. with 25 cm^3 of 10 % dilute hydrochloric acid. The insoluble matter was collected on an ash-less filter paper and washed with hot water and ignited to constant weight. The percentage of acid insoluble ash was calculated with reference to the dried total ash.

2.6 Digestion of Samples and Analysis

Wet ashing technique was used for the digestion of the samples for the analysis of specific process minerals (Miller-Ihli and Baker, 2000). The process was carried out by taking 1.00 g of each of the prepared sample into separate digestion tubes. Then 20.00 cm^3 of 69.5 % concentrated HNO_3 acid was added and heated in a tecator digestion block until about one third of each of the content is left. This was followed by the addition of another 10 cm^3 of the concentrated HNO_3 and 2.00 cm^3 of 60 % $HClO_4$ acids and the heating process continued until clear solutions were obtained. The digests were each diluted with about 20 cm^3 of double distilled water and boiled for another 15 minutes. The contents were allowed to cool and further transferred into 50 cm^3 volumetric flasks. These were all made to their marks with double distilled water. The solutions were then filtered using

Whatman No. 42 filter paper into separate screw capped polyethylene bottles (Audu and Lawal, 2006; Daniel, 2003). Similarly, the blank sample solution was prepared in the same way.

The concentrations of Cr, Cd, Mn, Cu, Fe, Pb, Zn and Ni in the digests of the medicinal plants were determined by using the hollow cathode lamps for the respective elements at the proper wave length and slit width (0.5nm) atomic absorption spectrophotometer (Model No. AA240FS, Varian). The flame type used for all the elements was air-acetylene.

2.7 Statistical data analysis

The heavy metal concentrations in the digests of the herbal plants were presented as mean ± standard deviation (SD). The data were analyzed by one-way analysis of variance (ANOVA), taking probability factor of 0.05 and the software used was Statistical Package for Social Sciences (SPSS) V.15.

3.0 Results and Discussions

Table 2: Moisture, Ash and Acid insoluble ash in the samples

Samples	**M C (%)**	**A V (%)**	**A I A (%)**
Cassia singueana (leaves)	4.83±0.23	17.3±0.24	7.2±0.24
Guiera senegalensis (leaves)	3.33±0.24	9.8±0.62	4.0±0.16
Combretum micranthum (leaves)	4.0±0.41	9.5±0.41	5.5±0.24
Senna italic (leaves)	4.33±0.24	14.8±0.24	3.5±0.08
Anogeissus leiocarpus (leaves)	3.67±0.24	10.8±1.02	2.5±0.33
Boswellia dalzielli (bark)	4.17±0.24	14.0±0.41	1.5±0.08
Cassia arereh (bark)	5.50±0.41	12.2±0.62	1.4±0.66
Prosopis africana (bark)	4.33±0.24	13.0±0.41	2.0±0.08
Anogeissus leiocarpus (bark)	4.17±0.24	12.5±0.82	2.0±0.41
Detarium microcarpum; (bark)	5.67±0.24	11.0±0.82	3.0±1.23

Key: M C= Moisture Content, A V = Ash Value, A I A = Acid Insoluble Ash, Mean±SD

The results of the Physico-chemical parameters analyzed were presented in Table 2. The results indicated the moisture, the total ash value and the acid insoluble ash of the samples. The moisture content ranges from 3.33 – 5.67 %. The values relatively indicate low moisture in the herbs; low moisture in herbs prevents bacterial, fungal and yeast growth **(**African Pharmacopoeia, 1986**)**. The moisture contents were found to be similar to 4.26 % reported by Gite *et al.,* (2010) on evaluation of physicochemical parameters of *Enicostemma axillare*. These values were within and in agreement with the 10 % maximum limit for moisture content in powdered medicinal plants prescribed in European Pharmacopoeia (2007).

The total ash values of the samples were in the range of 9.5% – 17.3 % in *Combretum micranthum* (leaves) and *Cassia singueana* (leaves) respectively. Though, only *Cassia singueana* and *Senna italic* (all leaves) were not in agreement with the 14 % maximum limit for total ash value in powdered medicinal plants (European Pharmacopoeia, 2007), but almost 80 % of the samples were in conformity with the standard. The acid insoluble ash also ranges from 1.4 % in *Cassia arereh* (bark) to 7.2 % in *Senna italic* (leaves). Only 40 % of the total samples were in agreement with maximum 2 % of acid insoluble ash in powdered medicinal plants (European Pharmacopoeia, 2007). The total ash values of the samples were all within the standard limit. Total ash content is usually attributed to be due to relative content of the carbonates, phosphates, silicates and silica. Ash value is useful in determining authenticity and purity of drug and also these values are important quantitative standards (Kokate, 2006). Acid-insoluble ash is a part of total ash and measures the amount of silica present, especially as sand and siliceous earth (Evans, 2002). These ash values are important pharmacognostic tool to standardize the crude drugs.

Table 3: Concentration of Heavy Metals in the Samples

Sample	Concentration (mg/Kg)							
	Cr	Cd	Mn	Cu	Fe	Pb	Zn	Ni
RH (L)	ND	0.038±0.001	18.136±0.001	0.127±0.001	5.519±0.001	0.576±0.001	0.480±0.001	0.212±0.001
SB (L)	0.112±0.002	0.030±0.001	10.648±0.001	0.218±0.001	15.010±0.001	0.624±0.001	0.535±0.001	0.197±0.001
GZ (L)	ND	0.028±0.001	10.122±0.001	0.110±0.001	4.580±0.001	0.659±0.001	0.447±0.001	0.201±0.001
FK (L)	ND	0.027±0.001	4.598±0.001	0.136±0.001	7.100±0.001	0.707±0.001	0.500±0.001	0.062±0.001
MK(L)	ND	0.026±0.001	8.097±0.001	0.099±0.001	4.443±0.001	0.685±0.001	0.577±0.001	0.237±0.001
HN (B)	ND	0.023±0.001	4.417±0.001	0.062±0.001	4.939±0.001	0.766±0.001	0.318±0.001	0.083±0.001
MG (B)	0.039±0.001	0.029±0.001	8.871±0.001	0.042±0.001	4.328±0.001	0.736±0.001	0.385±0.001	0.157±0.001
KY (B)	ND	0.028±0.001	5.076±0.001	0.070±0.001	6.928±0.002	0.676±0.001	0.151±0.001	0.096±0.001
MK(B)	ND	0.027±0.001	10.775±0.001	0.066±0.001	15.138±0.001	0.943±0.001	0.164±0.002	0.107±0.001
TR (B)	ND	0.030±0.001	11.401±0.001	0.060±0.001	4.740±0.001	0.794±0.001	0.111±0.001	0.147±0.001

The results in Table 3 shows the concentrations of Cr, Cd, Mn, Cu, Fe, Pb, Zn and Ni in the samples,

with Mn having an overall concentration of 18.136±0.001 mg/Kg in *Cassia singueana* (leaves) and Cd the least (0.023±0.001 mg/Kg) in *Boswellia dalzielli* (bark). In this study, the concentrations of Cr, Cd, Mn, Cu, Fe, Pb, Zn and Ni in almost all the samples collected were within the WHO permissible limits. The exceptions were Chromium concentration (0.112mg/kg) in *Guiera senegalensis* (leaves) and manganese concentration in about 50 % of the total samples.

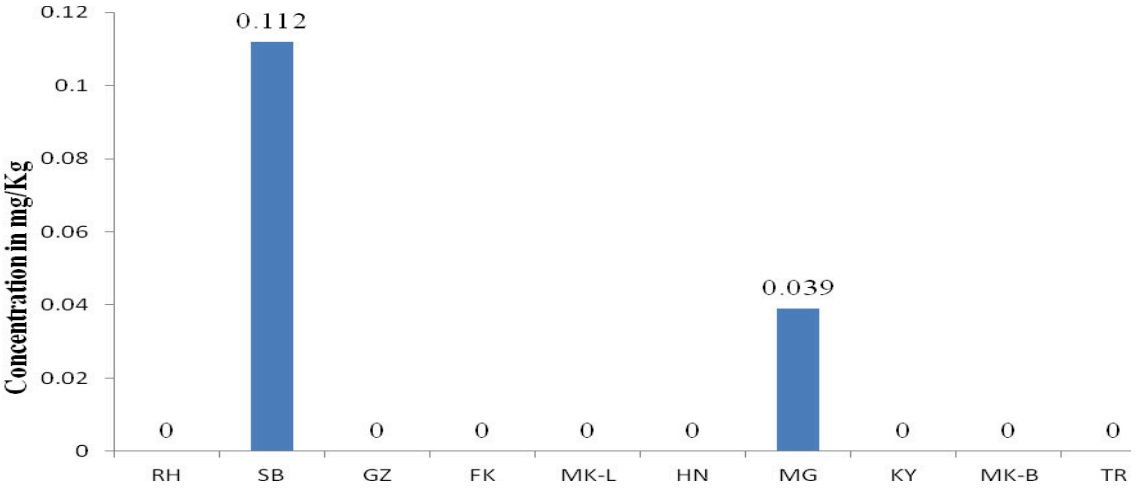

Figure: 2: Bar chart of Chromium concentrations in the samples

The bar chart (Figure 2), shows the relative chromium concentrations which was detected in only two samples; the leaves of *Guiera senegalensis* and the bark of *Cassia arereh* (0.039 mg/Kg). These amount though high (especially in *Guiera senegalensis* when compared to the sample array), is still much lower than 4.65 mg/Kg chromium reported by Shad *et al.,* (2008) on selected medicinal plants in Peshawar, Pakistan. However, lower values of chromium than observed here were also reported in literature; Umar *et al* (2014) reported 0.011 mg/Kg concentration of chromium in some medicinal plants commonly used in Kura Local Government Area of Kano State, Nigeria; which is tenfold lower than this work value. Significant differences in chromium (Cr) content at $p<0.006$ were not observed for plants parts used. The absence of chromium in majority of the samples may possibly be linked to its absorption and translocation profile which could be modified by soil pH, organic matter content and chelating agents, among others factors (Han *et al*., 2004).

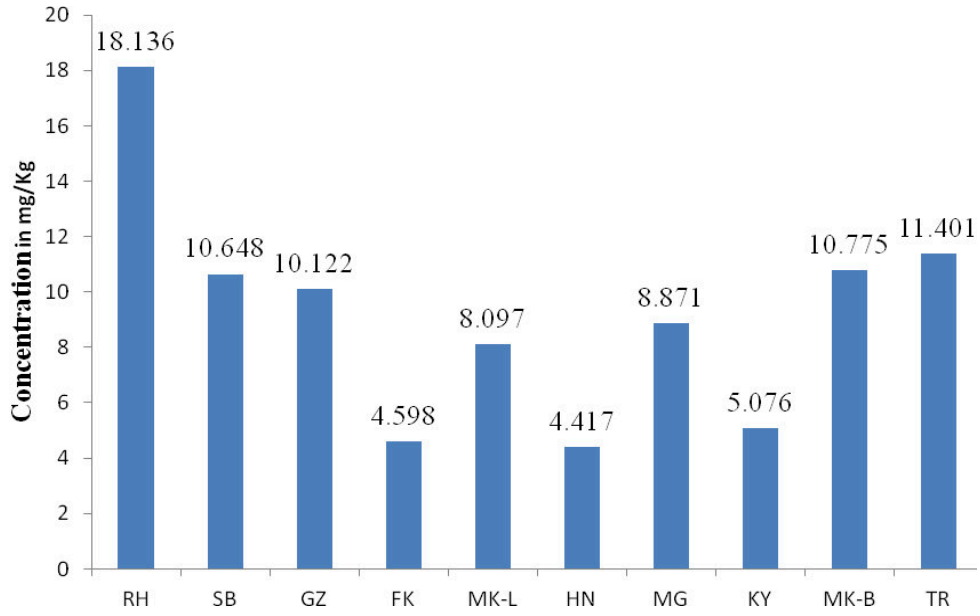

Figure: 3: Bar chart of Manganese concentrations in the samples

The Figure 3 illustrated the level concentration of Manganese to have slightly exceeded its 2 – 9 mg/Kg WHO daily allowable limit in 50 % of the total samples. However, the concentration (4.417 – 18.136 mg/Kg) is lower than 80.90 mg/Kg reported by Lasisi *et al.,* (2005). The result revealed a significant difference for magnesium among the plants at $p<0.006$ but no such difference for plant parts (between leaves and barks). Reason for the elevated manganese in some of the sample may not be so straight, but it has been shown that the

intake of manganese by plants increases in acidic soils (pH < 5.5) (Kabata-pendias and Pendias, 1999).

4. Conclusion

The plant herbs analyzed were found to be in good preservative condition but have also shown some level of contamination probably by silica material. The estimated heavy metals were below prescribed limits by world health organization (WHO) in almost all the samples. Some of these metals serve beneficial role as trace elements making the herbs additional sources of trace and microelements. While careful use of these herbs could be safe, prolong intake could be risk to the health of the users. It is therefore suggested that the quality, safety and efficacy of these herbal plants be improved through pharmacovigilance at different outlets.

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