Heavy metals contamination of the soil – water – vegetables chain in the Ilfov region

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Abstract. Dietary exposure to several heavy metals such as Cd, Cr, Pb, As represents a risk to human health through the consumption of vegetables. Due to the possible risks for the human body, contamination of soils as well as drinking and irrigation water has been the subject of many researches.
In this study, the analysis of heavy metals content from soil, water and vegetable samples from households in Ilfov County it was carried out.
As a result, no contamination of soil and water with heavy metals was observed.
Cadmium content is above the maximum allowable limit for all analyzed vegetables, excepting cabbage and green onion. Two lettuce samples have an alarmingly high content of lead, the values being even 10 times higher than the maximum admissible limit of 0.3 mg/kg. The high values obtained for chromium content in lettuce and radish samples raise serious questions about possible contamination. Arsenic content values ranged between 0.87 and 7.69 mg/kg, which also represents high values.
Based on the transfer factor (TF) calculated the strongest accumulation of the metals was in lettuce.

Key words: Heavy metals, contamination, soil, water, vegetables

1 Introduction

Ilfov County is the smallest county in Romania with a total area of 158.328 hectares and is located in the Arges, Ialomita and Mostistea river basins. This county surrounds Bucharest as a ring. On the territory of this county there is a significant industrial and economic activity with a very good evolution. Representative industries of this county are: the food industry, tobacco processing, leather and footwear, paper and cardboard, rubber and plastics processing. The food, beverage and tobacco industries account for 72.5% of the total value of the county's total production.

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In the last 20 years there has been a socio-economic development of the county in an accelerated pace. This development, besides the positive aspects, also presents the disadvantage caused by the increase of sources of anthropogenic pollution of the environment.

There are many studies regarding the accumulation and origin of heavy metals in soil and the potential ecological hazards associated with this process [1-3]. Researches had attracted attention to the effects of heavy metals on human health. Among many toxic elements, lead, arsenic, and cadmium are considered to be potential carcinogens and are associated with the development of several diseases, especially cardiovascular, kidney, nervous system, blood, and bone diseases [4-8].

Heavy metals enter soil through a variety of sources, including include urban, industrial aerosols created by combustion of fuels, metal smelting, and other industrial activities. Other sources of soil contamination of heavy metals are excessive dose of pesticides, micronutrient fertilizers, and manures such as sewage sludge [9, 10].

Heavy metals can become a health risk via consumption of contaminated vegetables, fruits and drinking water. Vegetables are a necessary component of the human diet, providing a source of essential nutrients, antioxidants, dietary fibers and metabolites.

Absorption and accumulation of heavy metals in vegetables are influenced by many factors, including: concentration of heavy metals in soil, composition and intensity of atmospheric deposition, including precipitations, phase of plant vegetation, irrigation with wastewater, using organic and mineral fertilizers with the load of heavy metals, or application of pesticides [11].

The aim of this paper is to study the contamination with potential carcinogenic heavy metals (As, Pb, Cd and Cr) in soil – water – vegetables chain in the Ilfov region.

2 Materials and methods

This study aim was to investigate the degree of contamination by carcinogenic and toxic substances (heavy metals) of the water used for watering crops, of the soil of agricultural use as well as of the grown vegetables in some households from Ilfov County (Copaceni, Jilava, Berceni, Glina).

2.1 Water samples

The water samples collected were representative samples of the water quality at the time of sampling and the sampling site. Six samples of water from the wells of some households from the above mentioned places were analyzed.

Determination of heavy metals in water was done by induction coupled atomic emission spectroscopy (ICP-OES) according to SR EN ISO 11885:2009 [12]. Water samples were mineralized in acidic medium to eliminate interference and then were analyzed by ICP-OES.

2.2 Soil samples

Regarding soil analysis, 11 soil samples from the upper horizon (0 - 20 cm) of agricultural soils (vegetables) from the places above mentioned above were collected (Fig. 1).

Fig. 1. Places where soil and vegetables samples were collected

Thus, was analyzed the total content of chromium (Cr), cadmium (Cd), lead (Pb) and arsenic (As) in the hydrochloric acid solution obtained after solubilizing the residue resulting from the melting of soil samples with a mixture of perchloric acid ($HClO_4$) and nitric acid (HNO_3) (Milestone Digestor Method; SR ISO 11047: 1999 [13]).

2.3 Vegetable samples

11 samples of vegetables (lettuce – 4 samples, green onion – 2 samples, cabbage – 2 samples, spinach – 1 sample, radish – 2 samples) corresponding to the 11 soil samples listed above were harvested and analyzed (Fig. 2).

Fig. 2. Analyzed vegetables samples

2.4 Heavy metals analysis of vegetable samples

Analysis of the heavy metal content involves two phases: preparation of the samples and proper dosing by atomic absorption spectrometry. Sample preparation was carried out by microwave mineralization according to SR EN 14084: 2003 [14] using a Berghoff MWS-2 microwave oven. The mineralization process was carried out according to the program described below:

Step 1 – 145 ºC – 10 minutes – 80 % power;
Step 2 – 160 ºC – 10 minutes – 80 % power;
Step 1 – 190 ºC – 20 minutes – 80 % power;

The content of lead (Pb), cadmium (Cd), total chromium (Cr) and arsenic (As) was determined using a graphite furnace atomic absorption spectrometer (GF-AAS) AAnalyst 600 - Perkin Elmer, provided with Zeeman background noise correction.

3 Results and discussions

In Table 1 are shown the values of the heavy metals content (Pb, Cd, Cr, As) from the water samples. All water samples were taken from wells in different households, having depths between 7 and 15 m.

Table 1. Heavy metals analysis of water samples

Code	Place	Type	Appearance	Heavy metals content (μg/L)			
				Pb	Cd	Cr	As
W1	Copaceni	Groundwater (well) – 8 m depth	Clear, without suspended solids	< 1	< 0.12	1.2	< 0.2
W2	Copaceni	Groundwater (well) – 7 m depth	Clear, without suspended solids	< 1	< 0.12	< 1	< 0.2
W3	Jilava	Groundwater (well) – 7 m depth	Clear, without suspended solids	< 1	< 0.12	< 1	< 0.2
W4	Berceni	Groundwater (well) – 7 m depth	Clear, without suspended solids	< 1	< 0.12	2.3	< 0.2
W5	Berceni	Groundwater (well) – 8 m depth	Clear, without suspended solids	< 1	< 0.12	2.6	< 0.2
W6	Glina	Groundwater (well) – 15 m depth	Clear, without suspended solids	< 1	< 0.12	< 1	< 0.2

The maximum admissible concentrations (Pb – max 10 μg/L; Cd – max 5 μg/L; Cr – max 50 μg/L; As – max 10 μg/L), according to Law no. 458/2002 [15] on the quality of drinking water, updated version, for none of the 4 metals analyzed were exceeded. All the values obtained were extremely low, showing no contamination.

In Table 2 are shown the values of the heavy metals content (Pb, Cd, Cr, As) from the soil samples.

Table 2. Heavy metals analysis of soil samples

Code	Place	Type	Relief unit	Heavy metals content (mg/kg)			
				Pb	Cd	Cr	As
S1	Copaceni	Aluviosoil	Arges-Sabar Meadow	37	0.532	26	2.46
S2	Copaceni	Aluviosoil	Arges-Sabar Meadow	12	0.423	36	3.62
S3	Copaceni	Aluviosoil	Arges-Sabar Meadow	9	0.426	34	3.39
S4	Copaceni	Aluviosoil	Arges-Sabar Meadow	17	0.383	36	3.84
S5	Jilava	Preluvosoil	Bucharest Plain	25	0.420	27	2.63
S6	Jilava	Aluviosoil	Bucharest Plain	14	0.472	28	3.05
S7	Berceni	Preluvosoil	Bucharest Plain	20	0.318	43	3.80
S8	Berceni	Preluvosoil	Bucharest Plain	22	0.300	32	3.21
S9	Berceni	Preluvosoil	Bucharest Plain	26	0.324	33	3.97
S10	Berceni	Faeoziom	Bucharest Plain	19	0.420	33	3.99
S11	Glina	Cernoziom	Bucharest Plain	18	0.351	30	3.39

Concerning the heavy metal content, normal values were obtained for As, Cd, Cr and Pb. The lowest values, ranging between 0.300 and 0.532 mg/kg, were obtained for cadmium, while the highest values, ranging between 26 and 43 mg/kg were obtained for total chromium. The analyzed soils are not polluted with heavy metals.

11 samples of vegetables: 4 samples of lettuce, 2 samples of green onion, 2 samples of cabbage, 1 sample of spinach and 2 samples of radishes were analyzed (Figure 2). The results obtained for the heavy metals content (Pb, Cd, Cr and As) are presented in Table 3.

Table 3. Heavy metals analysis of vegetable samples

Code	Place	Vegetable	Heavy metals content (mg/kg)					
			Pb	ML_{Pb}	Cd	ML_{Cd}	Cr*	As*
S1	Copaceni	Lettuce	**3.65**	0.3	**0.86**	0.2	**11.17**	3.47
S2	Copaceni	Cabbage	< 0.002	0.3	0.20	0.2	1.11	4.68
S3	Copaceni	Lettuce	< 0.002	0.3	**1.92**	0.2	< 0.0013	3.22
S4	Copaceni	Green onion	< 0.002	0.1	< 0.0002	0.2	< 0.0013	3.59
S5	Jilava	Lettuce	< 0.002	0.3	**1.350**	0.2	**9.75**	7.69
S6	Jilava	Cabbage	< 0.002	0.3	< 0.0002	0.2	< 0.0013	0.87
S7	Berceni	Spinach	< 0.002	0.3	**1.66**	0.2	**2.27**	1.70
S8	Berceni	Radishes	< 0.002	0.1	**0.26**	0.05	**7.70**	1.32
S9	Berceni	Green onion	< 0.002	0.1	< 0.0002	0.2	0.74	2.64
S10	Berceni	Lettuce	**10.05**	0.3	**0.65**	0.2	**60.79**	5.39
S11	Glina	Radishes	< 0.002	0.1	**0.11**	0.05	**18.74**	0.88

ML_{Pb} – Maximum allowed limit for lead (Pb), stated by Regulation (EU) no. 1881/2006;
ML_{Cd} – Maximum allowed limit for cadmium (Cd), stated by Regulation (EU) no. 1881/2006;
* - for chromium (Cr) and arsenic (As) there are no maximum allowed limits;

The lead content in green onion, radishes, cabbage and spinach samples are extremely low, well below the maximum permitted level laid down in Regulation (EU) no. 1881/2006 [16]. Two lettuce samples (S1 and S10) showed extremely high lead content, exceeding the maximum permitted level laid down in Regulation (EU) no. 1881/2006.

Regarding cadmium content, excepting green onion and cabbage samples, all other recorded values exceed the maximum permitted level laid down in Regulation (EU) no. 1881/2006.

Despite the fact that there is no maximum limit for chromium, the extremely high values recorded for lettuce and radish samples raise serious questions about possible contamination.

Arsenic content values ranged between 0.87 mg/kg and 7.69 mg/kg. For this element there are no maximum limits.

The plants ability to take up the metals from soil was measured by the ratio between the concentration of element in plant and in soil, representing the biological absorption coefficient (BAC) or the transfer factor (TF) [17, 18]. TFs for each sample and each element are presented in Table 4.

Table 4. Transfer factors (TFs) for each heavy metal

Type	Transfer factor (TF)			
	TF_{Pb}	TF_{Cd}	TF_{Cr}	TF_{As}
Lettuce	0.1	**1.62**	**0.43**	**1.41**
Lettuce	0	**4.51**	0	**0.95**
Lettuce	0	**3.21**	**0.36**	**2.92**
Lettuce	**0.53**	**1.55**	**1.84**	**1.35**
Cabbage	0	**0.47**	0.03	**1.29**
Cabbage	0	0	0	0.29
Green onion	0	0	0	**0.93**
Green onion	0	0	0.02	**0.66**
Spinach	0	**5.22**	0.05	**0.45**
Radishes	0	**0.87**	0.24	**0.41**
Radishes	0	0.31	**0.62**	0.26

The higher transfer factor of heavy metal indicates the stronger accumulation of the respective metal by that vegetable. A transfer factor of 0.1 indicates that plant is excluding the element from its tissues [19]. The greater the transfer factor value than 0.50, the greater the chances of vegetables for metal contamination by anthropogenic activities will be and so the need for environmental monitoring of the area will be required [20]. Analyzing results it can be observed that the strongest accumulation of the metals is in lettuce.

4 Conclusions

The study shows the possible contamination with heavy metals of water, soil and vegetables samples collected from different places in Ilfov County.

Regarding water samples analyzed, no exceedances of the maximum admissible limits for any of the 4 metals analyzed were recorded.

For the soil samples, normal values were obtained for As, Cd, Cr and Pb, showing no contamination.

Excepting cabbage and green onion samples, cadmium content is above the maximum allowable limit for all other vegetables. Two lettuce samples have an alarmingly high content of lead, the values being even 10 times higher than the maximum admissible limit. Also, the strongest accumulation of the metals is observed in lettuce. Despite the fact that there is no maximum limit for chromium, the extremely high values recorded for lettuce and radish samples raise serious questions about possible contamination. Arsenic content values ranged between 0.87 mg/kg and 7.69 mg/kg. For this element there are no maximum admissible limits.

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