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HERAKLION2019
7th International Conference on Sustainable Solid Waste Management
26-29 June 2019 | Heraklion, Crete Island, Greece

INFLUENCE OF FLOOD ON LEVEL OF THE HEAVY ELEMENTS IN AGRICULTURAL SOIL AND THE PLANT CROPS

Biljana Škrbić, Jelena Živančev, Igor Antić, Maja

University of Novi Sad, Faculty of Technology Novi Sad,
Bulevar cara Lazara 1, 21000 Novi Sad,

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, resulting in elevated heavy element uptake by vegetables.

Thus, the main aims of this study were:

a) to determine the concentration and occurrence of selected heavy elements in the investigated flooded region;

b) to assess the current state of soil using several indexes; and….

c) to quantify uptake and accumulation of selected elements in different vegetables and further to evaluate the health risk through daily consumption of the analyzed plants.

The present study was carried out in region of the northern Serbian province of Vojvodina heavily flooded in May 2014,

as it is the area of intensive agricultural production,

in order to establish direct relationship of level of elements in flooded arable soil and the vegetable crops

- Sampling was performed in autumn 2016.
- A total of 21 topsoil samples (0-30 cm) were collected from selected flooded locations.
- Each sample was a composite of 10 subsamples collected from a 100 m x 100 m grid using a stainless steel 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.

Nine elements were analyzed in soil and vegetable samples:

As (arsenic), Pb (lead), Cd (cadmium), Ni (nickel), Co (cobalt), Cr (chromium), Mn (manganese), Cu (copper), Fe (iron)

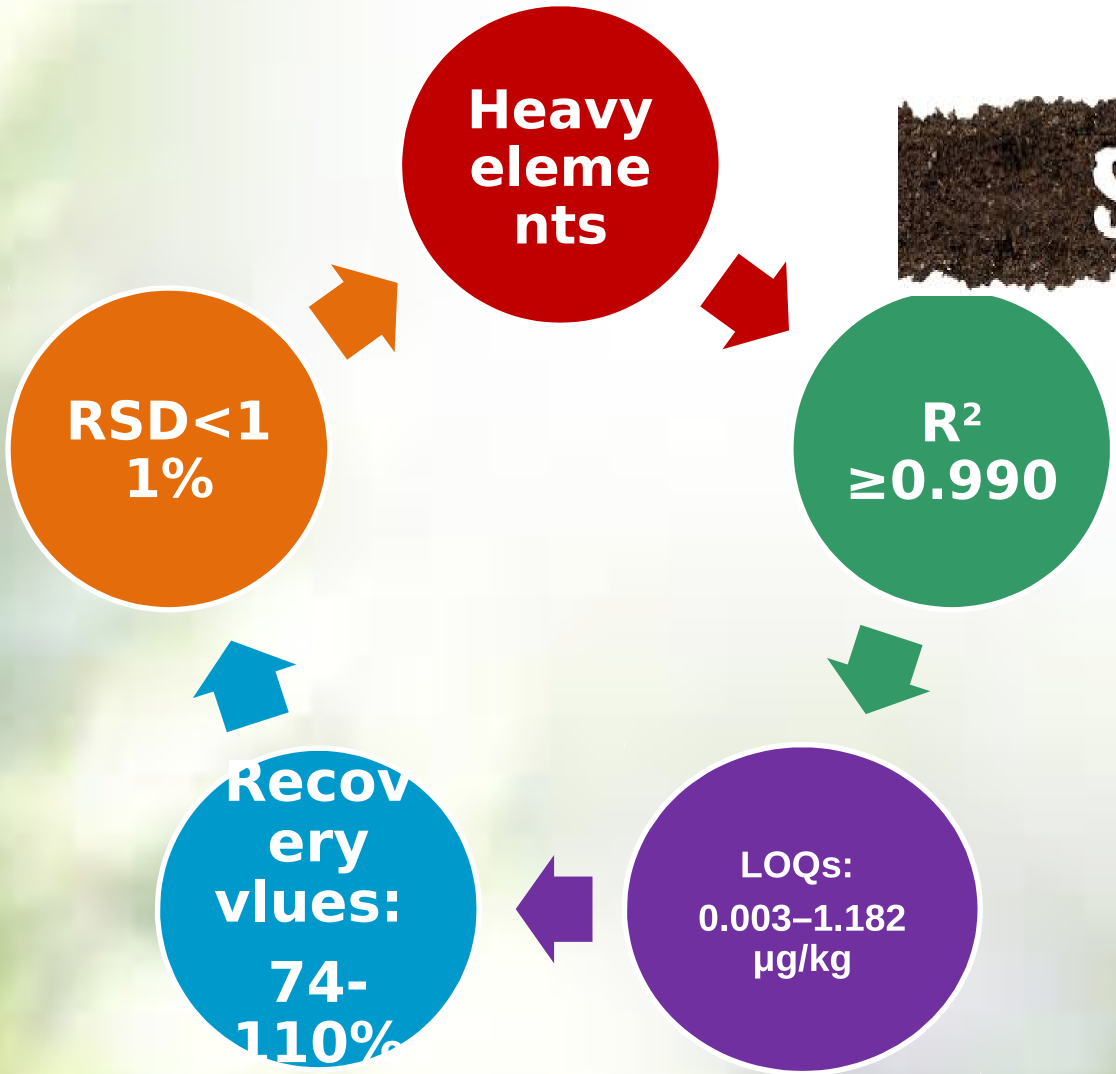
For heavy elements analysis, microwave unit (Ethos One, Milestone, Italy) was used for digestion of the samples.

The operational conditions and the heating program of the microwave system

Step	Time (min)	T1	P	Power
1	00:15:00	200 °C	45 bar	1200 W
2	00:15:00	200 °C	45 bar	1200 W

Contents of heavy elements were determined by atomic absorption spectrometry with a graphite furnace (Varian AA240/GTA120)

Summary of the validation data of the GFAAS method



Summary of the validation data of the GFAAS method

Heavy eleme nts

R^2 ≥0.990

LOQs: 0.003–1.182 µg/kg

Recov ery vlues: 73-102%

RSD<8 %

Quantification of soil pollution

Contamination factor (Cf)

$$C_f = \frac{C_i}{C_{ref}}$$

Potential ecological risk index (RI)

$$RI = \sum_{i=1}^{n} Er^i$$

Pollution load index (PLI)

$$PLI = (PI_1 \times PI_2 \times PI_3 \times \ldots \times PI_n)^{1/7}$$

Potential ecological risk factor (Er)

$$Er^i = Tr^i \times P_i$$

Geo-accumulation index (I_{geo})

$$I_{geo} = \log_2\left(\frac{C_i}{1.5 \times B_n}\right)$$

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, was calculated as follows:

$$BF = C_{plant}/C_{soil}$$

where Cplant and Csoil represent the heavy element concentrations in the edible part of plant 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, celery and parsnip, 31 g/day for onion and 144 g/day for potato.

Target hazard quotient

The target hazard quotient (THQ) was determined by the following equation:

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

where E_f is the exposure frequency (365 days years^{-1});
E_d is the exposure duration (70 years);
F_{ir} is the food ingestion rate (g person^{-1} day^{-1});
C is the metal concentration in vegetable samples (mg kg^{-1});
R_{fd} is the oral reference dose (mg kg^{-1} day^{-1});
W_{ab} is the average body weight (60 kg for adults); and
T_a is the average exposure time (365 days year^{-1} x 70 years).

The oral reference doses for selected elements are 0.004 mg kg^{-1} day^{-1}, 0.001 mg kg^{-1} day^{-1}, 0.04 mg kg^{-1} day^{-1}, 0.02 mg kg^{-1} day^{-1}, 0.00005 mg kg^{-1} day^{-1}, 0.7 mg kg^{-1} day^{-1} for Pb, Cd, Cu, Ni, Mn and Fe (EPA, 2016).

Hazard index

When more than one kind of heavy metals appear, the health risk associated with all measured heavy metals ingested through the vegetables should be additive.

Thus, the hazard index (HI) can be expressed as the sum of the hazard quotients (HQ) for all heavy metals and the HI is calculated as follows:

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$$HI = \sum_{i=1}^{n} TQHi$$

A **HI less than 1** indicates no obvious health risk to adults through vegetables consumption.

If the **HI is greater than 1**, it means there is a potential health risk to humans.

Heavy element contamination in soil

Descriptive statistic of heavy elements (mg kg^{-1}) on a dry weight basis

	As	Pb	Cd	Co	Cr	Cu	Ni	Mn	Fe
Flooded arable soil									
Minimum	1.47	9.14	0.16	0.09	16	12	12	538	610
Maximum	8.57	44	14	19	66	29	44	1550	2793
Mean	5.15	19	1.30	2.74	35	19	19	1037	1242
Median	4.83	18	0.43	0.29	37	19	15	1013	1240
Kurtosis	-0.48	3.17	16	2.71	-0.68	-0.60	3.24	-0.31	3.19
Skewness	0.17	-1.06	3.95	2.08	0.12	0.36	1.76	0.41	1.14
Background values[a]	2.19	14.81	0.48	-	2.41	10.82	4.26	-	-
Target values[b]	29	85	0.8	9	100	36	35	-	-
Intervention values[b]	55	530	12	240	380	190	210	-	-

[a]**Background metal concentrations for unpolluted agricultural soils of the region (Ubavić et al., 1993).**
[b] **Serbian standard target values for soil (OG RS 80/10, 2010).**

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 samples exceeded the maximum permissible value.

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The remediation values were not exceeded for any of the studied elements in any of the studied locations.

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In comparison with the background values, notably enrichment is found for most of the analyzed elements in flooded soil samples.

Heavy element contamination in soil

Pollution assessment of soil elements using different indices (contamination factor, potential ecological risk factor, potential ecological risk index, geo-accumulation index and pollution load index)

	Pb	Cd	Cr	Cu	Ni	
Flooded arable soil	Contamination factor (Cf)					
	0.63	3.51	0.43	0.84	0.52	
	Potential ecological risk factor (Er)					Risk index
	6.41	81	29	9	22	148
	Geo-accumulation index (Igeo)					
	0.13	0.71	0.09	0.17	0.11	
	Pollution index (PI)					Pollution load index (PLI)
	0.63	3.51	0.43	0.84	0.52	1.00

The Cf average based on background values for these elements indicates medium degree of contamination with Cu as well as strongly pollution for Cd.

As observed, Cf values calculated for other analysed elements classified the soil in category 1 (with none to medium pollution).

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Based on calculated Er, it should be mentioned that low degree of pollution was found for analyzed soil, with the exception for Cd (80≤Eri<160, considerable risk) in flooded soil.

However, the Er values for Cd were less than 40 for 86% of the flooded locations, indicating that most of the affected area had a low ecological risk of this element.

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The RI is calculated as sum of Er for each individual element and the obtained results showed that analyzed soil undergo considerable contamination (124≤RI<248) by PTEs.
The results highlighted that the highest contribution to the RI of all elements for the flooded soil gave Cd.

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The mean values of I_{geo} calculated for all analyzed elements in investigated soil showed that all sampling sites were unpolluted to moderately polluted and that soil belonged to class 1.

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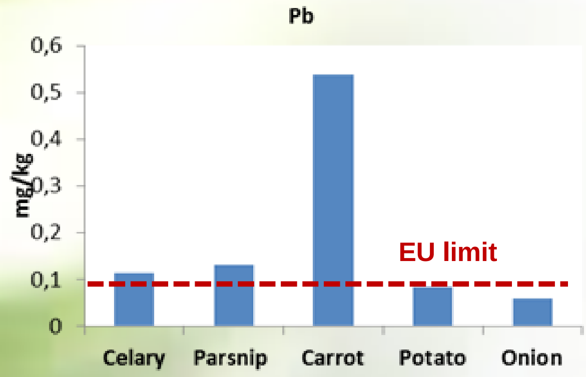
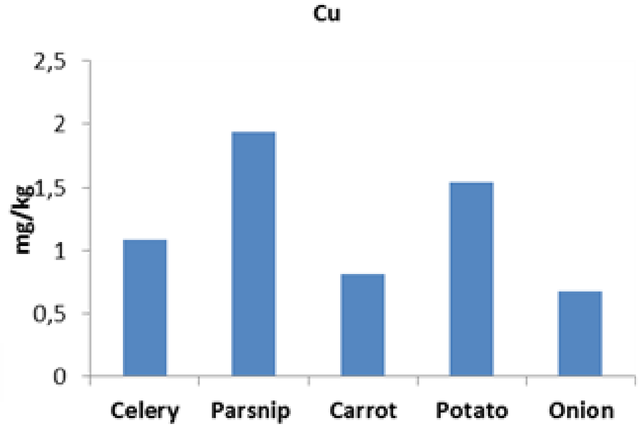
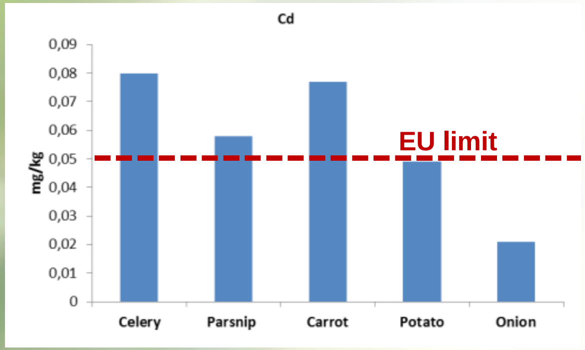
	0.63	3.51	0.43	0.84	0.52	1.00

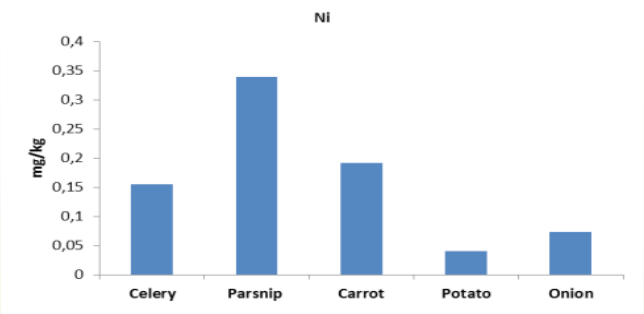
The obtained value for PLI indicated that pollution degree for soil was in unpolluted domain (PLI≤1), i.e. the investigated soil was not contaminated with the studied elements.

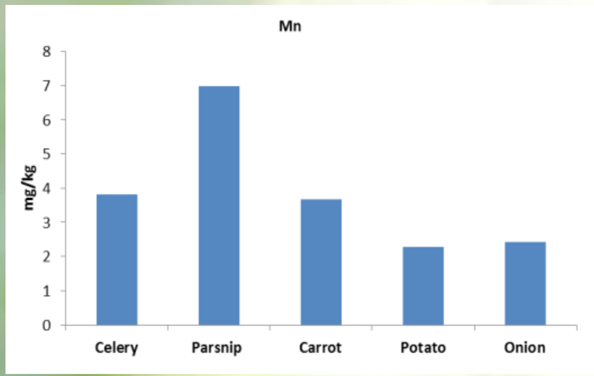
Heavy element contamination in vegetable crops

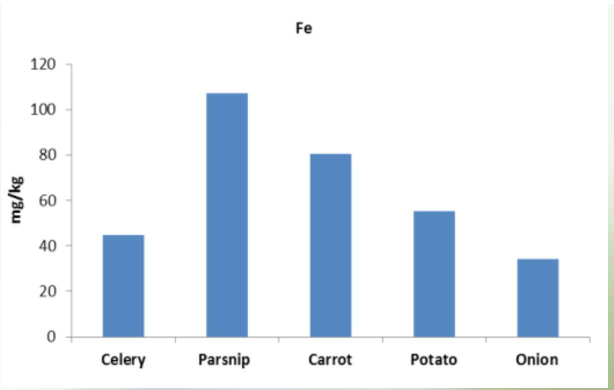






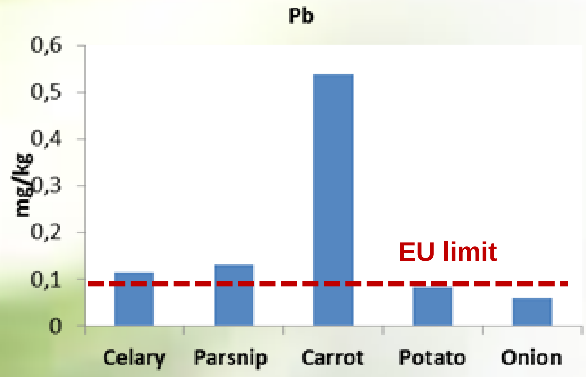


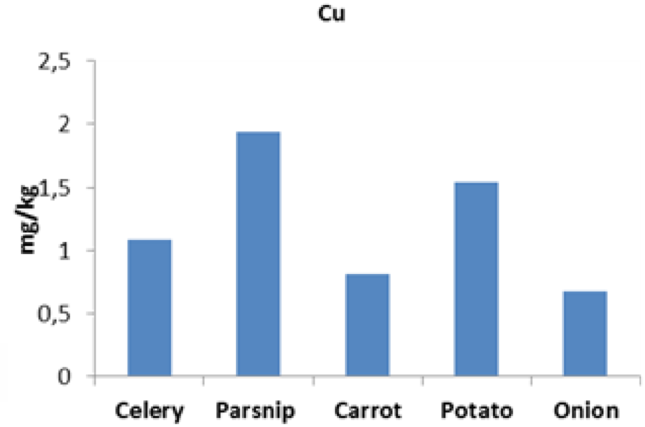


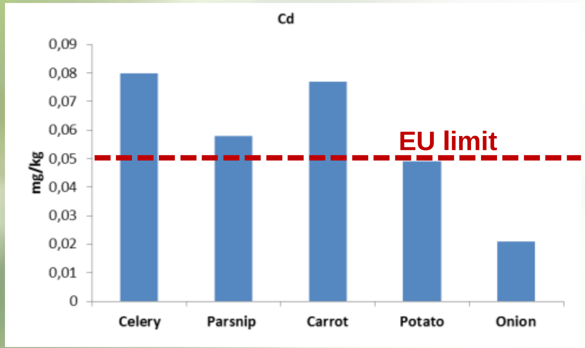


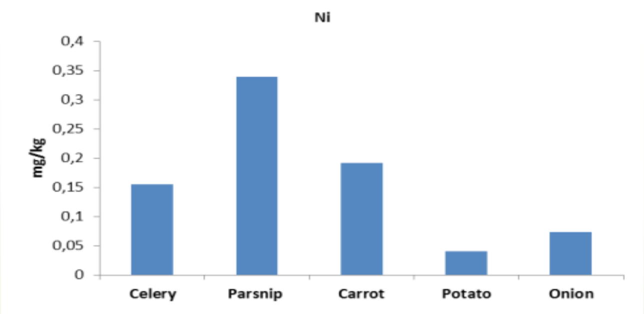
The highest average concentrations of Cu, Ni, Mn and Fe were found in parsnip, while the highest average levels of Pb and Cd were detected in carrot and celery, respectively.

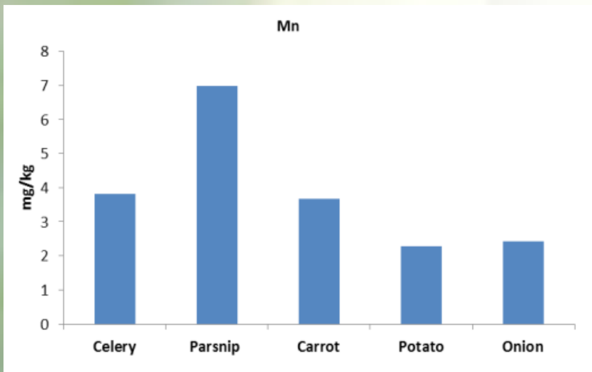
Heavy element contamination in vegetable crops

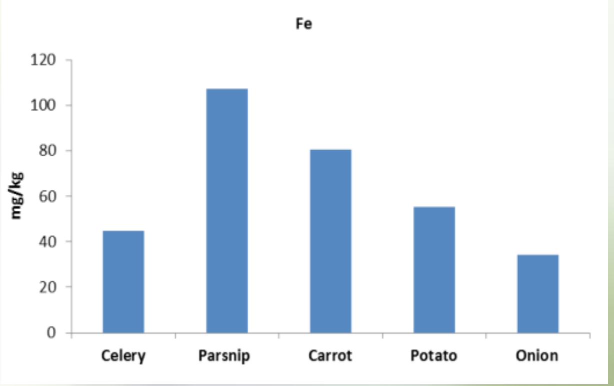






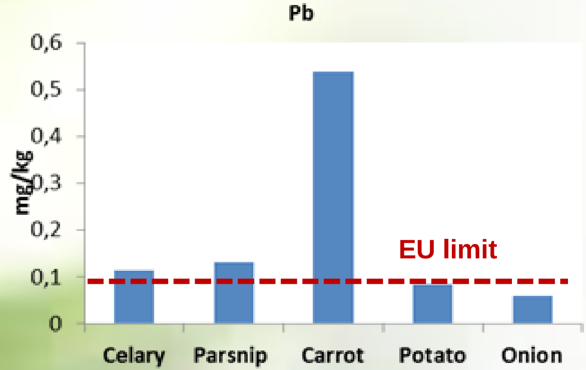


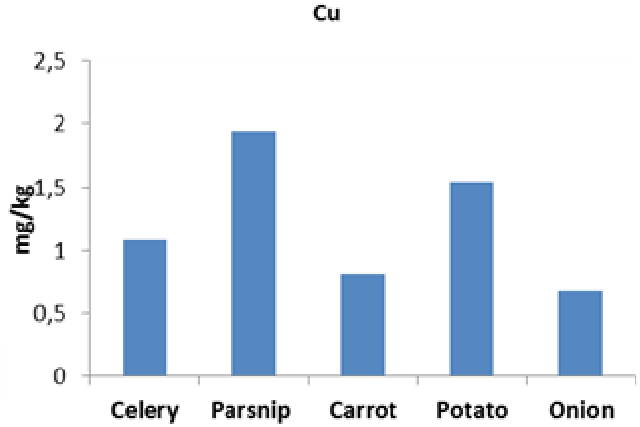


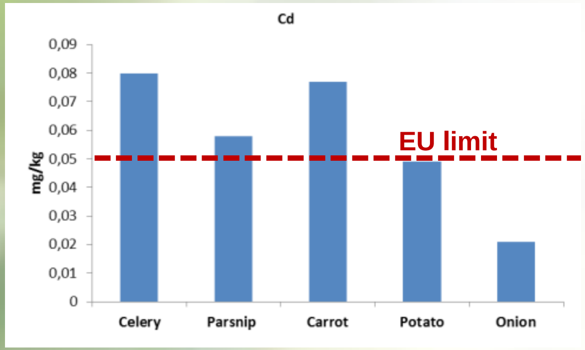


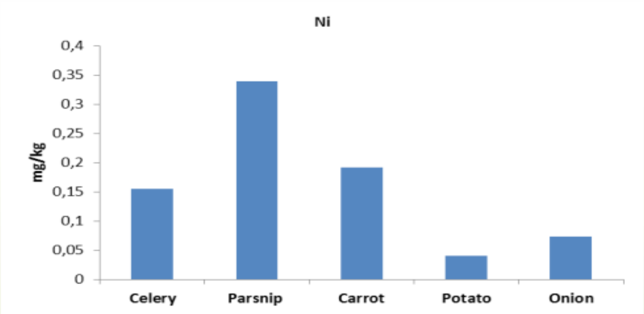
Generally, the lowest average concentrations of detected elements were in onion.

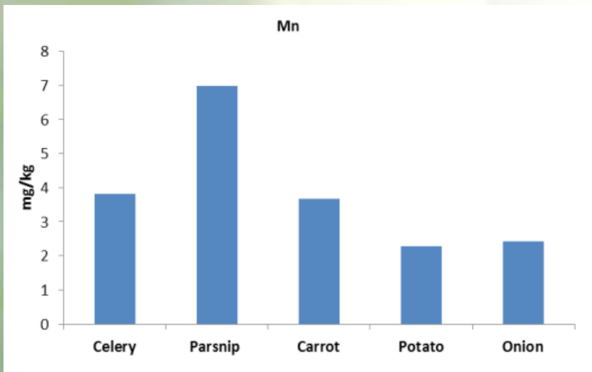
Heavy element contamination in vegetable crops

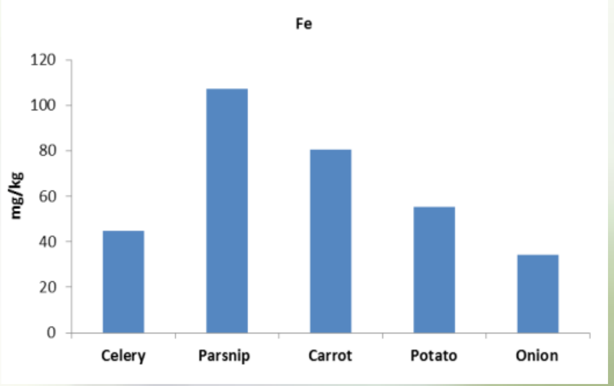






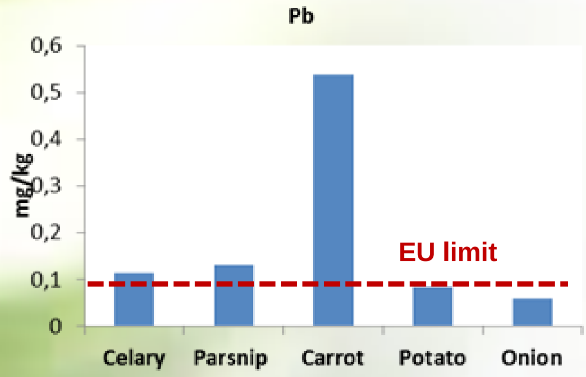


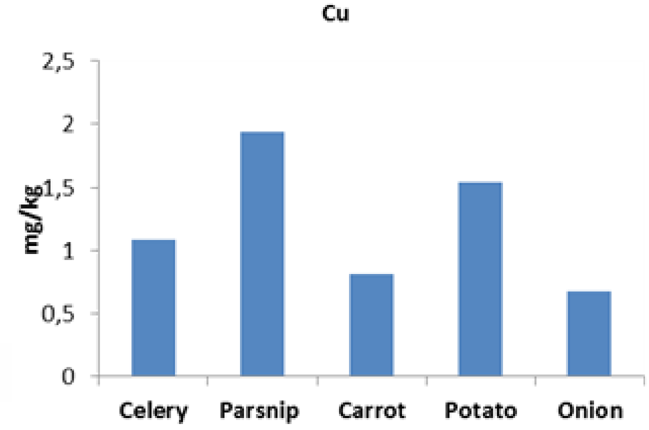


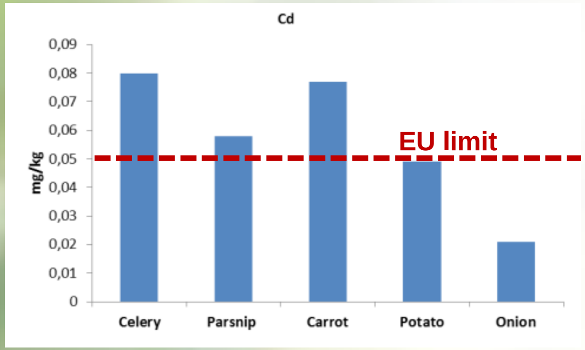


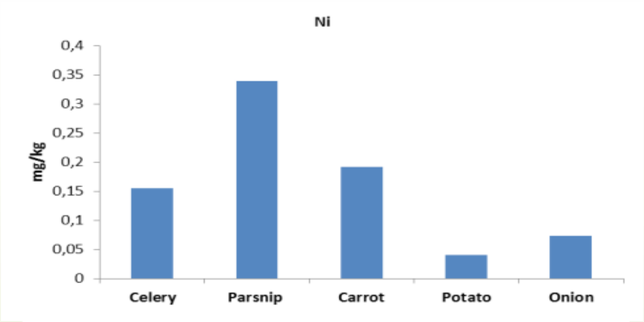
The Pb was found in carrot samples at the level of 0.54 mg/kg, which was almost 5 times higher than the maximum residue level of 0.1 mg/kg set by EC/Serbian regulation.
In other vegetables it was at level of maximum allowable concentration or below.

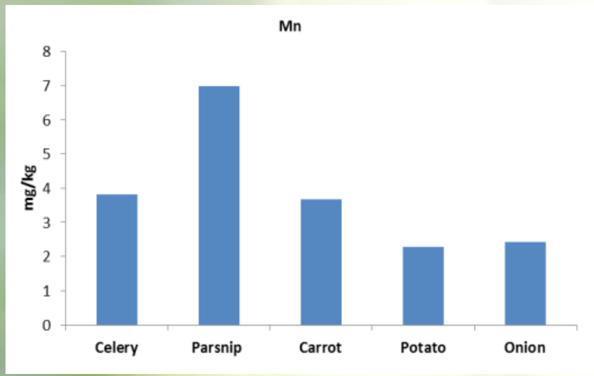
Heavy element contamination in vegetable crops

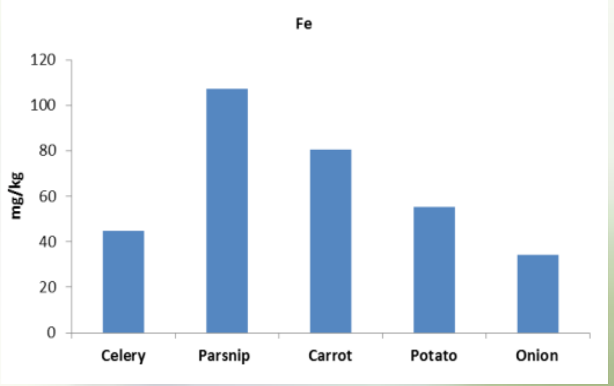






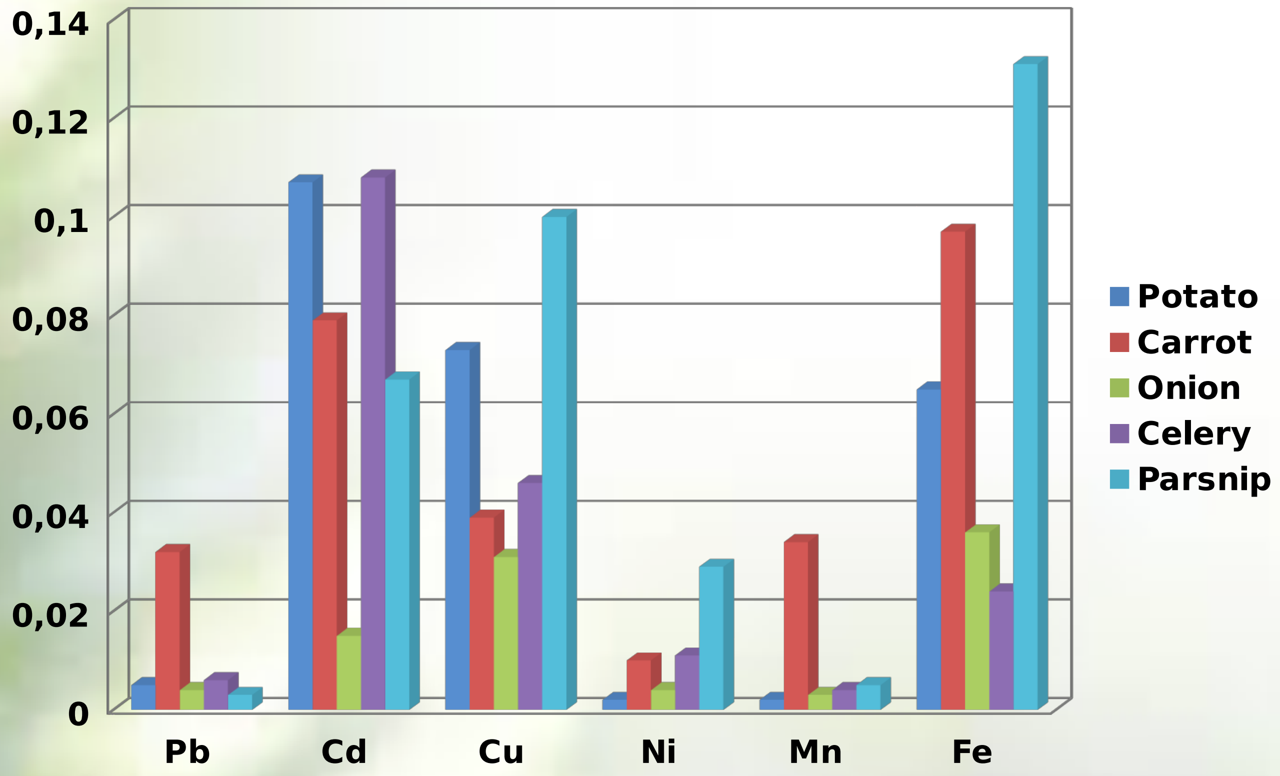






The Cd detected above ML in samples of celery, parsnip and carrot.
The lower concentrations Cd were found in samples of potato (0.05 mg/kg) and onion (0.02 mg/kg).

Average bioaccumulation factor (BF) of selected heavy elements from soil to different vegetable crops



As can be seen from Fig. element accumulation and translocation potential varied upon element to element and plant to plant in analysed vegetable crops.

The value of BF for Fe was the highest in parsnip taking into account all analysed heavy elements and vegetable crops.

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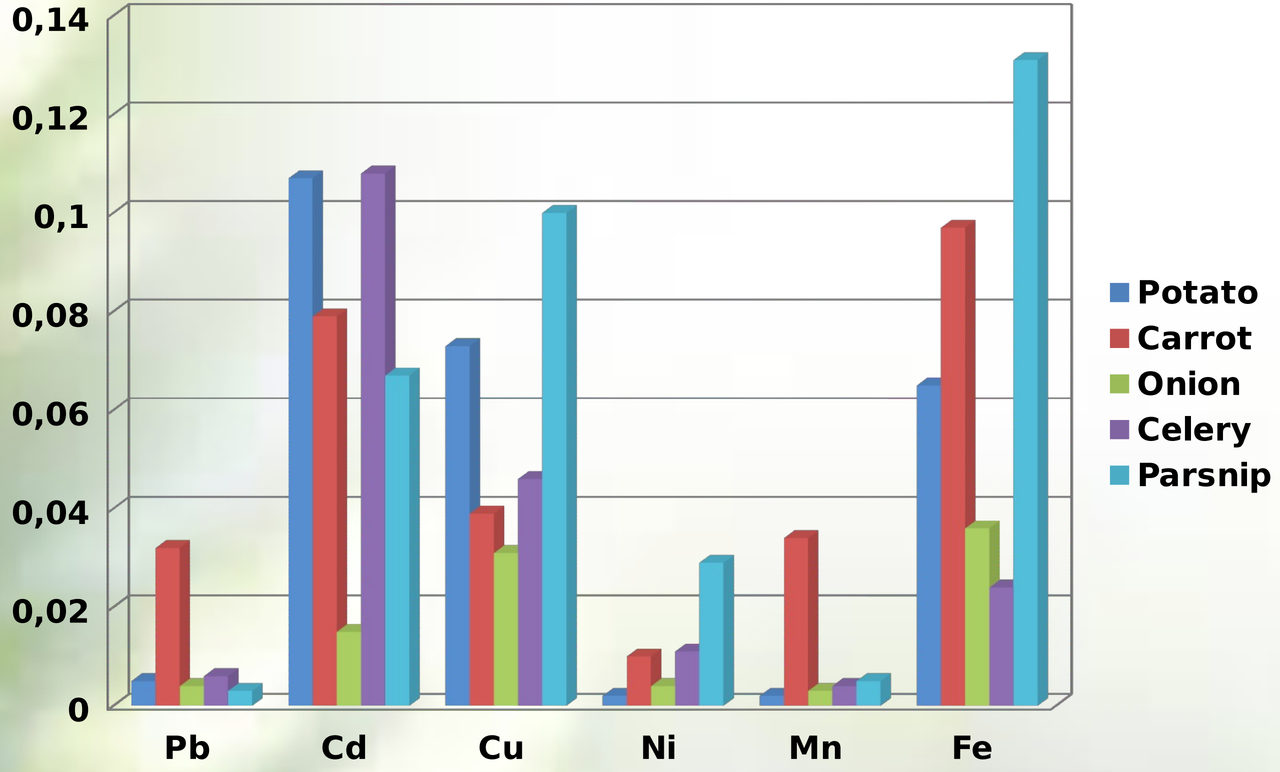

The BF value for Pb was the highest in the carrot, while for other analysed crops it was quite equable.

The BF values obtained for Cd in potato and celery were similar that for Cu in parsnip.

Risk assessment

The food chain (soil-plant-human) is recognized as one of the major pathways for human exposure to soil contamination.

Estimated daily intakes (EDI, mg day^{-1}) of selected elements through consumption of analysed vegetables for Serbian adult consumers

Vegetables	Consumption rate (g day^{-1})	EDI of analysed elements (mg day^{-1})					
		Pb	Cd	Cu	Ni	Mn	Fe
Potato	144	0.012	0.006	0.22	0.006	0.33	7.94
Carrot	18	0.009	0.001	0.01	0.003	0.06	1.37
Onion	31	0.002	0.002	0.02	0.002	0.08	1.07
Celery	18	0.002	0.001	0.02	0.003	0.07	0.76
Parsnip	18	0.002	0.001	0.03	0.006	0.12	1.82
Total intake		0.027	0.011	0.31	0.02	0.65	13
Recommended safe limits		0.044*/ 0.105**	0.058	3	0.1-0.3	11	48

*nephrotoxic effects, **cardiovascular effects

The calculated daily intakes based on the average detected concentration and daily consumption rate were compared with recommended safe limits reported by EU.

In this study, the highest daily intake was estimated for Fe through consumption of all analysed crops compared to other elements.

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Recommended safe limits		0.044*/ 0.105**	0.058	3	0.1-0.3	11	48

*nephrotoxic effects, **cardiovascular effects

Additionally, the greatest daily contribution to the total intake of Fe gave potato which is consequence of its highest consumption rate among the analyzed crops.

The estimated daily as well as total intakes of studied elements were far below recommended safe limits, not representing significant risk to Serbian adult population.

Risk assessment

Additionally, the potential health risk was assessed through target hazard quotation for each element as the ratio of determined dose of contaminant to a respective dose level.

The target hazard quotation (THQ) and health risk index (HI) of analyzed elements in different vegetable crops

Vegetables	THQ						
	Pb	Cd	Cu	Ni	Mn	Fe	TTHQ*
Potato	0.05	0.12	0.09	0.001	1.09	0.19	1.54
Carrot	0.04	0.02	0.01	0.003	0.22	0.03	0.32
Onion	0.01	0.001	0.01	0.001	0.25	0.03	0.30
Celery	0.01	0.01	0.08	0.01	0.01	3.36	3.48
Parsnip	0.01	0.004	0.15	0.03	0.52	8.04	8.75
$TTHQ_{analyt}$	0.12	0.16	0.34	0.05	2.09	12	HI=14

*TTHQ (individual food)= THQ

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.

Risk assessment

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*TTHQ (individual food)= THQ

Total of THQ calculated for each element had the following trend:

Fe˃Mn˃Cu˃Cd˃Pb˃Ni.

Potential health risk evaluated as HI was 14 (˃1) and it cannot be ignored, particularly,

keeping in mind other foodstuffs which were not subject of analysis as well as potential sources in the environment.

Conclusions

This study presents the first insight into the concentrations of 9 heavy elements in flooded arable soil, their translocation and accumulation in edible parts of selected crop plants as well as potential health risk.

Conclusions

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 of element concentration from soil.

Conclusions

- Although, the THQ values for most elements were below 1, total element THQ was above 1.

- The potential health risks of analysed elements from exposure to the vegetables are therefore of some concern.

- Furthermore, Fe and Mn are the elements with the highest contribution to the health risk.

Conclusions

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 these contaminants in different and the most consumable crop plants which grown in this region.

Thank you for your kind attention!