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Transfer of Metals in Food Chain: An Example with Copper and Lettuce

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Abstract **– Present study investigated the possible transfer of metals in the food chain (from soil to edible plants). The experiment was done with lettuce *Lactuca sativa* grown in different types of soil contaminated with copper (Cu^{2+}) in various concentrations, with or without addition of humic substances. The highest content of copper was detected in lettuce samples grown in soils with lower levels of organic matter, thus indicating the importance of soil organics in metal transfer routes and accumulation rates in plants. It was found that copper accumulation in lettuce grown in contaminated soils can be significantly reduced by the addition of humic substances.**

Keywords **– copper, food chain contamination, lettuce, metal accumulation**

I. INTRODUCTION

Element transfer from basic natural sources (soil, water and air) to the biota in ecosystems is, to a great extent, done by plants [1]. Such elements as Cu, Fe, Mn, Mo, Ni and Zn are known as micronutrients that are essentially necessary for plant physiological processes in trace quantities. While As, Cd, Cr, Hg and Pb are elements that can be assessed as non essential and potentially harmful contaminants. However, increased presence of trace elements in the environment and particularly in soils can affect plant development as well as may influence the elemental composition of harvested crops and, in case of food or feed plants, can lead to contamination of the food chain [*e.g.*, 1-3].

Availability of elements for plants is a complex system of complicated biochemical processes and reactions that are dependent on biogeochemistry and soil properties as well as are influenced by climatic and seasonal conditions. Sequestration, soil weathering, pH, oxidation-reduction potential are just some attributes that are to be taken into account [1, 4-6].

Soil contamination and possible subsequent site and vegetation pollution with potentially toxic elements may occur due to the natural environmental processes and anthropogenic activities. Respectively, volcanic releases, atmospheric depositions, mining and use of chemicals in agricultural practices can be mentioned as well recognized examples [4, 5, 7]. In agricultural areas, as well as in areas used for agriculture in the past, natural soil composition can be altered by frequent applications of fertilizers and other agrochemicals. Use of mineral fertilizers may lead to higher content of Sr and I in soils but application of organic fertilizers conveys significant amounts of As, Cu, Ni and Zn into the soils. Phosphorous fertilizers are the ones that substantially may affect soil element content by input of such elements as As, Cd, Cr, F, Ni, Pb, Sr and Zn [8].

Trace metals can be taken up by plants if they are present in the soil as soluble ions in the forms of organic or inorganic complexes. In addition, not only concentration of ions but also type and chemical character of complexes formed are important in case of plant ability to accumulate potentially toxic elements [9]. Depending on plant capacity to transfer and accumulate elements in a higher or lower extent, a relative classification can be applied as follows: a) hyperaccumulators: plants that can accumulate high concentrations of elements in their vegetative parts; b) accumulators: plants that tend to accumulate elements in their vegetative parts; c) indicators: plants that are able to take up elements and to reflect the ambient environmental content of these elements; d) excluders: plants that do not tend to take up and accumulate elements from contaminated environments [2, 10]. However, such properties of plants are widely studied for phytoremediation purposes at contaminated sites with polluted soil but less has been attributed to the investigation of capacity of metals' accumulation in food plants.

Nowadays the problem of possible health hazards by consumption of contaminated food plants has been recognized not only for agricultural production but also concerning allotment or community gardens. Increase of urbanization constrains the set up of family gardens at sites that have been polluted by industry in the past or that are under the influence of daily urban contamination such as construction dust or traffic exhaust [6, 11]. Vegetables and fruits grown in such conditions mostly are consumed long term by small groups of people and therefore potential health impacts are not considered important within these communities.

Apart from the food chain contamination that may occur as a consequence of excessive transfer of trace metals from soils to edible plants, environmental effects such as extinction of vegetation cover induced by plant intoxication can also occur [4, 5].

The aim of the study was to investigate the transfer of metals into the food chain from different types of contaminated soils to food plants, using the example of copper transfer from soil to vegetative parts of leafy lettuce.

II. MATERIALS AND METHODS

A. Soil contamination and field experiment

The study was carried out by using five different types of soils: S1 low marsh peat soil; S2 turf podzolated soil / sandy loam; S3 turf podzolated soil / sandy with low organic matter content; S4 turf podzolated soil / sandy with relatively higher organic matter content; S5 turf podzolated soil / sandy clay. Piles of selected soils were contaminated with $CuSO_4 \times 5\ H_2O$ solutions of three different target Cu^{2+} concentrations: 70, 100 and 200 mg/kg, as well as the control samples of uncontaminated soils were kept. Copper among the other trace elements is known as a metal that easily forms complex compounds with dissolved organic matter [9]. Therefore, copper was selected as an experimental metal for the current study. Soil contamination procedure was done as it has been described in literature, *i.e.*, soils were humidified by spraying with calculated amounts of copper sulphate water solutions, following by mixing several times [6]. After the contamination soils were left to equilibrate for two weeks, as well as repeated mixing was done before filling of soils into pots.

In addition, half of each of contaminated soils was saturated with the solution of concentrated humic substances (3 g/kg).

Soils were loaded into the pots where leafy lettuce was sown as an experimental food plant. Leaf vegetables, particularly spinach and lettuce in many studies of metal accumulation in plants have been referred to as the most abundant species to accumulate trace metals [6]. Therefore, and also due to the rapid growth and moderate requirements for growth conditions, lettuce *Lactuca sativa* L. var. Grand Rapids was chosen as a target plant within the present study. Plants were grown under partly opened-air conditions, *i.e.*, when needed the pots were covered with a plastic shield to protect them from wind, heavy rainfall and excessive sunlight.

B. Sampling and analysis

Lettuce samples were harvested 35-45 days after sowing. Consequently, samples were cleaned, air-dried and crushed. For trace element analysis it is important to avoid any contact of samples with contaminants, particularly metals. Therefore, crushing of samples was done by using a ceramic knife but sample solutions were kept in polypropylene tubes. Until analyses samples were stored in closed disposable plastic bags in a dry and dark place. Heating was performed in chemically persistent glass beakers.

Lettuce samples were mineralized by wet digestion as it is widely applied for cleavage of biological and environmental samples [*e.g.*, 6]. The pre-treatment procedure of samples was implemented as follows: a) 0.1000 ± 0.0020 g of dry lettuce sample was weighted on analytical balances; b) 5 ml of analytically pure concentrated HNO_3 and 2 ml of analytically pure concentrated H_2O_2 was added; c) after holding the samples overnight, sample solutions were digested by heating at 160 °C temperature; d) after digestion, sample solutions were filled up to 10 ml with ultra pure deionised water. For the accuracy of data, every sample was prepared in triplicate.

Quantitative analysis of copper content in analytical samples was performed using a flame atomic absorption spectrometry (AAS). Measurements were done by AAS apparatus "Perkin Elmer AAnalyst 200" with flame atomization. Absorption was measured by background correction. Characteristic values for copper detection with available methodology were determined by using blank samples, *i.e.*, limit of detection 0.20 mg/kg, level of quantification 0.65 mg/kg and uncertainty 4%.

III. Results and Discussion

The basic step of trace metal transfer into food chain is soil-plant interaction within the certain ambient environment. Sustainable micronutrient cycling is an important issue in case of essential micronutrient transfer as well for the assessment of possible human health risks caused by potentially toxic elements in daily nutrition [12].

Within the current study lettuce samples grown in contaminated soils of different types (with or without addition of humic substances) and were analyzed for copper content and the results were compared with the control samples, *i.e.*, lettuce samples grown in uncontaminated soil. Values regarding copper content in lettuce samples are expressed in units of dry mass (mg/kg DM).

While copper concentration in lettuce grown in uncontaminated soils of every selected type (control soil samples) on average was only 5.07 mg/kg DM, the highest average value for samples grown in soils contaminated with 70 mg/kg of Cu^{2+} was detected for lettuce grown in soil S3 that is sandy soil with low organic matter content (19.47 mg/kg DM) but the lowest concentrations were detected in lettuce grown in soils S4 and S1 that were soils with higher content of organics. Obvious difference were observed for the copper content in lettuce grown in soils addition with solution of humic substances (Fig. 1) that affirmed the importance of organic matter in element transfer from soil to plants.

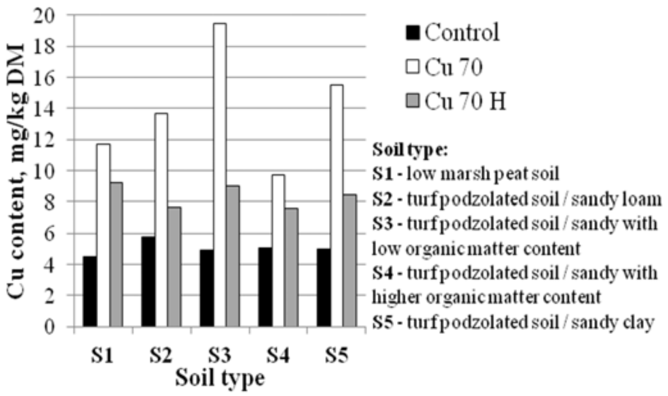

Fig. 1. Detected content of copper in lettuce samples grown in different soil types contaminated by Cu^{2+} at target concentration of 70 mg/kg, with (Cu 70 H) or without (Cu 70) addition of solution of humic substances.

It has been proved that natural substances (*e.g.*, humic acids) and synthetic solvents (*e.g.*, ethylenediamine tetraacetic acid EDTA or diethylenetriamine pentaacetic acid DTPA) used as chelators may influence metal accumulation in plants and can be used for metal removal from polluted soils [9]. However, treatments by humic acids, if compared with synthetic chelators, in case of copper contamination showed the highest potential to reduce copper toxicity by involving metal ions in complex compounds in plants [9, 13]. Heemsbergen *et al*. outlined that copper availability for plants is dependent on speciation of substance applied, *i.e.*, is it salt or not, however, copper solubility can be increased by complex formation with dissolved organic matter but bioavailability in this case can be not changed or even can be reduced [13].

In lettuce samples grown in soils contaminated with 100 mg/kg of Cu^{2+} similar tendencies of copper content changes were detected regarding comparison of samples grown in soils with or without addition of solution of humic substances. The highest copper concentrations were detected for lettuce samples grown in soils S5 and S2 but the lowest concentration was detected in lettuce grown in soil S1 (peat soil) that is naturally rich with organics (Fig. 2).

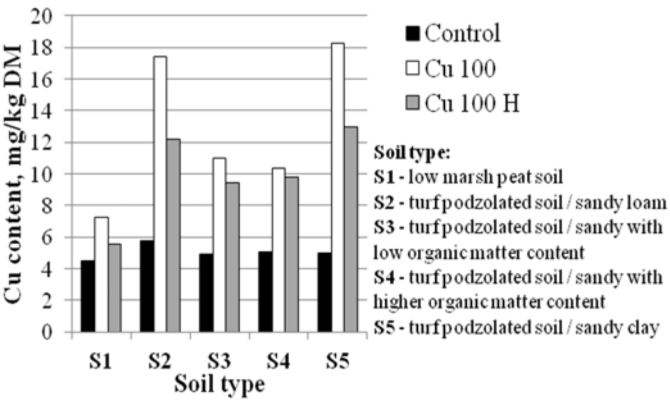

Fig. 2. Detected content of copper in lettuce samples grown in different soil types contaminated by Cu^{2+} at target concentration of 100 mg/kg, with (Cu 100 H) or without (Cu 100) addition of solution of humic substances.

In a study done by Alexander *et al.* quite similar results has been obtained for lettuce. Lettuce samples of different varieties were grown in soil contaminated with target concentration 130 mg/kg of Cu^{2+}. Copper content in lettuce was detected in range 6.73-12.55 mg/kg DM (control values 4.19-7.07 mg/kg DM) but no significant differences were statistically detected between selected lettuce cultivars [6]. The highest concentration applied for soils within the present study was 200 mg/kg of copper. Copper content in lettuce grown in soils contaminated at this level reached up to 94.03 mg/kg DM for samples derived from soil S2, following by samples derived from soil S5 (66.23 mg/kg DM). The lowest copper concentration contained lettuce samples grown in soils S1 and S4. The tendency of humic substances to reduce metal content in plants was clearly detectable, *e.g.*, for lettuce samples grown in soil S2 copper content was about 11 times lower in case of soil addition with humic substances than without it (Fig. 3).

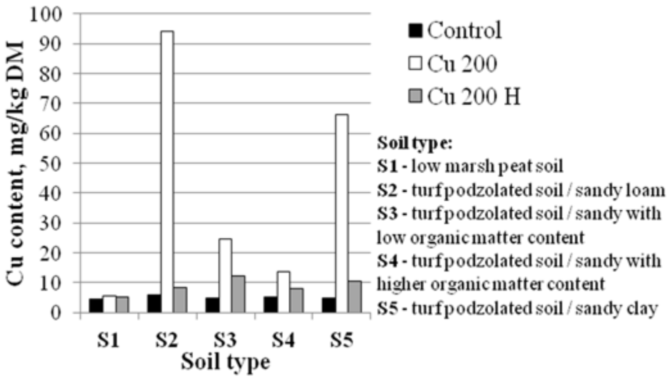

Fig. 3. Detected content of copper in lettuce samples grown in different soil types contaminated by Cu^{2+} at target concentration of 200 mg/kg, with (Cu 200 H) or without (Cu 200) addition of solution of humic substances.

Metal transfer from soil to plants is dependent on various chemical processes such as chelation, absorption and desorption, precipitation and dissolution. He *et al.* defined that 'chelation is the process during which trace elements form stable complexes with organic or inorganic ligands' [14]. It is supposed that chelation is the main factor that affects copper accumulation in lettuce grown in soils added with solutions of humic substances.

In several studies it was described that characterization of quantitative transfer of metals from soil to plants can be estimated by so called transfer factor (TF) or soil-plant partition coefficient [1, 6, 7].

Theoretical transfer factor calculation was performed for lettuce samples grown in soils of different types with various levels of copper contamination (Table I).

TABLE I

THEORETICAL TRANSFER FACTORS (TF) FOR CU^{2+} TRANSFER FROM SOIL TO LETTUCE PLANTS GROWN IN DIFFERENT TYPES OF CONTAMINATED SOILS

Soil type	TF at corresponding Cu^{2+} target contamination in soil			TF at corresponding Cu^{2+} target contamination in soil with addition of solution of humic substances		
	70 mg/kg	100 mg/kg	200 mg/kg	70 mg/kg	100 mg/kg	200 mg/kg
S1 - low marsh peat soil	0.167	0.073	0.027	0.132	0.055	0.027
S2 - turf podzolated soil / sandy loam	0.196	0.174	0.470	0.109	0.122	0.041
S3 - turf podzolated soil / sandy with low organic matter content	0.278	0.110	0.122	0.128	0.094	0.062
S4 - turf podzolated soil / sandy with high organic matter content	0.139	0.103	0.069	0.109	0.098	0.039
S5 - turf podzolated soil / sandy clay	0.222	0.183	0.331	0.121	0.129	0.053

Transfer factor reveals the ratio of contaminant concentration C_{plant} in plants *versus* contaminant concentration C_{soil} in soil, *i.e.*, $TF=C_{plant}/C_{soil}$ [1, 6, 7]. Higher values of transfer factor reflect greater productivity of plants to accumulate metal whereas lower values of transfer factor show the intensity of sorption of metal ions to soil colloidal particles [7].

The lowest values of transfer factor were determined for lettuce samples grown in soils with the highest contamination level of copper and with addition of solution of humic substances by that affirming intensity of metal sorption processes in soil connected with presence of organic matter.

Transfer factor can be variable due to several influencing factors, however, Kloke *et al*. has suggested mean transfer factor values for some metals, *e.g.*, 0.01-1.00 for Cu and Pb, 1-10 for Zn, to be used for the assessment of metal transfer from soil to food and feed plants [7, 15]. Calculated values for theoretical transfer factor in this study fall within the suggested mean boundaries. As stated by Hao *et al*. such soil properties as low pH and low content of organic matter as well as metal deposits from atmosphere and anthropogenic activities can lead to high values of transfer factor in case of copper in ambient environments [7].

IV. Conclusions and Future Work

The experiment with Cu^{2+} transfer from soil to lettuce was done as an example within the evaluation study of assessment of metal transfer in the food chain. The highest content of copper was detected in lettuce samples grown in soils with lower levels of organic matter, thus indicating the importance of soil organics in metal transfer routes and accumulation intensity in plants. If metals are involved in organic complexes, they become bounded and less mobile to be used freely within the physiological processes of plants. It was found that in lettuce grown in contaminated soils of all types when were added solution of humic substances, copper accumulation was detected in significantly less amount than in samples grown in contaminated soils without humic addition. The obtained results are useful for overall understanding of possible contamination of food plants with potentially toxic metals.

The development of the study is going to be expanded by taking into account certain soil properties and other influencing factors.

Acknowledgements

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