CONTAMINATION OF CULTIVATED VEGETABLES BY HEAVY ELEMENTS FROM FLOODED ARABLE SOIL: HUMAN EXPOSURE

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Abstract

The consumption of vegetables is one of the most important pathways for heavy elements to harm human health. Direct deposition of contaminants from the atmosphere onto plant surfaces and accumulation of heavy elements in flooded arable soil are of great concern because of the potential health risk to the local population. Thus, the present study was carried out to analyse distribution and soil-plant transfer of Pb, Cd, As, Co, Cr, Ni, Cu, Mn and Fe in potato, carrot, celery, parsnip and onion in order to evaluate their potential effects on human health. Total content of heavy elements in 26 vegetable samples collected from different flooded fields was analysed by atomic absorption spectrometry with a graphite furnace (AASGF) after microwave digestion of the analysed samples. Average concentrations of lead (Pb) and cadmium (Cd) in some of the investigated vegetable samples were higher than maximum allowable concentrations set by EC/Serbian regulation. On the other hand, arsenic (As) was not detected in any of the analysed samples. Accumulation and translocation of analysed elements were varied from element to element as well as among selected vegetable crops. The results showed that the parsnip had highest uptake for the most analysed elements (Fe (107 mg/kg) > Mn (6.98 mg/kg)> Cu (1.94 mg/kg)>Ni (0.34 mg/kg)> Pb (0.13 mg/kg) compared with the other investigated crops. The bioaccumulation factor (BA) for analysed elements in different vegetables was found in order of Cd (0.08)>Fe(0.07)>Cu (0.06)>Pb (0.01)=Ni>Mn (0.001), indicating that analysed crops are categorized as excluder (BA<1). The total health risk associated with the consumption of investigated vegetables grown in studied flooded arable soil was assessed using target hazard quotient (THQ). The THQ values estimated for investigated crops were notably below the safe limit of 1, except for Mn (2.10) and Fe (11.65).

Keywords: Soil contamination**,** plant uptake, risk assessment, bioaccumulation factor.

Introduction

Heavy elements are of great concern because of their persistence in the environment and toxicity to humans and other organisms. Sources of heavy elements in the environment include natural occurrence and contamination by anthropogenic sources (Xu et al. 2013). In the 20th century, agricultural activity led to an apparent increase in environmental pollution, especially in the concentration of toxic elements and agrochemicals in arable topsoil (Orlowski et al. 2014). Thus, the contamination of heavy elements in agricultural soils can also contribute to human health particularly taking into consideration the capacity to accumulate in edible parts of the plants. On this way, the heavy elements might be found in food chain and cause adverse toxicological effects for the consumers (Beccaloni et al. 2013). Also, the ability of plants to accumulate heavy elements into their organs could be used to monitor soil pollution, in particular the amount of heavy elements (Malizia et al. 2012). Therefore, plants can take up elements from soil by their root, transport them upwards to their shoots, and finally accumulate them inside their tissues, although there are large variations among different plant species in terms of metal accumulation ability (Luo et al. 2006). Oral ingestion of contaminated food has been proved to be an important pathway for the transfer of heavy elements from the environment to human bodies. Thus, there is the need to investigate the possible risk for the population due to the chronic exposure to heavy elements present in vegetables and fruits. The European Union has also published (EC, 2006) the regulation in which maximum levels have been derived for Cd and Pb in foodstuffs such as vegetables. Many studies have been conducted to investigate the heavy element contamination of soil and plants (Luo et al. 2011; Tiwari et al. 2011; Beccaloni et al. 2013; Inácio et al. 2014; Orlowski et al. 2014; Galal and Shehata, 2015). However, there is very little information from Serbia for heavy element contents in flooded arable soil and their accumulation and translocation to crop plants such as vegetables. In this context, the risk associated with consumption of contaminated vegetables grown in flooded region may be a potential health concern. Therefore, the presented study was carried out in region of intensive agricultural production - heavily flooded in May 2014, located in the northern Serbian province of Vojvodina in order to establish direct relationship of level of elements in flooded arable soil and the vegetable crops grown there in. Thus, the main objective of this investigation is to quantify the elements concentration in soil and their translocation in vegetables to evaluate health hazards which may be helpful in making policies for growing safe vegetables in flooded areas.

Material and methods

Reagents and solutions

All chemical was of analytical reagent grade. Ultra-pure water was produced by Milli-Q purification system (Simplicity, Millipore, Molsheim, France) and used for preparation of standards and sample solutions. Concentrated 69% nitric acid (ccHNO3) ("for trace metals analysis" grade) and 30% hydrogen peroxide (H_2O_2) were purchased from J.T. Baker (Deventer, Netherlands). All the plastic and glassware were cleaned by soaking in a 20% hydrochloric solution (J.T. Baker, Deventer, Netherlands) overnight then in 20% nitric acid overnight and finally rinsed with Milli-Q water. The As, Cd, Co, Cr, Cu, Pb, Fe, Mn and Ni stock standard solutions (1 g/L) were supplied by J.T. Baker (Deventer, Netherlands). The working standard solutions of 1 µg/mL for each element were obtained by diluting stock solutions in 3% nitric acid. The calibration curve was prepared using the so-called bulk solution prepared by mixing the standard solutions and the subsequent dilution. Automix option of the GFAAS was applied enabling automatic preparation of the calibration standards.

Sampling and sample preparation

Sampling was performed in autumn 2016. A total of 21 topsoil samples (0-30 cm) were collected from selected locations. Each sample was a composite of 10 subsamples collected from a 100 m x 100 m grid using a plastic hand trowel and transported to the laboratory. Subsamples were thoroughly mixed to provide a composite sample of 3 kg of soil. Soil samples were air-dried at room temperature (25 ^{O}C), then passed through a 2 mm polyethylene sieve and finally ground into fine powder with a pestle. The ground samples stored (at 4 ^{O}C) in hermetically sealed polyethylene bags for further analysis. Furthermore, available vegetables (potato, carrot, celery, parsnip and onion) were collected from selected sampling points. Vegetables (n=26) were washed with distilled water to remove residues of soil and then the samples were wiped. After that, only edible part of crops was analysed. Microwave (Ethos One, Milestone, Bergamo, Italy) with segmented rotor of high pressure (HPR-1000/10S) and internal temperature sensor was used for digestion of the samples. The method applied for heavy elements determination is previously used by Škrbić et al. (2013).

Instrumental analysis

A Varian AA240/GTA120 (Mulgrave, Australia) model atomic absorption spectrometer (AAS) with deuterium background correction, equipped with a graphite furnace (GF) for electrothermal atomization and an automatic sampler was used in this study. The assembly was operated from an interfaced computer running SpectrAA software. Varian hollow cathode lamps (Mulgrave, Australia) were used as line sources for all analytes. Argon (99.999%, Messer Tehnogas A.D., Belgrade, Serbia) was used as the inert gas. The wavelengths used for determination of the elements in analyzed samples were as follows: 193.7 nm for As; 228.8 nm for Cd; 283.3 nm for Pb; 240.7 nm for Co; 357.9 nm for Cr; 232 nm for Ni; 324.8 nm Cu; 372 nm for Fe; and 279.5 nm for Mn.

Quality control

The developed method was validated by in-house quality control procedure. The correlation coefficients obtained for calibration curves were all greater than 0.9950. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as the mean signal of five blanks plus three and ten times the standard deviation, respectively. LODs/LOQs (mg/kg) were as follows: 0.025/0.075 for As; 0.012/0.025 for Cd; 0.013/0.026 for Pb; 0.003/0.003 for Co; 0.043/0.076 for Cr; 0.005/0.005 for Ni; 0.010/0.026 for Cu; 0.565/1.182 for Fe; and 0.002/0.006 for Mn. Recoveries for analyzed elements were determined by spiking soil and plant sampleswith mixture of analytes of interest and ranged from 74 to 110%. The repeatability expressed as relative standard deviation of spiked samples ranged from 0.1 to 11%.

Data analysis

Bioaccumulation factor

The bioaccumulation factor (BF), an index of the ability of the plant to accumulate a particular metal with respect to its concentration in the soil substrate (Ghosh and Singh, 2005), was calculated as follows: $BF=C_{plant\ root}/C_{soil}$, where $C_{plant\ root}$ and C_{soil} represent the heavy element concentrations in the plant root and soil, respectively.

Estimated daily intake of analysed elements from vegetables

The estimated daily intake (EDI) of selected elements through vegetables was depended on both the element concentrations in vegetables ($C_{plant\ root}$, mg/kg) and the amount of daily intake of vegetables ($W_{vegetable\ intake,}$ kg/day), which was calculated as follows:

$EDI= C_{plant\ root} \times W_{vegetable\ intake}$

Average daily intake of vegetables for adult consumers was adopted according to the Serbian market basket (Statistical Office of the Republic of Serbia, 2015) as: 18 g/day for carrot, 31 g/day for onion and 144 g/day for potato. Consumption rate of celery and parsnip is not included in the Serbian market basket, but it is estimated as daily intake of carrot, considering the common habits of Serbian population to use the same quantity of both of these vegetables with carrot for meal preparation.

Target hazard quotient

The target hazard quotient (THQ) was conducted by considering the parameters according to Wu et al. (2016). THQ was determined by the following equation:

$$THQ = \frac{\mathrm{E_f E_d F_{ir} C}}{R_{fd} W_{ab} T_a} x10^{-3}$$

where E_f is the exposure frequency (365 days/years); E_d is the exposure duration (70 years); F_{ir} is the food ingestion rate (g/person/day); C is the metal concentration in vegetable samples (mg/kg); R_{fd} is the oral reference dose (mg/kg/day); W_{ab} is the average body weight (60 kg for adults); and T_a is the average exposure time (365 days/year x 70 years). The oral reference doses for selected elements are 0.004 mg/kg/day, 0.001 mg/kg/day, 0.04 mg/kg day, 0.02 mg/kg/day, 0.005 mg/kg/day and 0.7 mg/kg/day for Pb, Cd, Cu, Ni, Mn and Fe (EPA, 2016). A THQ less than 1 indicates no obvious health risk to adults through vegetables consumption. If the THQ is greater than 1, it means there is a potential health risk to humans.

Results and discussion

Heavy element contamination in soil

Table 1 summarizes the total concentration of analysed heavy elements in the top 0-30 cm of the flooded arable soil. According to the Serbian national target limits for heavy elements in soil (OG RS 80/10, 2010) only the average level of Cd in the flooded soil samples exceeded the maximum permissible value. The remediation values were not exceeded for any of the studied elements in any of the studied locations.

Table 1. Average content of heavy elements analysed in flooded arable soil

Elements mg/kg	As	Cd	Co	Cu	Cr	Pb	Ni	Mn	Fe
Mean	5	1.4	3.1	19	37	18	18	1015	1281
Target values[a]	29	0.8	9	36	100	85	35	-	-
Intervention values[a]	55	12	240	190	380	530	100	-	-

[a] Serbian standard target values for soil (OG RS 80/10, 2010)

Heavy element contamination in vegetable crops

Contents of heavy elements in the edible part of analysed vegetables are shown in Figure 1. The highest average concentrations of Cu, Ni, Mn and Fe were found in parsnip, while the highest average levels of Pb and Cd were detected in carrot and celery, respectively. Generally, the lowest average concentrations of detected elements were in onion. To ensure food safety, the European Commission Regulation (EC,1881/2006) has set maximum levels for some contaminants, including also heavy elements like Pb (0.1 mg/kg) and Cd (0.05 mg/kg) in vegetables, whereas for As the maximum allowed concentration has not yet been proposed. Similarly, the latest Official Bulletin of the Republic of Serbia No 29/14 (The Serbian regulation, 2014) has established the maximum levels (ML) for Pb and Cd in foodstuffs in line with the EC regulation, but it regulates wider spectrum of food commodities and it also set the maximum level of As (0.3 mg/kg in vegetables). The Pb was found in carrot samples at the level of 0.54 mg/kg, which was almost 5 times higher than the maximum residue level of 0.1 mg/kg sets by EC/Serbian regulation. In other studied vegetables the determined concentrations were at the level of maximum allowable concentrations or below. The Cd detected above ML in samples of celery, parsnip and carrot. The lower concentrations of Cd were found in samples of potato (0.05 mg/kg) and onion (0.02 mg/kg).

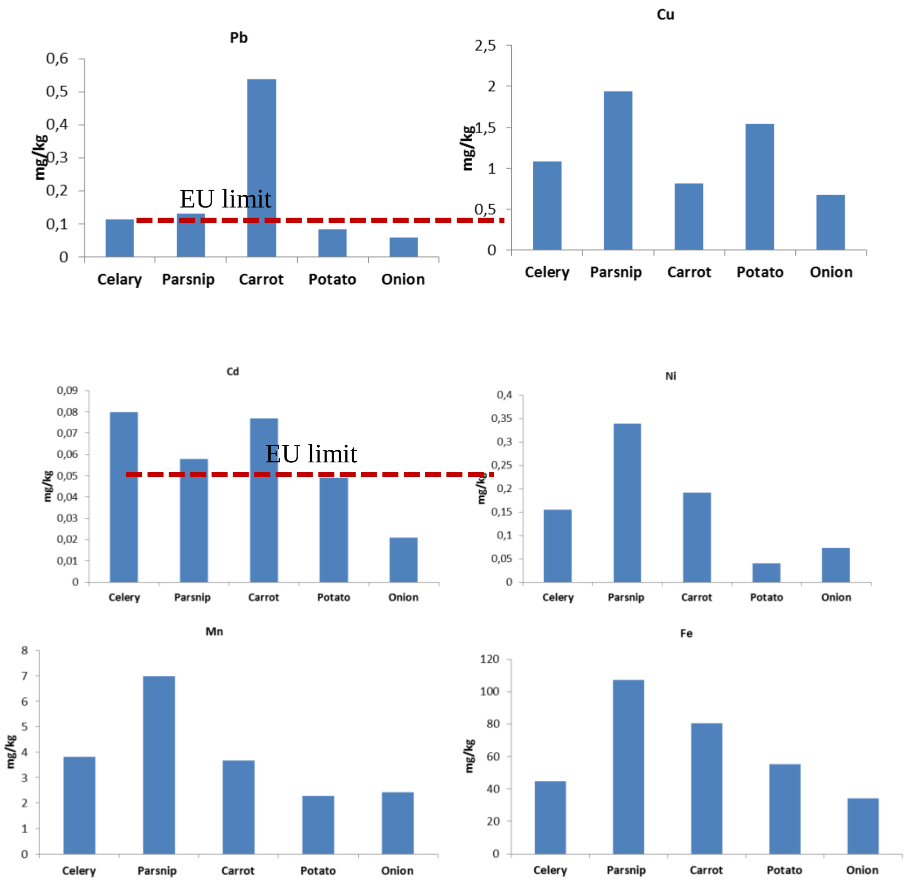

Figure 1. Average concentration of analysed heavy elements in different vegetables collected from analysed flooded arable soil

Table 2 presents the heavy element transfer from soil to vegetable crops i.e. bioaccumulation factors (BF). Elements with greater BF are more easily transferred from soil to the edible parts of plants than the ones with lower BF. The greatest accumulation of Fe was observed in parsnip followed by carrot and potato. The most dominant accumulation of Cd was found in potato and celery. The BF value of Cu was the greatest in parsnip. The presented results indicate low BF for other studied heavy elements in vegetables analysed. As can be seen from Table 2 there are difference in BF values among the analysed vegetables because heavy element uptake by plants depends on the plant type and their physiological character.

Table 2. Bioaccumulation factor, a ratio of concentration in edible parts of vegetables to that of the corresponding soil

Bioaccumulation factor	Pb	Cd	Cu	Ni	Mn	Fe
Potato	0.005	0.107	0.073	0.002	0.002	0.065
Carrot	0.032	0.079	0.039	0.010	0.034	0.097
Onion	0.004	0.015	0.031	0.004	0.003	0.036
Celery	0.006	0.108	0.046	0.011	0.004	0.024
Parsnip	0.003	0.067	0.100	0.029	0.005	0.131

Table 3. Estimated daily intakes (EDIs, mg/day) of selected elements and target health quotients (THQs) through consumption of analysed vegetables for Serbian adult consumers

Vegetables	Pb		Cd		Cu		Ni		Mn		Fe	
	EDI*	THQ	EDI*	THQ	EDI*	THQ	EDI*	THQ	EDI*	THQ	EDI*	THQ
Potato	0.012	0.05	0.006	0.12	0.222	0.09	0.006	0.001	0.327	1.09	7.939	0.19
Carrot	0.009	0.04	0.001	0.02	0.014	0.01	0.003	0.003	0.062	0.22	1.371	0.03
Onion	0.002	0.01	0.002	0.001	0.021	0.01	0.002	0.001	0.075	0.25	1.068	0.03
Celery	0.002	0.01	0.001	0.01	0.018	0.08	0.003	0.01	0.065	0.01	0.762	3.36
Parsnip	0.002	0.01	0.001	0.004	0.033	0.15	0.006	0.03	0.119	0.52	1.822	8.04

*The recommended safe limits (mg/day) are: 48, 3, 11, 0.1-0.3, 0.058 and 0.044-0.105 for Fe, Cu, Mn, Ni, Cd and Pb respectively, (JECFA, 1999, 2011, National Research Council, 1989, WHO, 1994, EFSA, 2010).

The EDI and THQ of the analysed elements calculated through the consumption of investigated crops in this study by Serbian adult consumers are shown in Table 3. The calculated EDIs of heavy elements (Pb, Cd, Cu, Ni, Mn and Fe) through consumption of vegetables were lower than the recommended safe limits reported by EU. The greatest daily intake was estimated for Fe through consumption of potato which is in consequence of its highest concentration found, and therefore highest consumption rate among the analysed crops. The THQ of each element through consumption of analysed vegetables decreased in the order of Fe>Mn>Cu>Cd>Pb>Ni. The THQ values for most analysed elements were below 1, (except for Mn and Fe), indicating that intake of a single element through consumption of vegetables does not pose a significant potential health hazard. The Mn and Fe exhibited higher THQ (2.10 and 11.56, respectively) compared to all other elements in the investigation region, and these elements are major components contributing to the potential health risk. The total element THQ value (sum of individual element THQ for vegetables) was 14.40 (>1) and it might be associated with potential health risk which cannot be ignored.

Conclusions

This study presents the first insight into the concentrations of investigated 9 heavy elements in flooded arable soil, their translocation and accumulation in edible parts of selected crop plants as well as potential health risk. The study highlights the fact that levels of Pb and Cd were above MLs in some plant crops, although, only the average content of Cd in flooded arable soil exceeded the maximum permissible value. The BF was less than 1 for all elements, indicating that edible parts of plants did not show great capacity to absorb element from the investigated soil samples. Although, the THQ values for most elements were below 1, total element THQ was above 1. The potential health risks of analysed elements presented in investigated vegetables are therefore of some concern. Furthermore, Fe and Mn are the elements with the highest contribution to the health risk. However, health risk can be increased with consumption of other contaminated crop plants that was not analysed in this study. Thus, a long-term risk assessment needs to be carried out in order to determine the migration potential of the studied elements in different and the most consumable crop plants which grown in this region.

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