Analysis of Heavy Metals in Selected Medicinal Plants from Dir, Swat and Peshawar Districts of Khyber Pakhtunkhwa

[1]IQBAL HUSSAIN*, [1]MUNEEB UR REHMAN KHATTAK, [1]FARHAT ALI KHAN, [2]INAYAT UR REHMAN, [1]FARMAN ULLAH KHAN AND [2]FARID ULLAH KHAN
[1]Department of Chemistry Kohat University of Science and Technology Kohat, Khyber Pakhtunkhwa.
[2]PCSIR labs Complex Jamrud Road Peshawar, Khyber Pakhtunkhwa.

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Summary: Essential and non-essential heavy metals like Manganese, Zinc, Iron, Nickel, Copper, Chromium, Lead and Cadmium were analyzed quantitatively in selected medicinal plants including, *Acorus calamus*, *Artemisia annua, Chenopodium foliosum, Cupressus arizonica,* Euphorbia helioscopia L, *Lepidium sativum, Nerium oleander, Ranunculus mariculatus , Tecoma stans, Urtica dioica* by using atomic absorption spectrometry. The main purpose of this study was to quantify essential and non-essential heavy metals in selected herbs, which are extensively used in the preparation of herbal products and standardized extracts. The high conc. of iron, Mn was found in *Nerium oleander*26.52 mg/kg, 94.40 mg/kg. Zn in *Lepidium sativum* 77.00 *mg/kg* and high conc. of K 94600 and Na 400 mg/kg was found in *Tecoma stans*. The concentration of other heavy metals particularly Cu, Ni and Pb were also found in higher conc. in the selected herbs. The main purpose of the present study was to evaluate the contents of toxic metals and their concentration level which may have adverse effect on human health, besides providing a scientific data.

Introduction

Recently there has been an increasing attention using herbal products for combating diseases. One of the reasons that people prefer herbal medicines over modern chemicals is their low price, easy availability, more effective and with lesser side effects. While another reason is their safety compared to the chemical drugs, ignoring the fact that there are chemical materials in plants as their active ingredients. Because the plants are directly in contact with air, water and soil, the constituents of these sources might contaminate the plants. In addition to toxic elements such as mercury, arsenic, lead, nickel and cadmium which might be present in some plants and threaten the consumer health, especially the children and elderly, useful elements such as calcium, magnesium, zinc, manganese and iron are also usually present in plants, which helps the good health. In continuation to our interest regarding heavy metal analysis in medicinal plants with regard to toxic metals [1-5].

The heavy metals are mobilized by human activities such as mining and discarding industrial waste in nature, and they pose a potential threat to organisms [6-7]**.** Heavy metals are known to affect biological communities [8-11]. When the levels of heavy metals exceed in plants and animals, it can induce a variety of acute and chronic effects in wide range of organisms in various ecosystems. The presence of heavy metals beyond the allowed upper and lower limits can cause metabolic disturbance. [11] Thus Deficiencies of essential minerals particularly those which involve in the metabolism of carbohydrates for example chromium, manganese, zinc, potassium and magnesium are found in diabetics**.** Chromium helps to lower cholesterol and triglyceride levels and increases insulin sensitivity. The excess iron can cause oxidative stress and damage the pancreas and thus affect insulin secretion, Manganese is involved in energy metabolism High levels of zinc may increase glycosylation [12]. WHO recommends that medicinal plants which form the raw materials for the finished products may be checked for the presence of heavy metals, anti bacterial and anti fungal activities and other contaminants. Further it regulates maximum permissible limits of toxic metals like arsenic, cadmium and lead, which amount to 1.0, 0.3 and10 ppm, respectively [13-14] Medicinal herbs are easily contaminated during growth, development and processing. After collection and transformation into dosage form the heavy metals confined in plants finally enter the human body and may disturb the normal functions of central nervous system, liver, lungs, heart, kidney and brain, leading to hypertension, abdominal pain, skin eruptions, intestinal ulcer and different types of cancers.

The main purpose of the present study was to quantify the heavy metals in the selected medicinal herbs and to provide a scientific data base line for local practitioners as well as for pharmaceutical industries.

Results and Discussion

Concentration of essential and non-essential heavy metals in medicinal plants beyond permissible limit is a matter of great concern to public safety all over the world. The problem is rather more serious in Pakistan, because medicinal plants which form the raw materials for the finished products are neither controlled nor properly regulated by quality assurance parameters.

Table-1 summarizes pharmacognostic features of the selected medicinal herbs used as herbal remedy. The concentrations of Mn, Zn, Fe, Ni, Cu, Cr, Pb and Cd in selected medicinal plants are appended (Table-1).

Iron

Iron is an essential element for human beings and animals and is an essential component of hemoglobin. It facilitates the oxidation of carbohydrates, protein and fat to control body weight, which is very important factor in diabetes. Results in Table-1 reveal that maximum concentration of Fe was found in *N. oleander* 26.52 mg/kg, *T. stans* 24.48 mg/*kg*, E. helioscopia L 19.44 *mg/kg*, *A. calamus* 16.16 mg/*kg*, *C. foliosum* 13.00 *mg/kg*, *U. dioica* 12.96 *mg/kg*, *L. sativum* 11.40 mg/kg, *Ranunculus* 8.52 *mg/*kg, *Cupressus* 3.52 mg/kg. The results suggest that high amount of Fe in plants may also be due to the foliar absorption from the surroundings air. The dietary limit of Fe in the food is 10-60 mg/day [17] Low Fe content causes gastrointestinal infection, nose bleeding and myocardial infarction [15].

Chromium

The concentration of Cr Table-1 found in different plants was in *E. helioscopia* L 50.6 mg/*kg*, *C. foliosum* 47.60 mg/kg, *N. oleander* 46.00 mg/kg, *A. calamus* 44.20 mg/kg, *A. annua* 43.40 mg/kg, *C. arizonica* 42.20 mg/kg, *T. stans* 36.80 mg/kg, *L. sativum* 32.6 mg/kg, *U. dioica* 29.8 mg/kg, *Ranunculus* 24.2 mg/kg. With the exception of fall out of atmospheric pollutants through rain and accumulation in plant, it is probable that the metal was translocated through air dust blowing from nearby. The toxic effects of Cr intake is skin rash, nose irritations, bleeds, upset stomach, kidney and liver damage, nasal itch and lungs cancer, chromium deficiency is characterized by disturbance in glucose lipids and protein metabolism [17]. The daily intake of Cr 50-200 µg has been recommended for adults by US National Academy of Sciences [18].

Zinc

As evident from Table-1, high concentration of Zn was found in *L. sativum* 77.00 mg/kg followed by *C. foliosum* 50.00 mg/kg, *E. helioscopia* L 45.00 mg/kg, *T. stans* 43.20 mg/kg *N. oleander* 42.20 mg/kg, *A. calamus* 39.2 mg/kg, *A. annua* 34.4 mg/kg, *U. dioica* 28.8 mg/kg, *Ranunculus* 28.6 mg/kg. Zinc is an essential trace element for plant growth and also plays an important role in various cell processes Including normal growth, brain development, behavioral response, bone formation and wound healing. Zinc deficient diabetics fail to improve their power of perception and also cause loss of sense of touch and smell. The dietary limit of Zn is 100 ppm.

Mn

The maximum concentration of Mn was found in *N.oleander* is 94.4 mg/kg, followed mg/kg. *C. foliosum* 82.8 mg/kg. *E. helioscopia* L 70.00 mg/kg *T. stans* 67.00 mg/kg, *L. sativum* 61.2 mg/kg *A. calamus* 51.40 mg/kg, *A. annua* 48.00 mg/kg, *U. dioica* 40.80 mg/kg, *C. arizonica* 29.60 mg/kg, *R. mariculata* 28.80 mg/kg. Mn deficiency in plants causes chlorosis. The estimated safe and adequate daily dietary intake in adults is 11 mg/day**).** Deficiency of Mn in human causes myocardial infarction and other cardiovascular diseases, also disorder of bony cartilaginous growth in infants & children and may lead to immunodeficiency disorder and rheumatic arthritis in adults

Table-1: Concentration of Heavy Metals in Selected Medicinal Plants mg/kg.

S No	S/No	Fe	Cr	Zn	Mn	Cu	Co	Ni	Na	K	Cd	Pb
1	***Lepidium sativum***	11.40	32.60	77.00	61.20	9.80	1.00	17.20	192	15400	0.200	0.60
2	***Chenopodium foliosum***	13.00	47.60	50.00	82.80	9.80	1.40	26.00	224	25800	0.40	1.40
3	***Ranunculus Mariculatus***	85.02	24.20	28.60	28.80	11.00	0.200	18.20	392	33600	0.60	1.20
4	***Urtica dioica***	12.96	29.80	28.80	40.80	7.40	0.400	15.80	100	11400	0.00	1.40
5	***Euphorbia helioscopia L***	19.44	50.60	45.00	70.00	16.80	0.400	28.60	152	21000	0.20	2.20
6	***Acorus calamus***	16.16	44.20	39.20	51.40	10.00	0.200	24.20	148	19000	0.20	2.20
7	***Tecoma stans***	24.48	36.80	43.20	67.00	8.60	1.20	22.60	400	49600	0.00	2.00
8	***Nerium oleander***	26.52	46.00	42.20	94.40	9.00	1.00	2.008	244	27400	0.00	1.00
9	***Cupressus arizonica***	35.20	42.20	33.20	29.60	9.60	0.20	22.20	466	49800	0.20	3.20
10	***Artemisia annua***	83.20	43.40	34.40	48.00	11.60	1.20	22.40	318	29600	0.20	0.60

Copper

Although Cu is an essential enzymatic element for normal plant growth and development but can be toxic at excessive levels. Phytotoxicity can occur if its concentration in plants is higher than 20-100 ppm DW (dry weight). As can be seen from the data (Table-1) high concentration of Cu was found in *E. helioscopia* L 16.80 mg/kg, followed by *A. annua*11.60 mg/kg, *R. mariculata* 11.00 mg/kg, *C. arizonica* .8.00 mg/kg, *A. calamus* 10.00 mg/kg. *N. oleander*, *L. sativum and C. foliosum* 9.80 mg/kg, *C. arizonicas* 9.60 mg/kg, *N. oleander* 9.00 mg/kg, *T. stans* 8.60 mg/kg, and *U. dioica* 7.40 mg/kg The concentration of Cu in the selected herbs is high but it is beyond then critical level in plants. High levels Cu may cause metal fumes fever with flue like symptoms, hair and skin decoloration, dermatitis, irritation of the upper respiratory tract, metallic taste in the mouth and nausea. Copper deficiency results in anemia and congenital inability to excrete copper resulting in Wilson's disease [19].

Nickel

In case of Ni the concentration in different plants was in descending order of *E. helioscopia* L 28.60 mg/kg, *N. oleander* 28.00 mg/kg, *C. foliosum* 26.00 mg/kg, *A. calamus* 24.2 mg/kg, *T. stans* 22.6 mg/kg, *A. annua* 22.40 mg/kg, *C. arizonica* 22.20 mg/kg, *R. mariculata* 18.20 mg/kg, *L. sativum* 17.20 mg/kg, and *U. dioica* 15.80 mg/kg. The higher concentration of Ni in plants may be due to anthropogenic activities.

The most common ailment arising from Ni is an allergic dermatitis known as nickel itch, which usually occurs when skin is moist, further more Ni has been identified as a suspected carcinogen and adversely affects lungs and nasal cavities. Although Ni is required in minute quantity for body as it is mostly present in the pancreas and hence plays an important role in the production of insulin. Its deficiency results in the disorder of liver [20].

Lead and Cadmium

Lead and cadmium are non-essential trace elements having functions neither in human's body nor in plants. They induce various toxic effects in humans at low doses. The typical symptoms of lead poisoning are colic, anemia, headache, convulsions and chronic nephritis of the kidneys, brain damage and central nervous system disorders. Cadmium accumulates in human body and damages mainly the kidneys and liver [23]. Prescribed limit for Pb contents in herbal medicine is 10 ppm while the dietary intake limit for Pb is 3 mg/week. The lowest level of Cd which can cause yield reduction is 5-30 mg/kg, while the maximum acceptable concentration for food stuff is around 1 mg/kg [21]. Surprisingly no Pb or Cd were detected in plant samples (Below detection)

Experimental

Collection and Post Harvest Treatment of Plant Material

Plants *A. calamus, A. annua, C. folsilium, E. helioscopia L, L. sativum, N. oleander, R. mariculata T. stans,* and *U. dioica* were collected from natural habitat of Khyberpakhtunkhwa including Dir, Swat and Peshawar disricts during the appropriate season. Plant parts, especially roots were washed in fresh running water to eliminate dust, dirt and possible parasites and then treated with deionized water and was dried in shade at 25-30 $^{\circ}$C. During this sample processing, necessary measures were taken in order to avoid any loss or contamination of heavy metals.

Acid Digestion of Plant Samples

Weighed quantities of crushed and powdered portion 1g from whole part of each plant including root, stem, leaf and flower in a china dish were heated in an oven at 110 $^{\circ}$C to remove moisture. The dried sample after charing was heated in a furnace for 4h at 550 $^{\circ}$C. The contents of china dish were cooled in desiccator and 2.5 mL 6M HNO_3 was added into the dish to dissolve its contents. The solution was filtered and transferred to a 20 mL flask and diluted to the mark

Estimation of heavy metals was carried out on flame atomic absorption Spectrophotometer [FAAS] (Polarized Zeeman Hitachi 2000 was used.)

Calibration of Equipment

For the elements under investigation we established the following sensitivity and detection limits respectively of the used FAAS apparatus.

Table-2:

1.	**Pb**	**0.2 and 1.0 ppm**
2.	**Cr**	**0.5 and 3.0 ppm**
3.	**Cd**	**0.2 and 1.0 ppm**
4.	**Fe**	**0.5 and 5.0 ppm**
5.	**Cu**	**0.5 and 3.0 ppm**
6.	**Mn**	**0.5 and 2.50 ppm**
7.	**Zn**	**0.05 and 5.0 ppm**
8.	**Co**	**1.0 and 5.0 ppm**
9.	**Ni**	**0.5 and 4.0 ppm**

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