RESEARCHES ON SOIL CONTAMINATION WITH HEAVY METALS AND THEIR REMANENCE IN VEGETABLES

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ABSTRACT

The paper presents the results of experimental researches on soil contamination with heavy metals (copper, lead, zinc) in different concentration each (c_1=1.5 %; c_2=3.0 %; c_3=4.5 %; c_4=6.0 %). The contaminated soil was placed in pots, where spinach and radish seeds were planted. The vegetables were grown in a greenhouse until the end of the vegetation period, afterwards being harvested and the remanence of each heavy metal for each concentration was determined for each plant. The results obtained were compared with the blank sample where the soil was not contaminated.

The purpose of the study was to identify the levels of heavy metals (Cu, Zn and Pb) transfer/absorption from the soil into spinach leaves respectively radish roots.

INTRODUCTION

Metal contamination in agricultural soils is of increasing concern due to food safety issues and potential health risks. Accumulation of Heavy and trace metals in vegetables occur by various sources but soil is considered the major one. Consumption of vegetables containing (heavy/trace) metals is one of the main ways in which these elements enter the human body. Soil-to-plant transfer is one of the key components of human exposure to metals through food chain [4].

Heavy metal elements, such as lead (Pb), cadmium (Cd), arsenic (As), etc., have toxic effects on human health. Toxic metals can accumulate persistently in the body over a lifetime. Pb can adversely influence the intelligence development of children, cause excessive lead in blood, and induce hypertension, nephropathy and cardiovascular disease [9]. Chronic Cd exposure can cause acute toxicity to the liver and lungs, induce nephrotoxicity and osteotoxicity, and impair function of the immune system [8, 9]. The element As is a metalloid and is associated with angiosarcoma and skin cancer. Other metal elements such as copper (Cu) and zinc (Zn) are important nutrients for humans, but excessive ingestion can also have adverse effects on human health. For example, a Cu surplus can cause acute stomach and intestine aches, and liver damage, and Zn can reduce immune function and levels of high-density lipoproteins [9].

Source of heavy metal contamination in soil and vegetables can be arised by many ways such as: mining and processing metal ore [8], untreated wastewater for irrigation [7], the harvesting process, storage and/or at the point of sale [3]. Once the heavy metals, such as Cd and Pb were dispersed into water, soil and air, they could be accumulated by the crops. For example, [10] reported the high Pb level (386 mg/kg), Cd (5.5 mg/kg), Zn (1100 mg/kg), Cu (703 mg/kg) in the contaminated soil from Dabaoshan mine. [2] observed the 17.79 mg/kg for Cd and

57. 63 mg/kg for Pb in radish collected from wastewater irrigated suburban area in Titagarh, Indian.

The paper [5] presents potential health risk of heavy metals accumulation in vegetables irrigated with polluted river water. The mean concentrations of heavy metals found in the agricultural soil were in the order of Ni (96.343 mg/kg) > Cr (69.746 mg/kg) > Cu (69.013 mg/kg) > Zn (45.726 mg/kg) > Pb (28.129 mg/kg) > Cd (0.9654 mg/kg). The mean concentrations of heavy metals in edible parts of selected vegetables were in the order of Zn (19.762 mg/kg) > Cu (9.373 mg/kg) > Pb (3.699 mg/kg) > Ni (2.92 mg/kg) > Cr (1.127 mg/kg) > Cd (0.168 mg/kg).

In Romania, the paper [6] presents heavy metal content in vegetables and fruits cultivated in Baia Mare mining area and health risk assessment, the results showed the heavy metals are more likely to accumulate in vegetables (10.8–630.6 mg/kg for Zn, 1.4–196.6 mg/kg for Cu, 0.2–155.7 mg/kg for Pb, and 0.03–6.61 mg/kg for Cd) than in fruits (4.9–55.9 mg/kg for Zn, 1.9–24.7 mg/kg for Cu, 0.04–8.82 mg/kg for Pb, and 0.01–0.81 mg/kg for Cd). Parsley, kohlrabi, and lettuce proved to be high heavy metal accumulators.

The present work, deals with the determination of heavy metal concentrations from farmland soils and some of the vegetables grown in greenhouses, in pots with contaminated soil in different concentrations.

MATERIAL AND METHOD

Two types plants were studied in order to identify the levels of minerals absorbed by the plants during vegetal development after planting them in farmland soil mixed with heavy metals mixtures (copper, zinc and lead).

Ten kg of soil was homogenized with 100 mL of heavy metal each (Cu, Zn, Pb) with a concentration of 1.5%, 3.0%, 4.5% and 6.0%. This contaminated farmland soil was introduced into pots and three plants of spinach and radish were planted. The blank sample was made by planting three plants of spinach and radish using uncontaminated soil. The physical and chemical properties of the soil (pH, humidity, total nitrogen, total phosphorus, total potassium and conductivity index) were also observed during the experiment. The soil moisture was maintained during the experiments by watering the plants weekly.

1. Soil samples

Basic properties of the farmland soil under study were: pH 5.0-7.0; total nitrogen 1.9 %, total phosphorus 0.5%, total potassium 0.9%, electrical conductibility 1.2, particle elements of over 20 mm maximum 5%, moisture 14.7%.

2. Plant material

The plant species chosen for this study are spinach (*Spinacia oleracea* L.) for leafy (fig.1) and radishes (*Raphanus sativus* L.) for roots (fig. 2) because they are the most consumed vegetables for their nutrient-rich. Also, the option for spinach was made also because among vegetables, it has the greatest capacity for heavy metal accumulation, without showing any visible symptoms of phytotoxicity, which enhances the risk to human health.

Spinach (*Spinacia oleracea L.*) [1] is an annual herbaceous grown plant, having a pivoting root in the soil, up to 180 cm deep, with lateral ramifications. The leaves a long or short petiolate, big, dark-green, smooth with a prominent median nervure. There are 8-12 leaves in the rosette. The cylindrical floral stem is 60-80 cm tall, poorly ramified. Flowers are united at the basis, several grouped in one place, the male ones in 4-5 stamina, and the female ones are axillar. The fruit is a spherical achene, rugged or spiny, yellow with green tones.

Is grown throughout the entire country, it prefers middle texture soils that

are fertile permeable, loose, rich in humus and with high moisture. As active principles it contains: protids, carbon hydrates, lipids, chlorophylls, Na, K, Ca, Mg, Cu, I, vitamins A, B1, B2, C.

Radish (*Raphanus sativus L,)* [1] is a grown herbaceous plant, annual and biannual, which presents a pivoting root in the soil. The straight cylindrical floral stem, up to 100 cm tall. The inferior leaves are petiolate, big, pubescent, and the stem ones are lanceolate, more or less sectioned. Flowers are white, pink or violet, grouped in a raceme, it blooms in May-September, the fruit is a capsule.

Is grown in all the country, is pretentious to moisture, prefers middle texture soils that are loose and rich in humus. As active principles it contains proteins, fats, cellulose, mineral salts, carbon hydrates, sodium, potassium, calcium, phosphorus, vitamins A, B1, B2, C.

Fig. 1 Spinach - Spinacia oleracea L.

Fig. 2 Radish - Raphanus sativus L.

3. Determination of heavy metals in the contaminated soil

The farmland soil is contaminated with multiple metals (Pb, Cu, Zn) in this study.

The method by which the heavy metals (Cu, Zn, Pb) from soil samples (uncontaminated, contaminated with solutions of 1.5 %, 3.0 %, 4.5 % and 6.0 % concentration) was represented by x-ray fluorescence analysis.

An x-ray fluorescence (XRF) spectrometer was used, measuring the peak line emission was obtained a value, which represented the concentration of the analyte. The concentration of the sample to be analyzed was correlated with the net measured value.

4. Determination of heavy metals in vegetable leaves

The plant samples were dried (60° C, 72 h), grinded and then were digested with nitric acid (65 %) in a microwave digestion system as follow:

-weigh 300 mg of the sample into the digestion vessel and add 7.5 ml of nitric acid.

-heat in the microwave oven with the following program.

• First step: T 150° C, power (%) – 50, time - 5 min.

• Second step: T 190° C, power (%) – 70, time 5 min.

The metal content was measured using a flame atomic absorption spectrometry (FAAS, GBC 932AA or GFAAS, GBC Savant AAZ).

RESULTS AND DISCUSSIONS

Table 1 presents the results of determinations on metals content (Cu, Pb, Zn) from uncontaminated and contaminated soil samples (mg/kg ds) with various concentration (1.5 %, 3.0 %, 4.5 %, 6.0 %).

Table 2

Results from determining the heavy metals content in soil samples (mg/kg su)

Metal	Uncontaminated soil	Concentration in the contaminated soil			
		c_1 = 1.5%	c_2 = 3.0%	c_3 = 4.5%	c_4 = 6.0 %
Cu (mg/kg)	17.6	58.9	267.2	525.1	680.8
Pb (mg/kg)	6.75	48.7	84.7	117.7	285.2
Zn (mg/kg)	39.8	202.7	534.8	921.7	1052.3

The concentration of contaminated soil compared to the uncontaminated soil with the three heavy metals were varied as follows: Cu 58.9÷680.8 mg/kg; Pb 6.75÷285.2 mg/kg; Zn 39.8÷1052.3 mg/kg.

The results regarding the remanence of heavy metals from the soil in the spinach leaves and radish roots are represented graphically in figure 3. The data shows the mean ± standard error of three replicates.

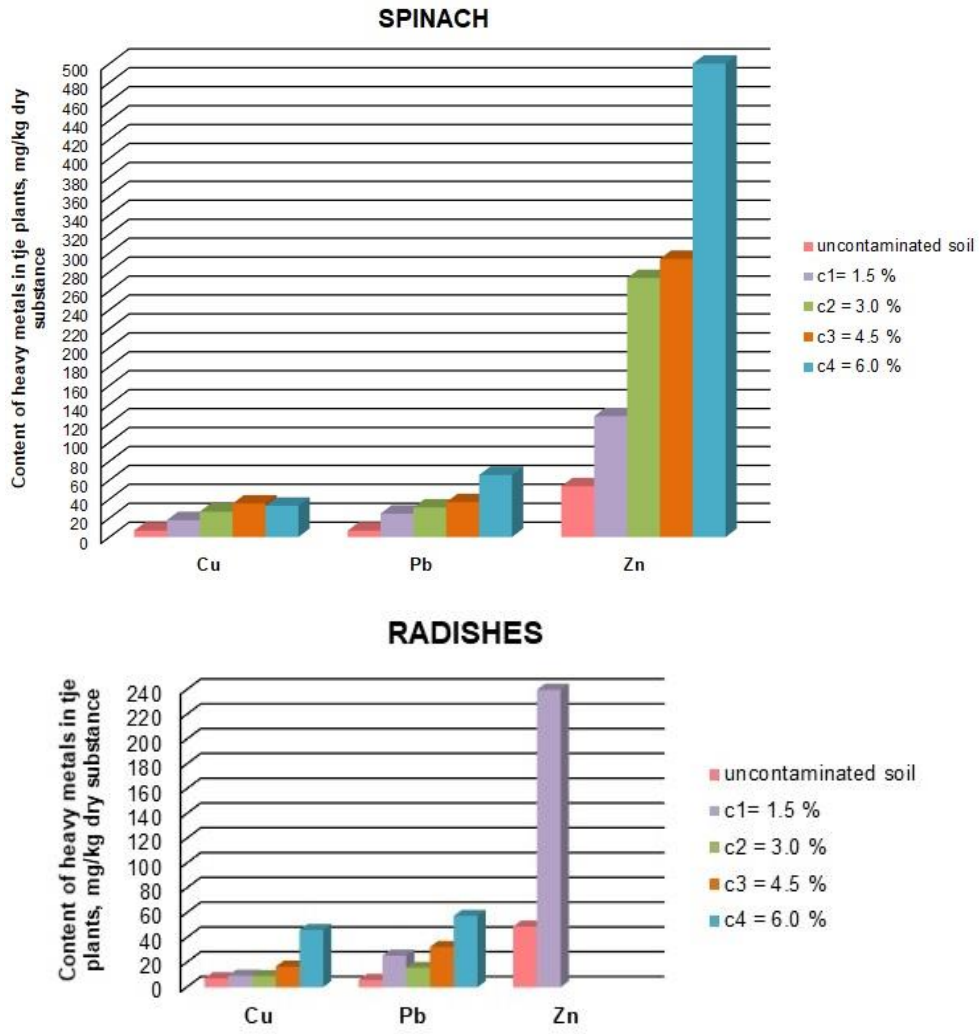

Fig.3 - Concentrations of heavy metals (Cu, Zn, Pb) in vegetable edible parts

After conducting the analysis of heavy metals in plants grown in pots inside a greenhouse, a higher heavy metal absorption was noticed for spinach leaves than for radish leaves. Also, as the heavy metals concentration increase, an increase in the plants' absorption level is noticed.

For spinach, the most absorbed metal was zinc, no matter the concentration, then copper and the least lead.

In the case of radishes, it was found that at concentrations of 3.0%, 4.5% and 6.0% zinc, plants did not develop a root. Pb and Cu were well absorbed for all concentrations.

For both plants, in the uncontaminated soil, heavy metals had very low concentrations, for spinach leaves 6.87 mg/kg Cu, 6.80 mg/kg Pb, 53.65 Zn and for radish roots 7.14 mg/kg Cu, 5.85 mg/kg Pb, 48.9 mg/kg Zn

CONCLUSIONS

Metal contamination in soil is receiving increasing attention all over the world. There are one major pathways (food chain) for human exposure to soil contamination: soil-plant-human.

From the experimental results obtained after contaminating the soil with heavy metals and their absorption by plants, the following conclusion can be drawn:

- Cu, Pb and Zn content in the contaminated soil exceeded by far the heavy metals content in the uncontaminated soil; soil contaminated with 6.0% solution was heavily loaded, as follows: 680.8 mg/kg Cu, 285.2 mg/kg Pb, 1052.3 mg/kg Zn;
- for the two plants, the assimilation of the three metals (Cu, Pb, Zn) was progressive, no matter the metal concentration; Zn was the most assimilated in plants, followed by Cu and the least assimilated was Pb;
- it was found that at concentrations of 3.0%, 4.5% and 6.0% Zn, radishes did not develop normal roots, only leaves;
- a very small assimilation of metals was also noticed in the case of plants grown on uncontaminated soil;
- spinach leaves were more rich in heavy metals than radish roots, for example at concentration of 1.5%, spinach leaves had: 17.89 mg/kg Cu, 24.7 mg/kg Pb, 127.7 mg/kg Zn and radish roots had: 9.26 mg/kg Cu, 25.46 mg/kg Pb, 240.5 mg/kg Zn.

Based on the results obtained, further studies are necessary, at lower concentrations for the construction of mathematical models for describing Copper, Zinc and Lead translocation from soil to plants as single ions as well as combined ions.

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