Heavy Metal Contamination in Soil and Plant samples by Inductively Coupled Plasma-Optical Emission Spectrometry

Napattaorn Buachoon

***Abstract*—**The concentrations of heavy metals in the soil and plant samples collected from Pathumtani Province, Thailand have been determined by Inductively Coupled Plasma-Optical Emission Spectrometry. Good accuracy was assured by the analysis of standard reference materials. The relative standard deviations for all measured metal concentrations were lower than 18%. Metal accumulation factors were calculated for plant samples. High ratio of plants to soil copper zinc cadmium leads and iron.

***Keywords*—**Inductively Coupled Plasma-Optical Emission Spectrometry, Digestion, Heavy metals, Soil, Plant

I. INTRODUCTION

POLLUTION of the environment with toxic metals has increased dramatically since the onset of the industrial revolution [1,2,3]. Soil pollution by heavy metals, such as cadmium, lead, chromium, and copper, etc. is a problem of concern. Although heavy metals are naturally present in soil, contamination and comes, from local sources: mostly industry (mainly non-ferrous industries, but also power plants and iron, steel and chemical industries), agriculture (irrigation with polluted waters, sewage sludge and fertilizer, especially phosphates, contaminated manure and pesticide containing heavy metals), waste incineration, combustion of fossil fuels and road traffic. Long-range transport of atmospheric pollutants adds to the metals in the natural environment [4]. In recent years, it has been shown that lead levels in soil and vegetation have increased considerably due to traffic pollution, especially from usage of leaded petrol and exhaust combustion [5,6,7]. The problem worsens as daily traffic increases [8].

Heavy metal contamination of soil results from anthropogenic such as mining [9], smelting procedures [10] and agriculture [11] as well as natural activities. Chemical and metallurgical industries are the most important sources of heavy metals in the environment [12,13].

The metals are classified as ±heavy metals± if in their standard state they have a specific gravity of more than 5 g/cm^3. There are known sixty heavy metals. Heavy metals get accumulated in time in soils and plants and could have a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange, and nutrient absorption), determining the reductions in plant growth, dry matter accumulation and yield [14,15,25]. In small concentrations, the traces of the heavy metals in plants or animals are not toxic [16]. Lead, cadmium and mercury are exceptions; they are toxic even in very low concentrations [17]. Every 1000 kg of ±normal soil±contains 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium, theoretically [18]. Monitoring the endangerment of soil with heavy metals is of interest due to their influence on groundwater and surface water [19,20,21,25] and also on plants[22,23,24,25], animals and humans [25,26,27].

The accumulation of these heavy metals in the soils, however, may have lessened over time as a result of the metals being up taken by creosote bushes. To date, no studies have been performed demonstrating creosote bushes as metal scavengers. Because creosote bushes are so prevalent throughout the southwest and because they are able to grow in such contaminated soil environments, they possess the qualities necessary for utilization as phytoremediation resources.

Decomposition of solid samples is an important step in combined analytical methods. In most cases, when using highly sensitive measuring methods, such as flame atomic absorption spectrometry (FAAS), graphite furnace AAS, ICPAES, ICP-MS. Combined analytical methods are favoured for multi element analysis of environmental and biological samples at very high speed. In this study, the levels of heavy metals in soil and plant samples collected from Pathumtani Province, Thailand were determined by Inductively Coupled Plasma-Optical Emission Spectrometry after various digestion methods.

II. MATERIALS AND METHODS

A. Sampling

Soil (control) samples were taken at random at the location of plant sampling from uncontaminated agricultural lands. The other soil samples were taken at measurement points located near high-density traffic roads and near the textile plants in Pathumtani Province, Thailand.

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B. Reagents

All reagents were of analytical reagent grade unless otherwise stated. Deionized water . HNO_3, H_2O_2 and $HClO_4$. The element standard solutions used for calibration were prepared by diluting a stock solution of 1000 ppm (Cu, Pb, Cd, Zn, Fe) supplied by Sigma.

C. Preparation of sampling

Soils were also sieved to -100 Tyler mesh to remove unwanted rock and sediment materials from the matrix. After the tissues were obtained, three replicate one gram samples of each tissue were acid digested according to EPA method 3050. A fourth replicate sample was also prepared and digested but was spiked with either 1.0 or 5.0 ppm each of copper, lead, cadmium, zinc and iron, which were the metals of interest. A blank was also prepared to ensure the integrity of the analytical procedure. The EPA protocol that was adopted for the acid digestion of the soil and tissue samples here can be described as follows: A 1.00-2.00 gram homogenous representative sample was obtained and placed in conical beakers. Sample slurries were prepared by adding 10 ml of 1:1 nitric acid. The slurries were then covered with watch glasses, heated to near boiling, and refluxed for 15 min. After refluxing, the slurries were cooled and then 5 ml of concentrated HNO_3 were added and the solution was again allowed to reflux for an additional 30 min. This last step was repeated to ensure complete oxidation of the metals. After the third refluxing period, the sample was cooled to room temperature and 2 ml of deionized water and up to 10 ml of 30% v/v hydrogen peroxide were added. The samples were then filtered to remove any particulates which might interfere with ICP-OES analysis. The filtrates were collected in 100 ml volumetric flasks and were diluted with deionized water to volume. The samples, which were approximately 5.0% v/v nitric acid, were now ready for ICP-OES analysis.

D. Data Analysis

The experiments were performed in triplicate, and the samples were analyzed in triplicate. For each set of given data, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples to determine the error margin.

III. RESULTS

The range of linearity of concentration vs. absorbance curve is of great importance in determining the elemental concentration of the soil and plant samples. The calibration curves for Copper (Cu), Lead (Pb) ,Zinc (Zn) Cadmium (Cd) and Iron(Fe) are shown in Fig. 1

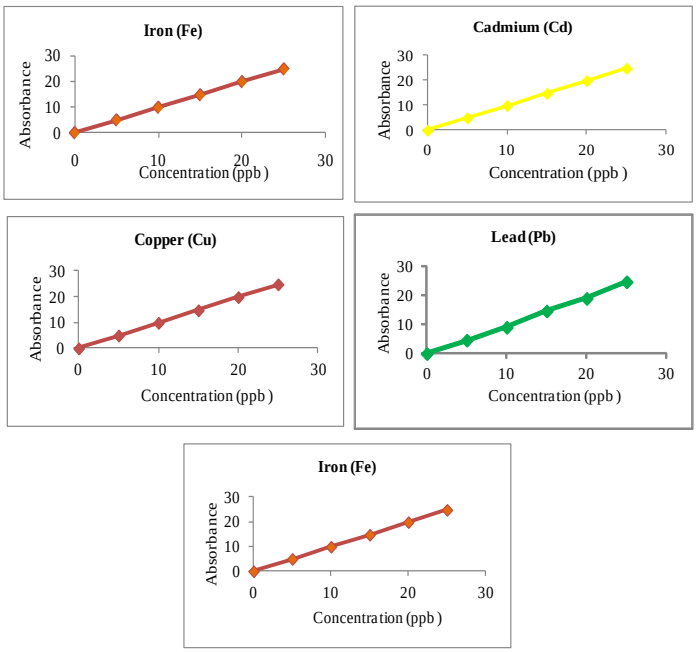

Fig. 1 Concentration versus absorbance curves for Copper (Cu), Lead (Pb) ,Zinc (Zn) Cadmium (Cd) and Iron(Fe)

Heavy metal levels in the analysed samples are given in Table I. All metal concentrations were determined on digest by acid. In general, heavy metal levels in the soil samples taken from roadside were found to be higher than those of soil samples near the plants. Control samples were taken from remote areas which are not influenced by the traffic and textile plants. Minimum values are consisted of control station. The lead concentration in the samples increased with increasing traffic volume.

TABLE I
OBSERVED AND CERTIFIED VALUES (µg/g) OF ELEMENTAL CONCENTRATIONS IN SRM (GBW 08303 POLLUTED FARMLAND SOIL) AS AVERAGE±S.D.

ELEMENT	CERTIFIED VALUE	OBSERVED VALUE OF DIGESTION	RECOVERY (%)
Cu	110±5.5	118± 5.7	95
Pb	83±4.1	70 ±4.2	96
Zn	230±9.8	252±10	95
Cd	1.15±0.05	1.14±0.05	98
Fe	2.55±0.10	2.88±0.15	98

*Each value is the average of five separate digestions.

Plant samples were collected from uncontaminated agricultural lands. The highest metal concentrations were found in Soybean. Metal accumulation factors in plants were calculated as 1.2, 0.003, 0.14, 0.080 and 0.001 for Cu, Pb, Zn, Cd and Fe, respectively. The results are shown in Table II.

TABLE II
OBSERVED AND CERTIFIED VALUES (µg/g) OF ELEMENTAL CONCENTRATIONS IN SRM (NIES, No. 3 *Chlorella*) AS AVERAGE±S.D.

ELEMENT	CERTIFIED VALUE	OBSERVED VALUE OF DIGESTION	RECOVERY (%)
Cu	2.9±0.5	2.5±0.8	97
Pb	0.67±0.07	0.63±0.09	97
Zn	27.1±1.2	26.1±1.3	96
Cd	0.026±0.006	0.017±0.009	95
Fe	0.168±0.04	0.151±0.07	98

*Each value is the average of five separate digestions.

TABLE III
CONCENTRATION OF HEAVY METALS IN SOIL AND PLANT SAMPLES COLLECTED FROM PATHUMTANI PROVINCE, THAILAND

NO.		Cu	Pb	Zn	Cd	Fe
SOIL						
1	CONTROL	6.21±0.21	14.5±1.1	41.5±2.4	0.28±0.02	6821±121
2	NEAR ROADSIDE	39.2±1.5	46.2±3.4	62.1±5.2	1.51±0.11	10121±380
3	NEAR TEXTILE PLANTS	29.1±0.3	21.4±1.5	61.2±6.1	4.31±0.28	8135±281
PLANT						
4	CORN	7.5±0.7	42±3.5	2.3±0.1	18±1.2	4.9±0.3
5	TOMATO	6.7±0.2	42±2.1	7.7±0.3	21±1.6	7.2±0.7
6	SOYBEAN	8.2±0.6	51±4.1	8.7±0.5	31±2.1	8.5±0.9

Heavy metal levels in the analysed samples are given in Table III . All metal concentrations were determined on digest by acid. In general, heavy metal levels in the soil samples taken from roadside were found to be higher than those of soil samples near the plants. Control samples were taken from remote areas which are not influenced by the traffic and textile plants. Minimum values are consisted of control station. The lead concentration in the samples increased with increasing traffic volume.

TABLE IV
BIO-ACCUMULATION FACTORS OF HEAVY METALS FROM SOIL TO PLANTS, N=5

PLANT	Cu	Pb	Zn	Cd	Fe
CORN	1.2	0.003	0.07	0.052	0.0001
TOMATO	1.1	0.003	0.17	0.070	0.001
SOYBEAN	1.4	0.004	0.19	0.117	0.002
MEAN	1.2	0.003	0.14	0.080	0.001

Plant samples were collected from uncontaminated agricultural lands. The highest metal concentrations were found in Soybean. Metal accumulation factors in plants were calculated as 1.2, 0.003, 0.14, 0.080 and 0.001 for Cu, Pb, Zn, Cd and Fe, respectively. The results are shown in Table IV.

Metal bio-accumulation factors in this study are lower than those reported in Refs. [29,30,]. While Cd, Cu and Zn were being accumulated at a high ratio by Soybean, the other elements were being accumulated at a low ratio. The mean concentrations of metals in plant samples were generally similar to those found in other studies [31,32,33]. The fact that toxic metals are present in high concentrations in the fruiting bodies of fungi, from an area greatly favoured by plants, is of particular importance in relation to the FAO/WHO [34] Standards for Pb and Cd as toxic metals. The maximum permissible dose for an adult is 3 mg Pb and 0.5 mg Cd per week, but the recommended doses are only one-fifth of those quantities.

The amount of heavy metal contents are related to species of mushroom, collecting site of the sample, age of fruiting bodies and mycelium, and distance from the source of pollution [30]. According to Stijve and Besson [35], the mechanism by which some heavy metals are accumulated is somewhat obscure although it seems to be associated with a chelation reaction with the sulfhydryl groups of protein and especially with methionine.

IV. CONCLUSIONS

The use of wet digestion system in soil and plant samples provides a better, safer and cleaner method of sample preparation. The accuracy of the method was checked and confirmed by SRMs. Good accuracy was assured by the analysis of standard reference materials. The relative standard deviations for all measured metal concentrations were lower than 18%. Metal accumulation factors were calculated for plant samples. High ratio of plants to soil copper zinc cadmium leads and iron. Creosote bush plants have succeeded in demonstrating the ability to uptake heavy metals such as copper and Zinc from contaminated soils. The metal concentrations in the plant with the highest concentration found in the Soynean. These data demonstrate the potential of phytoremediation via creosote bush as a low-cost, effective means of removing heavy metals from contaminated soils. The nature of the chemical groups that are responsible for the binding of the metals, however, is not fully understood and will be the purpose of further investigation.

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2. Determination of the Content of Hazardous Heavy Metals on Curcuma longu Grown around a Contaminated Area
3. Determination of Heavy Metals in Thai Herbal Plants
4. Determination of Heavy Metals Concentrations in Soil and Plant Samples by Inductively Coupled Plasma-Optical Emission Spectrometry
5. Herbal Extract of Efficiency For Metal Reduced From Vegetables Washing Water
6. Contamination of Microbial in Thai Traditional Medicines