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Review Article on Detection of Heavy Metals by ICP-Mass Spectroscopy

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ABSTRACT— The decontamination of soils polluted with heavy metals presents one of the most intractable problems for soil clean-up. In this paper the use of metal-accumulating plants is explored for the removal of heavy metals (Cu, Co, Pb, Hg, As, Cd) from superficially-contaminated soils by fly ash releasing through thermal plant. Heavy metals concentration was analyzed by ICP-MS (Inductively coupled plasma – mass spectrometry). Eight plant samples namely Ganda (Tagetes spp.), Jamun (Syzgium spp.), Gudhal (Hibiscus species), Rose (Rosa indica L.), Sudarshan (Crinum spp.), Sadabahar (Catharanthus Roseus), Kela (Musa spp.) and Guldawari were collected from Guru Nanak Dev Thermal Plant, Bathinda and Suratgarh Super Thermal Power Station, Suratgarh. Cu was maximum found in s Syzgium spp. Stem (21.6ppm) GNDP, Bathinda, Co was maximum found in Guldawari root (1.27ppm) in SSTP Suratgarh, Pb is maximum found in leaf of Musa spp (7.9ppm) in GNDP, Bathinda, Hg is maximum in Hibiscus species leaf (7ppb) from GNDP Bathinda, As is maximum found in Hibiscus species leaf (1.99ppm) from GNDP Bathinda and Cd was maximum found in root of Syzgium spp. (0.14ppm) in SSTP Suratgarh.

Keywords-Heavy metal, plants, ICP-MS, GNDP Bathinda, SSTP Suratgarh.

I. INTRODUCTION

Heavy metals are considered one of the major sources of soil pollution. Heavy metal pollution of the soil is caused by various metals, especially Cu, Ni, Cd, Zn, Cr and Pb (Karaca et al.2010). Some heavy metals (like Fe, Zn, Ca and Mg) have been reported to be of bio-importance to man and their daily medicinal and dietary allowances had been recommended. However, some others (like As, Cd, Pb, and methylated forms of Hg) have been reported to have no known bio-importance in human biochemistry and physiology and consumption even at very low concentrations can be toxic (Duruibe et al.2007). Heavy metals exert toxic effects on soil microorganism hence results in the change of the diversity, population size and overall activity of the soil microbial communities (Ashraf et al.2007). Elevated Pb in soils may decrease soil productivity and a very low Pb concentration may inhibit some vital plant processes i.e. photosynthesis, mitosis and water absorption with toxic symptoms of dark green leaves, wilting of older leaves, stunted foliage and brown short leaves, stunted foliage and brown short roots (Bhattacharyya P., Chakrabarti K et al.2008).

The metal plant uptake from soils at high concentrations may result in a great health risk considering food-chain implications (Jordao et al., 2006). Uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to human health. The consumption of heavy metal contaminated food can seriously deplete some essential nutrients in the body that are further responsible for decreasing immunological defenses, intrauterine growth retardation, disabilities associated with malnutrition and high prevalence of upper gastrointestinal cancer rates (Khan et al.2008). The pollution of heavy metals is one of the forms ofenvironmental pollution resulting from industrial oragricultural human activity. in recent years scientists havebeen interested in studying the heavy elements in termsof their presence in the environment and its biologicaleffects and its relation to human health. food is one ofthe main sources of human exposure to these elements,so many studies have been interested in developingappropriate methods to determine the extent of foodcontamination of these elements and their suitability forhuman use (Kennish, 1992) and to determine theminimum or critical concentration of these pollutants infood without causing damage (Zawir, Zaynab abed Al-Hussian. 2009). The percentage of pollution is increasingin developing plants near roads,bridges and denselypopulated areas, and the source of this pollution is soil,water or air (Giyath Saminon and Aljuba Malak, 2002;Naser et al, 2012).The proximity of these areas to the production areasof petroleum products, the spread of factory waste andcar exhausts cause the spread of these pollutants overthe places of sale and distribution of vegetables, anotherreason for direct pollution (Zawir, Zaynab Abed Al-Hussian, 2009).Some soil properties such as acidity, salinity andelectrical conductivity affect the ability to absorb affectsthe contamination of vegetables and fruits,especially papercrops, which in turn affects human health (Kachenko andSingh, 2006). Studies have confirmed that fertilization hasa role in pollution and the accumulation of heavy metals,such as in the use of phosphate fertilizers that increasethe accumulation of cadmium (Williams and David, 1977).It is also noteworthy that vegetative groups growing inan environmentwith accumulative content of heavyelements are more susceptible to contamination comparedto less polluted soils, it is worth mentioning that theseelements are not dangerousif they are taken within thelimit allowed by the world health organization and the worldfood organization (Nazemi, 2012).The risk of these elements is directly influenced bythe accumulation in the body organs such as the liver andkidneys and attack the protein compounds of manyenzymes by eating these vegetables fresh or indirectlycanned food (Itoda Adems and Itoda, 2010).Lead enters many industries such as gasoline, paint,water pipes, etc. and the accumulation of damage to healthand leave a negative impact on plant. Animals and humans it affects organs such as the nervous, digestive circulationand reproductive systems and is responsible for 10% ofthe global burden of disease, especially in areas that aremalnourished and lack protein (Sixth session of theintergovernmental forum on chemical safety, 2008).Studies have shown that cadmium is a heavy elementthat accumulates in plant tissues. the plant works to collectthem in special locations in the vegetative part or convertthem to other forms and the paper crops that contain themost cadmium are the leaves of lettuce, parsley andcelery especially in the farms surrounding the factories(Memon, et al, 2001), when ingested by humans causehealth damage through its impact on the liver and kidneys,especially women who suffer from iron deficiency, it wasalso found that areas lacking calcium are osteoporosis toreplace cadmium with calcium (Sixth session of theintergovernmental forum on chemical safety, 2008) copperis a necessary element and has good qualities in theindustry such as high electrical conductivity and themanufacture of alloys, which is necessary forphotosynthesis and chlorophyll formation, and the processof oxidation and reduction, it is important for humansbecause it enters in to the formation of enzymes and thebuilding of blood plasma and deficiency leads to anemia,especially in children, it is toxic to humans if it exceedsthe allowable quantity, whether through food or drinkingwater. the world health organization (WHO) has identifiedthis concentration as 1 mg/L for drinking water and 0.05– 1.5 mg /kg for food (Al-Maliki, 2006).The risk of nickel comes from entering the body whenthe availability of low concentrations in food (4 mcg / kgfood), it causes liver damage with reduced iron absorptionand a decrease in the activity of many enzymes, while inthe case of human exposure to high concentrations ofnickel, it causes toxicity and cancer, and the rate of humantake of nickel in the daily diet to about 200- 300 mcg(E.ssamMuhamad Abdel Moneim and Ahmed bin IbrahimAl-Turki, 2012).Iraqi soil is the most important causes of pollutionafter it was one of the cleanest environments in the worldin the seventies of the last century because of the largenumber of wars and daily waste in the service andproduction sectors, which affected the pollution of air,water and soil, especially Pb, Cd, Ni, Co, Cu (Sultan,2010), therefore, the aim of this study is to know theeffects of this contaminated environment of soil, waterand air on the vegetable content of some minerals,especially heavy elements in the markets of the city centerof Babylon.

II. MATERIALS AND METHODS

Sampling

Random sampling of most usable part of three plants i.e. rhizome of ginger, leafy part of mint and fleshy modified stem of aloevera is done from fifteen different sites within and around the Kota city from different agricultural fields or kitchen gardens along with the soil in which these plants were grown or cultivated adopting standard methods from literature. The sites chosen for collection of samples were of different types of areas from industrial, commercial and residential types representing varied sources of heavy metal pollution. Plant and soil samples were kept classified and marked according to their collection or sampling sources. Sampling for mint was done in second week of June; rhizome of ginger was collected in second week of September and aloevera picked up in first week of November in the year 2009.

Processing

Plant part samples were thoroughly

segregated, washed and dried first in sunlight and then in oven at 40-50oC temperature for approximately 12 hrs. The dried samples were powdered in stainless steel mill obtaining fine particles that passed through a 2 mm mesh and kept in polypropylene pouches for analysis. Soil samples were also dried, powdered and sieved similar to above mentioned process and kept in polypropylene plastic pouches for further analysis. To determine heavy metal concentration, a wet digestion method of the dried samples was adopted. 1 g of each air dried and sieved sample was ashed in a muffle furnace at 460oC for 4 hrs. The ash was digested in 10 mL aquaregia (1 part conc. HNO3 + 3 parts HCl) in a digestion tube on the heating blocks at different temperatures for a total of nine hours spreading over 2 h at 25oC, 2 h at 60oC, 2h at 105oC and 3h at 125oC). After the digestion, the residue was transferred to a 100 mL volumetric flask. The clear solution was made up to the mark with double distilled water. A blank digestion solution was made for comparison. For calibration purpose, a standard solution for each element under investigation was prepared.

Analysis
Metal measurement was performed with a Perkin-Elmer model 2380 atomic absorption spectrophotometer with double beam and deuterium background correction.

III. RESULTS AND DISCUSSION

The results pertaining to the plant samples are given in Table 1, which include analysis data of heavy metals viz Cadmium (Cd), lead (Pb), zinc (Zn), iron (Fe), and copper (Cu) concentrations in various samples. Table 2 shows the concentration spectra of various heavy metals in different soil samples.

Table 1: Results of analysis of plant parts

Herbs	Samples	Elements in mg/Kg				
		Pb	Cd	Zn	Fe	Cu
Mint	1	1.33	0.20	0.58	4.76	7.95
	2	1.86	0.83	3.18	32.42	3.94
	3	7.26	1.02	2.56	28.2	3.88
	4	4.40	0.53	1.24	11.8	3.94
	5	3.92	1.01	4.50	32.84	0.49
Aloevera	1	0.56	0.28	1.80	20.60	0.72
	2	1.58	0.29	1.20	21.23	8.35
	3	8.34	0.42	0.68	19.80	0.94
	4	11.30	0.82	1.14	17.40	0.54
	5	12.60	0.97	1.61	1.64	0.66
Ginger	1	0.50	0.14	2.74	10.88	1.06
	2	2.09	0.56	0.64	5.64	0.84
	3	12.60	0.87	6.78	6.92	6.88
	4	11.07	1.07	0.46	5.64	1.68
	5	1.16	0.92	1.58	31.65	9.20

In present studies, Cd concentration ranges from 0.14 to 1.07 mg/Kg in variousplant samples. The maximum concentration (1.07 mg/kg) of Cd was recorded in fleshy stem of Aloevera, while minimum concentration (0.14 mg/kg) was registered in rhizome part of Ginger. Acute doses (10-30 mg/Kg/day) of cadmium to human body can cause severe gastrointestinal irritation, vomiting, diarrhea, and excessive salivation, and doses of 25 mg of Cd/kg body weight can cause death. Low-level chronic exposure to Cd can cause adverse health effects including gastrointestinal, musculoskeletal, renal, neurological, and reproductive effects. The main target organ for Cd following chronic oral exposure is the kidney[10]. Intake of Cd can double if one smokes cigarettes because each cigarette contains about 2 mg Cd.

Table 2: Results of analysis of soil in which different plants were grown

Soil Samples		Elements in mg/Kg				
		Pb	**Cd**	**Zn**	**Fe**	**Cu**
	1	21.4	0.56	1.48	15.72	13.40
	2	10.28	0.98	5.48	39.42	4.64
Mint	3	4.84	0.92	5.40	23.60	10.16
	4	26.16	1.08	6.70	10.16	1.84
	5	21.25	2.96	6.80	20.20	2.48
	1	10.08	0.28	3.78	21.23	21.74
	2	12.85	1.46	2.32	6.96	4.24
Aloevera	3	40.16	3.88	1.20	1.64	2.46
	4	3.12	1.92	1.82	4.98	5.96
	5	20.62	2.02	4.30	3.44	11.24
	1	0.50	1.88	6.34	18.68	3.96
	2	2.09	0.92	16.84	28.66	14.56
Ginger	3	12.60	1.97	6.0	19.34	4.20
	4	11.07	1.90	5.54	17.46	3.50
	5	1.16	2.27	4.57	18.50	3.06

Iron is an essential element in production of Red Blood Cells (RBCs). The concentration of iron (Fe) content was highest in leaves of mint (32.84 mg/kg), while it was found lowest (1.64 while high intake may results into hepatic megaly, cardiac infraction and nephric malfunction. The acceptable limit for human consumption of iron is 8 to 11 mg/day for infants as well as adults[11]. During present investigation, the value of Fe was found much higher, which is significant due to iron-rich soil of the area.

The acceptable limit for human consumption of copper (Cu) is 10 ppm[12]. When Cu exceeds its safe level concentration, it causes hypertension, sporadic fever, uraemia etc. Present investigation reveals that Cu varies from 0.49 to 9.20 mg/kg, which falls below the safe limits for mg/kg) in fleshy stem of aloevera. The Fe content ranges from 1.64 mg/kg to 32.84 mg/kg. Low intake of Fe may cause anaemia, tiredness and pallid physique,

human health and hygiene. The highest concentration of Cu was found in rhizome part of ginger (9.20 mg/Kg), while lowest concentration (0.49 mg/Kg) was recorded in leaves of mint plant. As it falls within safety limits (10 ppm), the plants, which contain Cu, can be used for edible purpose without any risk.

During the present study, lead (Pb) content varies from 0.50 mg/Kg to 12.60 mg/Kg, which is above safety limit (1.5 ppm) for human consumption. Pb content was found high in fleshy stem of aloevera (0.50 mg/kg), while rhizome part of ginger showed low concentration of Pb (12.60

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mg/Kg). It has been reported that most of the accumulated lead is sequestered in the bones and teeth[13]. This causes brittle bones and weakness in the wrists and fingers. Lead that is stored in bones can re-enter the blood stream during periods of increased bone mineral recycling (i.e., pregnancy, lactation, menopause, advancing age, etc.). Mobilized lead can get redeposited in the soft tissues of the body and can cause musculoskeletal, renal, ocular, immunological, neurological, reproductive, and developmental effects. Among all the metals, zinc (Zn) is the least toxic and an essential element in the human diet as it is required to maintain the proper functions of the immune system. It is also important for normal brain activity and is fundamental in the growth and development of the foetus. Zinc deficiency in the diet may be more detrimental to human health than too much zinc in the diet. Although the average daily intake of zinc is 7-16.3 mg per day, the recommended dietary allowance for it is 15 mg per day for men and 12 mg per day for women[15]. On the contrary, the high concentration of zinc may cause vomiting, renal damage, cramps etc. The acceptable limit for human consumption of Zn is 150 ppm. During present study, the concentration of Zn was found high in rhizome part of ginger (6.78 mg/kg), while low concentration of Zn was observed in fleshy stem of aloevera (1.61 mg/kg). The content of Zn ranges 1.61-6.78 mg/kg, which falls within the safe limit. Thus, the trend of concentration of various heavy metals in studied samples of plants is as follows: Fe > Cu > Pb > Zn > Cd

IV. CONCLUSION

The measured levels of heavy metals (Cu, Cd, Se, As and Cr) in all the investigated groundwater samples are less than the safe limit approved by USEPA (2011) except arsenic in one sample. The observed concentrations of Cu, Cd and As in our investigated groundwater samples are less, but concentration of Fe in six samples, As in one sample, Se in seven samples and lead in six samples is found to be higher than the permissible limit as recommended by WHO (2008). A good positive correlation between heavy metals (Se and Cu) with TDS and conductance in investigated water samples has been observed. The overall result shows that heavy metal concentration in nine drinking water samples cross the MCL as recommended by various protection agencies and therefore unsafe for drinking purposes which is harmful for health point of view.

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