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Elevated selenium in vegetables, fruits, and wild plants affected by Raša coal mine water chemistry

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Abstract

Selenium (Se), an essential trace element that is toxic when humans and animals are exposed to it in excess, is ubiquitous in coal. For centuries, superhigh-organic-sulfur (SHOS) Raša coal, enriched in S, Se, U, V, and Mo, was mined and processed across the Mediterranean Raša Bay area, located in the Istrian peninsula (northern Adriatic Sea, Croatia). There is a concern that Raša coal mine water is contaminating local water, soil, and crops. The aim of this monitoring study was to determine levels of Se and selected potentially toxic trace (As, Cd, Cu, Cr, Mo, Pb, U, V, and Zn), and minor (Fe and Mn) elements in Raša coal mine water, surface water, and associated vegetables, one fruit, and wild plants. Levels of Se in coal mine water were increased (up to 12 µg/L) compared to a maximum allowed water Se (10 µg/L). Compared to an EU average soil Se (1.15 mg/kg), Raša garden soil showed a 5-fold increase in Se. Compared to Croatian and Greek vegetable Se levels (low to normal), Raša vegetables showed 20-fold, and a 50-fold increase in Se, respectively. Although approximative only, estimates of daily intake (EDI) of Se for mixed Raša vegetables (n = 21) showed a high level (0.055 mg/day). Namely, recommended dietary allowances (RDA) of Se for females and males are 0.055 mg/day, and 0.070 mg/day, respectively. The EDI values of the analyzed vegetables contributed to averaged RDA levels as follows: garlic (183%), turnip (154%), parsley (147%), onion and gourd (76%), lettuce (74%), kale (62%), radicchio (51%), and potato (20%). Although the calculated EDI for the analyzed Raša vegetables was 1/8 the toxic dose (>0.4 mg/day), these results call for further research on dietary and nutritional status of the residents in terms of Se.

Keywords: Raša coal, water, vegetables, selenium, estimated daily intake

1. Introduction

Coal is one of the most important sources of energy across a large part of the globe. Due to its highly complex composition (**Rađenović, 2006; Dai et al., 2012, 2015; Hower et al., 2016; Singh et al., 2015**), coal mining, processing, and combustion processes are emission sources of potentially toxic trace elements (PTEs) such as As, Cr, Cu, Cd, Mo, Pb, Se, U, V, Zn, etc. (**Hower et al., 1999; Saikia et al., 2018**). Their environmental fate is a matter of great concern for humans. Their adverse effects on humans and animals largely result from drinking contaminated water, and consuming crops grown on contaminated land (**Barla et al., 2017; Majumdar et al., 2019; Sasmaz et al., 2019; Upadhyay et al., 2019**). Since Se is a very coalphile element (**Yudovich and Ketris, 2006**), it should be monitored in coal-affected areas due to its narrow range between dietary essentiality and toxicity for life forms (**Lemly, 1997**). Selenium is essential for humans and animals due to its role in a number of enzymes, such as glutathione peroxidase, in which selenocysteine serves as the catalytic site (**White, 2016**). Although Se is a beneficial element for plants, its excessive amounts can be toxic to both animals and plants (**Alexander and Meltzer, 1995**). High-sulfur coals are particularly enriched in Se, U, Mo, and V (**Yudovich and Ketris, 2006; Dai et al., 2015, 2017**).

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Soil pollution with coal-derived compounds has been reported across the globe (**Espitia-Pérez et al., 2018; Luo et al., 2019; Maqbool et al., 2019**). Soil is the most commonly encountered geomaterial. It is continually changed and formed, while at the same time it interacts with crops, aquifers, air, and humans. Humans are constantly exposed to soil particles during their daily activities. One coal-related example is the case of Se pollution of soil, water, and locally grown food in China decades ago (**Yang et al., 1983**). This pollution resulted in an acute intoxication of humans with Se, in parts of the population of the Chinese Enshi County. The morbidity rate was almost 50% among 248 inhabitants of the five most heavily affected villages during 1961-1964. This geomedical problem was interpreted by processes of weathering of local coal enriched in Se, and the Se uptake by crops consumed by villagers (**Yang et al., 1983**). An average concentration of Se in the earth's crust is 0.1 mg/kg (**James and Shupe, 1984**). Plants vary significantly in their ability to accumulate Se from the soil, and even different species of plants growing in the same area contain non-uniform amounts of Se (**James and Shupe, 1984**). Selenium levels in cultivated crops, grains, and native grasses grown on seleniferous soils are usually less than 20 mg/kg dry weight (d.w.). Poisoning is most common in grazing animals such as cattle, sheep, and horses, which may forage on seleniferous grasses or shrubs, and one of the consequences is a reduced animal reproduction (**James and Shupe, 1984**).

Upon exposure, Se is incorporated into human as well as animal enzymes which regulate normal body processes. Chronic exposure to Se results in a condition in livestock known as alkali disease, characterized by lack of vitality, anemia, stiffness of joints, deformed and sloughed hoofs, roughened hair coat and lameness. Chronic toxicity studies have shown that dietary items containing 5 mg/kg d.w. or more of Se result in chronic toxicity in laboratory animals (**Koller and Exon, 1986**). The pharmacokinetics and biochemical actions of Se are comparable for humans and animals. Symptoms of selenosis for humans are hair loss, brittle, thickened and stratified nails, garlic breath and skin, red, swollen skin of hands and feet that may blister or even ulcerate, excessive tooth decay and abnormalities of the nervous system inclusive of numbness, convulsions, and paralysis (**Koller and Exon, 1986**). A daily intake of Se varies considerably between countries and regions of countries largely owing to the variability of the Se content of plant foods (and hence of animal forage) from one part of the world to another (**Rayman, 2008**). Overt Se toxicity in humans is far less widespread than Se deficiency; chronic exposure to high levels of Se has been observed in several populations in seleniferous areas such as the northern great plains of the USA, parts of Venezuela and Colombia, and the Chinese Enshy county (**Rayman, 2008**). Low or deficient Se intakes are found in Eastern European countries, and parts of China (**Rayman, 2008**). For example, in eastern Croatia, low Se concentrations in agricultural soils and occurrence of deficiency disorders in animals were reflected by an inadequate daily intake of Se (0.027 mg/day) which was 61% of the recommended optimal values (**Klapec et al., 1998**).

In Croatia, a special class of coal, known as superhigh-organic-sulfur (SHOS) Raša coal, was mined across a Raša town county (**Figure 1**) for centuries (**Medunić et al., 2020a**). Its exploitation ceased in 1999, and 4.4 Mt of coal remains underground. Coal research in Croatia is quite scarce as the coal mining industry (SHOS Raša coal) ceased altogether 20 years ago. Coal studies have been mainly focused on detrimental consequences of SHOS Raša coal mining and combustion on the local environment (**Medunić et al., 2016, 2018, 2019, 2020a, b**). The local bedrock is composed of karst, overlain by thin terra rossa soil. Raša coal combustion resulted in soil pollution with sulfur, PTEs, and organic compounds (**Medunić et al., 2016; Dvoršćak et al., 2019**), and specific distribution patterns of rare earth elements in soil (**Fiket et al., 2016**). Following the closure of underground coal mine shafts, their voids were filled with groundwater, which has been discharged directly into local streams ever since (**Figure 1**). **Medunić et al. (2018)** found increased levels of PTEs, especially Se, in surface fresh- as well as seawater, stream and submarine sediment, soil, and locally grown lettuce and potato samples. Arguably, the local environment has been affected by leaching of Raša coal, induced by circulation of groundwater (**Medunić et al., 2020a, b**). The process is facilitated in the karstic and seawater environments, characterized by oxidative and alkaline conditions, which contribute to the mobilization of Se (**Dreher and Finkelman, 1992**).

Herewith, the overall objectives of this monitoring study were to determine levels of Se and selected PTEs in the Raša town environment, in order to alert local authorities to initiate cleanup activities in the foreseeable future. Namely, Raša coal mine discharges and surface water were newly sampled to see whether their chemistry was comparable with previous sampling campaigns conducted in 2017/18 (**Medunić et al., 2018**). Compared to the 2017/18 campaigns, garden soil was sampled together with much more available vegetables; i.e. kale, turnip, gourd, onion, radicchio, parsley, and garlic for the first time, while lettuce and potato for the second time. Wild plants, elderberry, nettle, and yarrow, and fruits (figs) were sampled and analysed for the first time. Due to financial restraints, only a limited number of edible items was collected, and therefore data analysis had no statistical significance. Hereby, estimated daily intake (EDI) of Se, calculated by using Croatian average consumption values of the analyzed vegetables, should be taken as an approximative (general) measure only.

2. Materials and methods

2.1. Sampling and sample preparation

The study area’s local as well as regional characteristics in terms of geology, pedology, geography, and climate are presented elsewhere (**Durn et al., 1999**). Three sampling campaigns were conducted in former, closely located coal-mining towns Krapan and Raša, connected with the Krapan stream (**Figure 1**). Along its right bank, three private gardens (Krapan: n = 2, and Raša: n = 1) were selected for the sampling of topsoil (down to depth of 10 cm), which was red to brown colored clay-loam soil. Local residents have different habits in terms of crop cultivation; some of them use neither chemicals nor irrigate crops, while other ones use chemicals occasionally, and irrigate crops either with Raša coal mine discharges or water stored in metal barrels. Soil samples were air-dried, sieved through 1 mm, and homogenized in an agate mortar.

Available vegetables were the following: kale (n = 4), turnip (n = 3), gourd (n = 1), onion (n = 4), radicchio (n = 2), parsley (n = 2), garlic (n = 2), lettuce (n = 2), and potato (n = 1). They were collected in November 2018 and February 2019. Close to a coal mine water effluent in Krapan, wild plants (elderberry, nettle, and yarrow), and fruits (figs), were collected in May 2019 (n = 2 per item). Plant samples were cleaned with tap water and Milli-Q water, and then separated into roots (tubers), stems, flowers, and leaves, depending on a plant. Following the drying at room temperature, they were grated with a polypropylene grater in the porcelain containers, and finally stored in plastic bags in a fridge. Plant PTE data are expressed as fresh weight (f.w. basis).

Water samples (n = 7) were collected (February 2019) inside of two spatially related underground Raša coal mine shafts, and also outside, where the water gets discharged into the nearby Krapan stream (**Figure 1, CME**). In the garden no. 1 there was an old metal barrel with water collected for the crop irrigation purpose (mix of rain water and coal mine water); it was also sampled (n = 1). Samples were collected from a maximum depth of 10 cm, in acid-cleansed plastic bottles, and analyzed the next day.

Figure 1: Map of the study area. A) The geographical position of the Raša county (east coast of the Istrian Peninsula, North Adriatic, Croatia); b) aerial view of the study area: three garden plots (no.1, no.2, and no.3) with vegetables along the Krapan stream (CME – coal mine effluent/discharges).

2.2. Multielement analyses

Measurements of Se and PTEs in soil, vegetable, fruit, and wild plant samples were conducted using inductively coupled plasma mass spectrometry (ICP-MS) technique. Each soil sample (0.5 g) was weighed into a pre-cleaned Teflon vessel. Then, 8-mL of aqua regia (digestion solution obtained by mixing 1 volume of nitric acid and 3 volumes of hydrochloric acid) was added and heated in a microwave oven using the following operating conditions: (I) 2 min at 250 W, (II) 10 min at 400 W, and (III) 10 min at 600 W. Homogenized plant samples (0.5 g) were weighed into a Teflon liner with the addition of 3 mL H_2O and 2.5 mL HNO_3 (65%). Wet digestion was performed using a highpressure microwave oven Multiwave 3000 (Anton Paar, Graz, Austria) by the digestion program in three potency steps: (I) 2.5 min at 500 W, (II) 20 min at 1000 W, and (III) 30 min at 1200 W. Following the cooling to room temperature, the digested clear solution was quantitatively transferred to a 50 mL volumetric flask and made up to the mark with Mili-Q water. A mix of internal standard (ISTD) solution containing In, Bi, and Sc (Inorganic Ventures, Blacksburg, VA, USA) was added on-line using the standard ISTD mixing tee-connector. Element concentrations were determined by ICP instrument with mass detector Agilent ICP-MS system Model 7900 (Agilent, Palo Alto, CA, USA). High-purity argon (99.99%, White Martins, Brazil) was used throughout the analysis. Calibration of the instrument was carried out using certified standards of 99.9% purity for all elements (Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, V, Zn), and concentration of 10 mg/L as a stock solution (Environmental Calibration Standard, Agilent Technologies, USA). Stock solutions for ICP-MS analysis were prepared by dissolving the multi-element standard mixture solution with Mili-Q water. Working solutions were prepared by serial dilution of stock solutions with 5.0% v/v HNO_3, and kept at room temperature until further use. Calibration concentration range was 0.1-100 µg/L. The accuracy of the analysis was checked using the standard reference material 1515 Apple Leaves in the case of plant sample analyses (National Institute of Standards & Technology, Gaithersburg, Maryland, USA). For soil analysis, ERM CC141 Loam soil (Institute for Reference Materials and Measurements, Geel, Belgium) was used. The reference material was treated in the same manner as samples, within each analytical run, and the obtained results were within ± 5% of the certified values.

Element concentrations in water samples were determined as follows: prior to analysis, all the samples were acidified with 2% (v/v) HNO_3 s.p., and In (1 µg/L) was added as an internal standard. Multi-element analysis of the prepared water samples was performed by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) using an Element 2 instrument (Thermo, Bremen, Germany). External calibration was used for the quantification. Standards for multi-element analysis were prepared by an appropriate dilution of a multi-element reference standard (Analytika, Prague, Czech Republic) containing Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Se,Sr, Ti, Tl, and V, in which single element standard solution of U (Aldrich, Milwaukee, WI, USA) was added. All the samples were analyzed for total concentrations of the following elements: Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Se, Sr, Ti, Tl, U, and V. Quality control of the analytical procedure was performed by simultaneous analysis of the blank and the certified reference material for water (SLRS-4, NRC, Canada). A good agreement between the analyzed and the certified concentrations within their analytical uncertainties for all elements was obtained (± 10%).

2.3. Data analysis

Data analysis was conducted with the free PAST software (**Hammer et al., 2001**). It included calculations of basic statistical parameters, Kendall's Tau correlation coefficients, and Kruskal-Wallis test. Level of significance was 0.05.

3. Results and Discussion

3.1. Concentrations of PTEs in Raša coal mine water

Basic statistical parameters of Raša coal mine water PTEs are shown in **Table 1**. It is clear that Al, Ti, Mn, Fe, Sr, Mo, V, U, and Se max as well as Q_{75} values exceeded the world stream water values (**Reimann and de Caritat, 1998**), and/or Croatian regulation on the karst and table water (**OG, 2008**). Similarly, **Medunić et al. (2018, 2019)** reported that PTEs in the local surface Krapan stream water were higher than regulation. Strontium values (**Table 1**), indicative of mixing of fresh groundwater and seawater, here also reflect complex karstic hydrogeological circulation processes reported by **Medunić et al. (2020b)**. Moreover, the levels of Mo, V, U, and Se are increased in surface water, thus indicating on the problem related to the leaching of SHOS Raša coal (**Dai et al., 2015; Medunić et al., 2020a**). This possibly serious environmental issue should be incorporated and elaborated in future Labin and Raša urban as well as communal planning actions aimed at improved water quality (**Studija izvedivosti, 2017**). Namely, simultaneous removal of Se and other PTEs from wastewater is quite challenging, yet efficient and promising technologies are underway (**Aman et al., 2011**).

Table 1: Levels of PTEs (µg/L) in Raša coal-mine water (n = 7). Q_{50} – median; Q_{25} and Q_{75} – quartiles. a – **Reimann and de Caritat (1998)**, b – **OG (2008)**. Bold underlined values exceed the world stream water values (column a), and/or Croatian regulative values for the karst water (column b)

	Min	Max	Mean	SD	Q_{50}	Q_{25}	Q_{75}	a	b
Li	0.51	1.22	0.74	0.3	0.59	0.56	0.88	3	
Be	0.002	0.02	0.01	0.01	0.01	0.01	0.02	0.1	
Rb	0.49	1.87	0.86	0.5	0.62	0.59	1.19	1.1	
Sn	0.01	0.27	0.06	0.1	0.03	0.01	0.05	0.01	
Tl	0.01	0.05	0.03	0.01	0.03	0.02	0.04	0.04	
Bi	0.005	0.013	0.01	0.003	0.01	0.01	0.01	0.005	
Al	12.3	**644**	155	240	23.4	17.6	**331**	300	200
Ti	0.51	**28.3**	6.68	11	0.91	0.70	**14.4**	3	
Mn	0.25	**15.5**	4.46	6.1	0.47	0.28	**10.2**	4	50
Fe	10.9	**713**	189	260	22.0	12.6	**285**	40	200
Co	0.02	0.30	0.09	0.1	0.03	0.02	0.19	0.2	
Sr	477	**791**	682	110	675	638	**773**	70	
Sb	0.13	0.31	0.19	0.1	0.17	0.14	0.28	0.1	5
Ba	12.9	25.8	22.0	4.2	23.3	22.3	24.3	20	700
As	0.24	0.70	0.39	0.2	0.33	0.31	0.48	4	10
Cd	0.01	0.12	0.09	0.04	0.09	0.09	0.12	0.02	5
Pb	0.01	0.91	0.23	0.3	0.03	0.02	0.45	3	10
Cr	0.10	2.66	1.08	0.8	0.79	0.70	1.67	0.7	50
Ni	0.29	2.30	1.00	0.7	0.72	0.60	1.60	0.3	20
Cu	0.36	2.98	1.05	1	0.46	0.41	1.51	3	2000
Zn	0.01	3.88	0.92	1.4	0.04	0.01	1.40	15	3000
Mo	1.53	**16.5**	12.9	5.3	14.0	12.4	**16.4**	0.5	
V	0.14	**6.30**	3.49	1.9	3.21	2.90	**4.95**	0.9	5
U	0.85	**2.26**	1.89	0.5	2.01	1.82	**2.20**	0.04	
Se	2.81	**12.1**	9.37	3.3	10.9	7.70	**11.9**	0.2	10

Selected element correlations ($p < 0.05$) were all positive, thus indicating similar geochemical behaviour (**Table 2**). They formed a descending order as follows: U-Cd = V-Cd = Sr-Cd = U-V = U-Sr = V-Sr > Mo-Cd = Mo-U = Mo-V = Mo-Sr = Mo-Se > Cd-Cr = Cd-Se = U-Cr = U-Se = V-Cr = V-Se = Cr-Sr = Sr-Se > Cr-Mo > Pb-Fe = Sr-Se. The results displayed in **Tables 1** and **2** clearly show that the groundwater (Raša coal mine discharges) from the Raša town area is contaminated with Se, U, V, and Mo (Al, Ti, Mn, and Fe in lesser extent as well), as a consequence of the Raša coal leaching processes (**Medunić et al., 2020a**). An ensuing problem is the fact that local residents, who assume that the water is pristine, use it for the crop irrigation. This practice is not advisible, based on the results of this study.

Table 2: Kendall's tau correlation coefficients (below the diagonal) of selected Raša coal mine water PTEs (bold italic ones are significant at $p < 0.05$; p values are displayed above the diagonal)

	Mo	**Cd**	**Pb**	**U**	**V**	**Cr**	**Fe**	**Sr**	**Se**
Mo		0.00	0.21	0.00	0.00	0.00	0.21	0.00	0.00
Cd	***0.98***		0.17	0.00	0.00	0.00	0.17	0.00	0.00
Pb	0.39	0.43		0.17	0.17	0.29	0.01	0.17	0.29
U	***0.98***	***0.99***	0.43		0.00	0.00	0.17	0.00	0.00
V	***0.98***	***0.99***	0.43	***0.99***		0.00	0.17	0.00	0.00
Cr	***0.88***	***0.90***	0.33	***0.90***	***0.90***		0.09	0.00	0.01
Fe	0.39	0.43	***0.81***	0.43	0.43	0.52		0.17	0.29
Sr	***0.98***	***0.99***	0.43	***0.99***	***0.99***	***0.90***	0.43		0.00
Se	***0.98***	***0.90***	0.33	***0.90***	***0.90***	***0.81***	0.33	***0.90***	

3.2. Concentrations of PTEs in garden soil and vegetables

3.2.1. Estimates of element accumulation and translocation from soil to vegetables

Total levels of PTEs in garden soil and vegetables are presented in **Table 3**. Compared to legislative and world data levels of PTEs in soil (**Kabata-Pendias, 2010**), only Se and Mo were increased in garden soil. Garden soil Se values were fairly comparable with Se levels (3-10 mg/kg) in technogenic soil reported by **Medunić et al. (2018),** and **Fiket et al. (2020**). Similarly, **Sasmaz (2009)** reported soil Se levels from a Keban Pb-Zn-F mining area (Turkey), ranging from 0.1 to 6.5 mg/kg (mean: 1.35 mg/kg). The author found the highest Se concentration (6.5 mg/kg) for a soil sample collected from a mineralized vein, and strong linear correlations among Se and PTEs (Cu, Pb, Zn, Co, Mo, As, Au, Fe, Cd, and Bi), explained by soil weathering processes.

Table 3: Levels of PTEs in soil (mg/kg), and vegetables (mg/kg fresh weight (f.w.)) collected from three (no. 1., 2., and 3.) private gardens in Krapan and Raša towns. Bold italic underlined vegetable PTE values are increased compared to respective published ones (**Klapec et al., 2004; Pappa et al., 2006; Broadly et al., 2012; Hasanuzzaman et al., 2014**)

	Cr	Mn	Fe	Cu	Zn	As	Cd	Pb	Mo	Se
soil (garden no. 1)	94.0	736	28,900	41.2	144	15.3	1.05	40.7	1.57	5.38
kale leaf	0.85	***13.6***	***256***	1.77	5.50	0.13	0.04	***0.65***	***0.45***	***0.16***
kale root	0.22	***10.1***	***64.5***	0.98	4.47	0.03	0.08	0.24	***0.09***	***0.11***
lettuce leaf	***8.41***	***34.4***	***695***	***4.06***	***11.3***	***0.35***	0.06	***1.28***	***0.32***	***0.25***
turnip root	0.02	0.15	3.04	0.22	2.96	0.01	0.01	0.01	***0.20***	***0.28***
soil (garden no. 2)	114	917	33,800	40.9	146	17.1	1.12	39.1	3.06	5.06
gourd	0.08	1.94	***23.4***	1.10	4.08	0.01	0.01	0.04	***0.28***	***0.24***
potato	0.21	0.62	10.2	***3.01***	1.93	0.01	0.08	0.02	***0.31***	***0.06***
onion leaf	0.14	***4.02***	***33.5***	1.29	1.52	0.02	0.01	***0.36***	***0.34***	***0.11***
onion root	0.07	1.01	12.7	2.17	3.27	0.02	0.02	0.09	***0.40***	***0.06***
radicchio leaf	0.27	***6.44***	***84.8***	2.51	6.42	0.04	0.04	0.15	***0.14***	***0.16***
radicchio root	0.10	2.02	***20.9***	1.84	4.76	0.02	0.06	0.03	***0.34***	***0.16***
parsley leaf	0.21	***7.20***	***49.9***	1.07	7.25	0.02	0.02	0.06	***0.35***	***0.54***
parsley root	0.07	3.52	***23.3***	***3.89***	9.52	0.01	0.09	0.06	***0.67***	***0.39***
soil (garden no. 3)	81.9	759	24,400	47.2	200	14.5	0.89	49.6	3.31	4.17
lettuce leaf	0.85	***13.0***	***169***	***4.17***	3.89	0.11	0.03	0.23	***0.20***	***0.22***
garlic leaf	0.61	***5.42***	***158***	2.45	8.93	0.08	0.03	***0.42***	***0.86***	***0.66***
garlic root	0.32	***4.98***	***90.4***	***3.47***	9.11	0.05	0.08	***0.40***	***0.85***	***0.49***
onion leaf	0.07	***4.44***	***22.6***	0.63	2.12	0.01	0.00	0.05	***0.27***	***0.43***
onion root	1.49	***9.88***	***329***	***6.33***	8.64	0.22	0.09	***1.04***	***0.29***	***0.35***
kale leaf	0.29	***16.6***	***82.3***	2.43	6.61	0.05	0.03	***0.34***	***0.27***	***0.38***
kale root	0.23	***10.0***	***54.7***	2.42	4.55	0.03	0.02	***0.39***	***0.08***	***0.14***
turnip leaf	0.37	***5.41***	***117***	2.11	7.28	0.06	0.04	***0.45***	***0.35***	***0.56***
turnip root	0.04	0.59	5.96	1.40	2.07	0.06	0.03	0.08	***0.09***	***0.61***

The values of Cr, Mn, Fe, Cu, Zn, As, Cd, and Pb in vegetables were compared with the respective Croatian regulative levels (mg/kg f.w.) (**OG, 2005**) as follows: 0.04-15, 2-4, 20, 1-3, 10-15, 0.3, 0.1-0.2, and 0.1-0.3, respectively. Except for Cd, all the analyzed PTEs were increased at least in one vegetable item. Generally, soft leafy items showed higher PTE levels compared to respective roots (tubers). The lettuce from the garden no. 1. was the most polluted vegetable, especially in terms of Pb, As, Zn, Fe, Mn, and Cr. Increased PTE levels could be explained by water stored in an old rusty barrel (in the garden no. 1.), occasionally used for the crop irrigation (**Sarwar et al., 2019**). Its PTE levels (μg/L) were following (world stream water levels published by **Reimann and de Caritat (1998)** are given in parentheses): Cd 1.15 (0.02), Sn 0.03 (0.01), Pb 5.02 (3), Cr 2.58 (0.7), Mn 164 (4), Fe 889 (40), Co 0.9 (0.2), Ni 0.8

(0.3), Cu 3.4 (3), and Zn 2992 (15). Herewith, it can be said that the irrigation water was anomalously polluted with Mn, Fe, and Zn.

Since Mo is associated with Se in SHOS Raša coal (**Medunić et al., 2020a**), its soil values were expectedly slightly above the world average of 1.8 mg/kg (**Kabata-Pendias, 2010**). Due to its mobility and availability in alkaline conditions, plants grown on Mo-contaminated land can exhibit increased Mo levels (**Kabata-Pendias, 2010**). World vegetable Mo levels (mg/kg f.w.) are generally from 0.005 to 0.099. By comparing the literature Mo values (**Kabata-Pendias, 2010**) of lettuce (0.005), potato (0.047), and onion (0.024) with respective ones shown in **Table 3**, it is clear that the analyzed Raša vegetables were enriched in Mo.

A special attention was paid to Se in analyzed vegetables as its levels were increased in SHOS Raša coal (**Medunić et al., 2020a**), Raša coal mine water (**Table 1;** and **Medunić et al., 2019, 2020b**), and garden soil (**Table 3**). **Klapec et al. (2004)** carried out a study at Croatian localities low in Se (some 500 km away from the Raša town), and found following vegetable Se values (mg/kg f.w.): cabbage, carrot, and red beet 0.008, onion 0.012, garlic 0.057, parsley 0.009, potato 0.007, and celery 0.014. Compared to them, the analyzed Raša vegetables showed 20-fold increase in Se levels. A Greek study (**Pappa et al., 2006**) reported following vegetable Se values (mg/kg f.w.): carrot 0.006, celery 0,002, garlic 0.0137, lettuce 0.0024, onion 0.0073, parsley 0.0072, and tomato 0.0023. Compared to them, the analyzed Raša vegetables showed 50-fold increase in Se levels. The highest Se values (**Table 3**) were found for garlic and turnip.

The Kendall's tau correlation coefficients among the vegetable PTE values were calculated for the each garden separately. In the case of gardens no. 2. and 3., correlations were highly variable, positive as well as negative ($p > 0.05$); e.g. the Se-Mo correlation coefficients ($p > 0.05$) were 0.11, and 0.48, respectively. In the case of the garden no. 1., Cr, Pb, Zn, Cu, Mn, Fe, and As were mutually highly correlated (0.99, $p < 0.05$), similarly to their waterborne correlations shown in **Table 2**. Their correlation coefficients with Mo and Cd were 0.33 ($p > 0.05$). However, the correlation coefficients among Se and the rest of the analyzed PTEs were 0 ($p > 0.05$), and even negative with Cd. This finding could indicate on specific biogeochemical processes in the case of the Se uptake by vegetables grown very close to the Raša coal mine water effluent. The Kruskal-Wallis test showed significant difference ($p < 0.05$) between vegetable Se levels for the gardens no. 2. and 3. (**Figure 2**). Vegetables from the garden no. 3., located most downstream, had the highest Se levels. They were affected by both, the Raša coal mine discharges, and untreated municipal wastewater from the Labin and Raša towns.

The relationships among the vegetables and respective garden soil samples were assessed by the accumulation coefficients (AC) as follows:

$$AC = C_{\text{root, leaf, tuber}}/C_{\text{soil}} \qquad (1)$$

where the former represents an element concentration in different plant parts, while the latter is an element concentration in soil. Also, the translocation factors (TF) were calculated according to the equation:

$$TF = C_{\text{leaf, tuber}}/C_{\text{root}} \qquad (2)$$

The AC and TF values for the analyzed vegetables are presented in **Table 4**. One caution is necessary here: since bioavailable fractions of PTEs in garden soil were not determined, their uptake and translocation are of informative value only. Plant species differ strongly in Se uptake and accumulation in their specific parts (**White, 2016**). Depending on their capacity to tolerate high Se concentrations in the rooting medium, plants are commonly classified into Se-accumulators, non-accumulators, and Se-indicators. Noteworthy, most agricultural (e.g. potato) and horticultural plants are non-accumulators (**White, 2016**). Accumulation of Se also differs greatly among the plant organs in the same plant species. Most of the plants, with some exceptions, accumulate more Se in the upper parts (stem and leaf) than in roots (**Broadley et al., 2012; Hasanuzzaman et al., 2014**). This was also found for the analyzed Raša vegetables (**Table 5, Figure 3**). Based on the median values (**Table 5**), calculated together for the leaves and roots (tubers), the highest AC values were found for the garden no. 1. (**Figure 3**). It was expected based on the highest PTE levels in its vegetables (**Table 3**). Selenium was an exception as it exhibited the highest AC value for the garden no. 3., resulting from higher Se levels in the respective vegetables (**Figure 2**). **Table 5** also shows how Mo had the highest AC values compared to other elements (except for Se in the garden no. 3.). As shown by **Table 4**, the highest Se uptake from Raša soil was exhibited by the following vegetables: garlic (leaf > root) > turnip (root > leaf) > parsley (leaf > root), and onion (leaf > root).

Table 4: The AC and TF values for the analyzed vegetable PTEs

	AC_{Cr}	TF_{Cr}	AC_{Mn}	TF_{Mn}	AC_{Fe}	TF_{Fe}	AC_{Cu}	TF_{Cu}	AC_{Zn}	TF_{Zn}	AC_{As}	TF_{As}	AC_{Se}	TF_{Se}	AC_{Mo}	TF_{Mo}	AC_{Cd}	TF_{Cd}	AC_{Pb}	TF_{Pb}
1 soil																				
1 kale leaf	0.009	3.91	0.018	1.34	0.009	3.97	0.04	1.81	0.04	1.23	0.008	4.14	0.03	1.49	0.29	5.20	0.04	0.52	0.016	2.69
1 kale root	0.002		0.014		0.002		0.02		0.03		0.002		0.02		0.06		0.07		0.006	
1 lettuce leaf	0.089		0.047		0.024		0.10		0.08		0.023		0.05		0.20		0.06		0.031	
1 turnip root	0.000		0.000		0.000		0.01		0.02		0.000		0.05		0.13		0.01		0.000	
2 soil																				
2 gourd	0.001		0.002		0.001		0.03		0.03		0.001		0.05		0.09		0.01		0.001	
2 potato	0.002		0.001		0.000		0.07		0.01		0.001		0.01		0.10		0.07		0.001	
2 onion leaf	0.001	2.09	0.004	3.99	0.001	2.63	0.03	0.60	0.01	0.47	0.001	0.98	0.02	1.88	0.11	0.87	0.01	0.46	0.009	4.04
2 onion root	0.001		0.001		0.000		0.05		0.02		0.001		0.01		0.13		0.01		0.002	
2 radicchio leaf	0.002	2.73	0.007	3.19	0.002	4.06	0.06	1.36	0.04	1.35	0.002	1.47	0.03	1.00	0.04	0.39	0.04	0.67	0.004	4.75
2 radicchio root	0.001		0.002		0.001		0.05		0.03		0.001		0.03		0.11		0.06		0.001	
2 parsley leaf	0.002	3.04	0.008	2.04	0.002	2.14	0.03	0.28	0.05	0.76	0.001	2.19	0.11	1.39	0.12	0.53	0.02	0.23	0.001	0.87
2 parsley root	0.001		0.004		0.001		0.10		0.07		0.001		0.08		0.22		0.08		0.001	
3 soil																				
3 lettuce leaf	0.010		0.017		0.007		0.09		0.02		0.008		0.05		0.06		0.03		0.005	
3 garlic leaf	0.007	1.90	0.007	1.09	0.006	1.75	0.05	0.71	0.04	0.98	0.005	1.41	0.16	1.35	0.26	1.02	0.03	0.37	0.008	1.03
3 garlic root	0.004		0.007		0.004		0.07		0.05		0.004		0.12		0.26		0.09		0.008	
3 onion leaf	0.001	0.05	0.006	0.45	0.001	0.07	0.01	0.10	0.01	0.25	0.001	0.06	0.10	1.22	0.08	0.92	0.01	0.05	0.001	0.05
3 onion root	0.018		0.013		0.013		0.13		0.04		0.015		0.08		0.09		0.11		0.021	
3 kale leaf	0.003	1.26	0.022	1.66	0.003	1.51	0.05	1.00	0.03	1.45	0.003	1.85	0.09	2.71	0.08	3.42	0.04	1.66	0.007	0.88
3 kale root	0.003		0.013		0.002		0.05		0.02		0.002		0.03		0.02		0.02		0.008	
3 turnip leaf	0.005	9.94	0.007	9.11	0.005	19.6	0.04	1.51	0.04	3.52	0.004	1.05	0.13	0.92	0.10	3.70	0.05	1.23	0.009	5.87
3 turnip root	0.001		0.001		0.000		0.03		0.01		0.004		0.15		0.03		0.04		0.001	

Table 5: Median values of the accumulation coefficients (AC), and the translocation factors (TF) of analyzed elements in three (no. 1., 2., 3.) private gardens of the Krapan and Raša towns (the highest values are in bold italic)

	AC_{Cr}	AC_{Mn}	AC_{Fe}	AC_{Cu}	AC_{Zn}	AC_{As}	AC_{Se}	AC_{Mo}	AC_{Cd}	AC_{Pb}
1	0.005	0.016	0.005	0.03	0.035	0.005	0.04	***0.165***	0.05	0.011
2	0.001	0.003	0.001	0.05	0.030	0.001	0.03	***0.110***	0.03	0.001
3	0.004	0.007	0.004	0.05	0.030	0.004	***0.10***	***0.080***	0.04	0.008
	TF_{Cr}	TF_{Mn}	TF_{Fe}	TF_{Cu}	TF_{Zn}	TF_{As}	TF_{Se}	TF_{Mo}	TF_{Cd}	TF_{Pb}
1	***3.91***	1.34	***3.97***	1.81	1.23	***4.14***	1.49	***5.20***	0.52	2.69
2	2.73	3.19	2.63	0.60	0.76	1.47	1.39	0.53	0.46	***4.04***
3	1.58	1.37	1.63	0.85	1.21	1.23	1.28	2.22	0.80	0.95

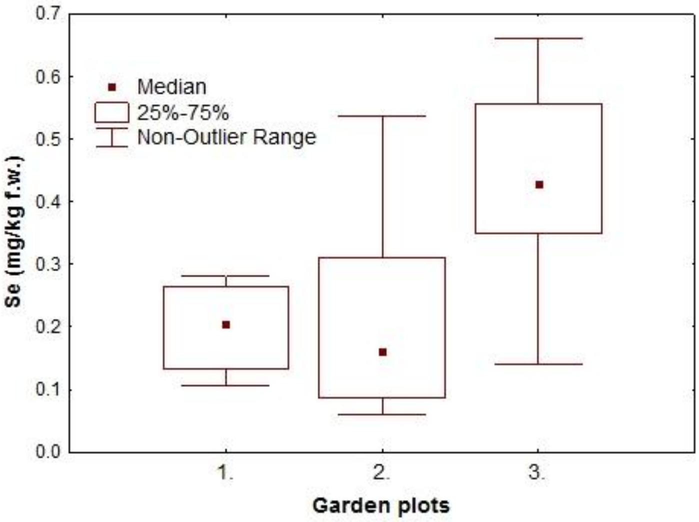
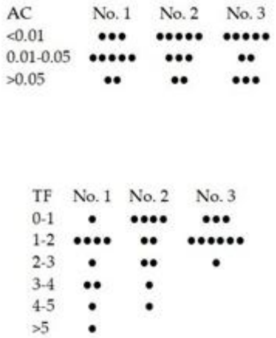


Figure 2: Box-plots of Se concentrations (mg/kg f.w.) in vegetables from the garden plots no. 1., 2., and 3.



AC	No. 1	No. 2	No. 3
<0.01	●●●	●●●●●	●●●●●
0.01-0.05	●●●●●	●●●	●●
>0.05	●●	●●	●●●

TF	No. 1	No. 2	No. 3
0-1	●	●●●●	●●●
1-2	●●●●	●●	●●●●●●
2-3	●	●●	●
3-4	●●	●	
4-5	●	●	
>5	●		

Figure 3: The AC and TF categories for vegetables from the three garden plots (no. 1., 2., and 3.). The black dots represent analyzed elements (n = 10). More details can be found in the text and **Table 5**.

Similarly to AC, the highest TF values (the PTE transfers from the roots (tubers) to the leafy parts) were found for the garden no. 1. (**Table 5, Figure 3**). The TF values for the gardens are listed in descending orders: garden no. 1./ Mo > As > Fe > Cr > Pb > Cu > Se > Mn > Zn > Cd; no. 2/ Pb > Mn > Cr > Fe > As > Se > Zn > Cu > Mo > Cd; and no. 3./ Mo > Fe > Cr > Mn > Se > As > Zn > Cu > Cd. Mostly, Mo, Fe, and Cr showed the highest transfers from the roots to the leafy parts of the vegetables. A few elevated TF values (outliers) were found in the case of turnip (garden no. 3.) for Cr, Mn, and Fe as follows: 9.94, 9.11, and 19.6, respectively. They could be ascribed to a possible contamination of an untreated municipal wastewater discharged to the Krapan stream, but specific biochemical mechanisms in vegetables can not be ruled out (**Hasanuzzaman et al., 2014**).

Finally, the following conclusions can be drawn from **Table 4**: 1/ the highest AC values of Cr, Mn, Fe, and Cu were found for lettuce, and onion and parsley roots as well; the highest AC values of Zn, As, Pb, and Mo were found for lettuce, and kale leaf, parsley root, and garlic leaf and root as well; 2/ compared to plant roots, the analyzed elements were generally increased in leafy parts (lettuce, kale, radicchio, parsley, and turnip), whereas mixed results (roughly 50:50, i.e. the PTE accumulation prevailed either in roots or leaves, depending on an element) were found for onion and garlic (e.g. their Mo and Cd were more accumulated in root parts than in leafy ones); and 3/ Se was more concentrated in garlic's (less pronounced by onion) leafy parts than in its roots.

3.2.2. Estimated daily intake of Se by vegetable consumption

Among all the elements, selenium has one of the narrowest ranges between dietary deficiency (< 0.04 mg/day) and toxic levels (> 0.4 mg/day) (**WHO, 1996**). The estimated daily intake (EDI) of Se via dietary intake of Raša vegetables was calculated according to the following equation (**Copat et al., 2013**):

EDI (mg/day) = [(element concentration; mg/kg) per meal (size or daily intake of food; kg)] (3)

In Croatia, the average consumption of vegetables and vegetable products is 174 g/day for an adult person, based on data for acute food consumption in grams per day (**EFSA Europa, 2011**). This data was approximated for Raša town residents, but future studies should include onsite questionnaires of their dietary habits. **Table 6** shows that the calculated EDI of Se for the mixed Raša vegetables (n = 21) was 0.055 mg/day. The RDA (Recommended Dietary Allowance) (**Institute of Medicine, 2000**) for females (F) and males (M) is 0.055 mg/day, and 0.070 mg/day, respectively (**WHO, 1996**). The calculated value was 1/8 the toxic level of 0.4 mg/day Se for the human and animal health. However, the EDI calculated for vegetables only was almost equal to the RDA for adults (**Institute of Medicine, 2000**). Moreover, the EDI values of all vegetables were used to calculate the contributions of Se to the RDA. It can be seen that they were very high in the case of garlic (183%), turnip (154%), and parsley (147%), followed by onion and gourd (76.4%), lettuce (74.5%), kale (61.8%), radicchio (50.9%), and potato (20.0%). For comparison, a Croatian study (**Klapec et al., 1998**), that was carried out some 500 km away from the Raša town (eastern Croatia), found that the average daily Se intake in the study area was inadequate, only 0.027 mg/day, as a consequence of low environmental Se levels there. The study (**Klapec et al., 1998**) included adults (F and M), and their dietary habits (fish, meat, eggs, milk, cereals, and vegetables). The authors noted that there was no evidence of health problems connected to low Se status though.

Table 6: Approximative estimates of daily intake (EDI) of Se and the contribution to reference nutritional values (a – EDI (mg/day) = [(element concentration; mg/kg) per meal (daily intake of food; kg)] (**Copat et al., 2013**); b – RDA for female (F) and male (M) Se, 0.055 mg/day (F/M) (**Institute of Medicine, 2000**)

	EDI (a) (mg/day)	Contribution of mean to RDA (b) (%)
mixed vegetables (n = 21)	0.055	96.4
kale (n = 4)	0.034	61.8 (F/M)
lettuce (n = 2)	0.041	74.5 (F/M)
turnip (n = 3)	0.085	154 (F/M)
gourd (n = 1)	0.042	76.4 (F/M)
potato (n = 1)	0.011	20.0 (F/M)
onion (n = 4)	0.042	76.4 (F/M)
garlic (n = 2)	0.101	183 (F/M)
radicchio (n = 2)	0.028	50.9 (F/M)
parsley (n = 2)	0.081	147 (F/M)

3.3. Concentrations of PTEs in figs, elderberry, nettle, and yarrow

Levels of Se, Mo, V, and U in fruits, i.e. figs (*Ficus carica*), and three wild plant species, i.e. elderberry (*Sambucus*), nettle (*Urtica*), and yarrow (*Achillea*), are displayed in **Table 7**. In Croatia, the three wild plants are commonly dried and used for making tea. Since Se concentrations in these items have been reported neither for Mediterranean countries nor for other parts of the world, the values in **Table 3**, along with the published ones from Croatia (**Klapec et al., 2004**), and Thailand (**Sirichakwal et al., 2005**) were used for their mutual comparisons. A caution is necessary as we used several countries/geographies, and various plant items in the consideration. The pedological, climatic, and other relevant conditions are certainly not similar to be able to make such comparison *sensu stricto*. Also, the methodologies used might not have been comparable. Nevertheless, **Klapec et al. (2004)** reported following fruit Se values (mg/kg f.w.): apple 0.008, plum 0.009, grape 0.013, and peach 0.011. Compared to them, the analyzed Raša fruits, i.e. figs, showed some 6-fold increase in Se levels. **Sirichakwal et al. (2005)** reported following fruit Se values (mg/kg f.w.): banana and apple (common) 0.003, grapes and guava 0.001, mango 0.006, and papaya 0.012. Compared to them, the analyzed Raša figs showed some 4- to 50-fold increase in Se levels. Similarly to vegetables (**Table 3**), figs had higher Se concentrations in leaves. Elderberry Se values were similar in the flower and stem parts, and almost identical to Raša lettuce (**Table 3**). Nettle Se values were similar to Raša onion, garlic, and parsley (**Table 3**). Yarrow flower and stem Se values were similar to those of nettle. Likewise the Raša vegetables, that are highly enriched in Se (**Table 3**), the Raša wild plants and figs were arguably enriched in Se. Similarly, **Sasmaz et al. (2015)** investigated selenium uptake and transport from soil to twelve wild plant species in an Ag-As mining area of Gumuskoy (Turkey). Their results indicate that all twelve plant species had the ability to transfer Se from the roots to the shoot. However, the Se transfer was more efficient in plants with higher enrichment coefficients for roots and shoots. Collectively, the Se values in collected Raša plants (grown and wild ones) are indicative of their phytoremediation potential which was elaborated by **Sasmaz et al. (2015)**. The latter paper showed how certain plants were particularly useful as biomonitors or hyperaccumulators for remediation of Se-contaminated soils. The Raša wild plant Mo values were also very similar to Raša vegetable Mo values. By comparing the Raša nettle Mo values with the published ones for lettuce, potato, and onion (**Kabata-Pendias, 2010**), they were increased 60-600 times. Regarding V, the following values (mg/kg f.w.) were reported by **Kabata-Pendias (2010)**: cabbage 0.008, lettuce 0.005, and apple 0.0001. Compared to them, Raša fig V concentrations were increased 20 times, while 3 times in the case of nettle. The U levels in analyzed wild plants were compared with respective results in the paper by **Anke et al. (2009)**, but approximately only, as their reported levels were expressed on dry basis. Uranium levels (mg/kg d.w.) from uranium mining and control locations were following, respectively: lettuce 0.073 and 0.034; parsley 0.054 and 0.028; cucumber 0.0085 and 0.007; apple 0.0028 and 0.0027; and onion 0.004 and 0.005. Since water content of fruits and vegetables can be more than 90-95%, the Raša wild plant U values were comparable or mostly lower regarding 1/10 of the U values in **Anke et al. (2009)**. It is clear from **Table 7** that figs had accumulated more Se, Mo, V, and U in their leaves than in fruits, while other plants had mixed relations among stems and flowers regarding the PTE levels.

Table 7: Levels of PTEs (mg/kg f.w.) in various parts of figs and wild plants collected between the Raša coal mine water effluent and its inflow into the Krapan stream (Fig. 1); the letters A-H indicate the corresponding plant parts

		Se	Mo	V	U
figs (fruit)	A	0.053	0.042	0.0023	0.0001
figs (leaf)	A	0.205	0.097	0.0609	0.0016
figs (fruit)	B	0.052	0.035	0.0019	0.0001
figs (leaf)	B	0.188	0.095	0.0566	0.0016
elderberry (flower)	C	0.229	0.631	0.0131	0.0005
elderberry (stem)	C	0.214	0.417	0.0326	0.0012
elderberry (flower)	D	0.228	0.638	0.0119	0.0004
nettle (leaf)	E	0.468	1.226	0.0187	0.0005
nettle (leaf)	F	0.382	1.800	0.0264	0.0007
yarrow (flower)	G	0.059	0.265	0.0095	0.0002
yarrow (stem)	G	0.039	0.093	0.0031	0.0001
yarrow (stem)	H	0.042	0.106	0.0042	0.0002

Concentrations of Cr, Mn, Fe, Cu, Zn, As, Cd, and Pb in the analyzed fruit and wild plant species are shown in **Table 8**. By comparison of the elderberry, nettle, and yarrow PTE values with respective vegetable ones (**Table 3**), it can be said that they were lower in the case of Cr, Mn, and Fe, either lower or equal in the case of Cu, and Zn, and much lower for As, Cd, and Pb. By comparing the figs' PTE values with respective fruit (apple and orange) ones (**Klapec et al., 2004**), it was found that only As was much lower, Pb equal, Cd either equal or higher, while other elements were either higher (Mn and Cu) or much higher (Cr, Fe, and Zn) in Raša plants. Generally, increased PTE values (**Tables 3, 7, and 8**) could be interpreted in the context of their increased levels in water (coal mine discharges, and water stored in barrels), and partly to geological setting of the Raša Bay estuary. Namely, **Medunić et al. (2020b)** elaborated an influence of complex karstic hydrological patterns on total PTE levels in the local environment.

Table 8: Levels of PTEs (mg/kg f.w.) in various parts of figs and wild plants collected between the Raša coal mine discharges and their inflow into the Krapan stream (Fig. 1); the letters A-H indicate the corresponding plant parts

		Cr	Mn	Fe	Cu	Zn	As	Cd	Pb
figs (fruit)	A	0.06	0.66	8.20	0.42	3.78	0.003	0.008	0.002
figs (leaf)	A	0.08	5.01	39.3	0.70	8.20	0.008	0.008	0.047
figs (fruit)	B	0.05	0.62	7.60	0.47	4.24	0.001	0.008	0.002
figs (leaf)	B	0.06	4.60	35.8	0.68	8.36	0.007	0.008	0.040
elderberry (flower)	C	0.01	4.12	10.7	1.61	6.59	0.002	0.001	0.009
elderberry (stem)	C	0.03	2.97	22.4	1.17	12.0	0.006	0.001	0.016
elderberry (flower)	D	0.01	4.20	10.5	1.57	6.60	0.002	0.000	0.015
nettle (leaf)	E	0.03	6.12	21.8	4.57	8.72	0.003	0.001	0.028
nettle (leaf)	F	0.06	6.66	28.1	4.34	8.96	0.005	0.001	0.041
yarrow (flower)	G	0.01	2.27	14.7	2.92	11.8	0.003	0.029	0.007
yarrow (stem)	G	0.12	1.05	13.1	1.10	3.36	0.001	0.010	0.004
yarrow (stem)	H	0.08	1.12	10.0	1.25	4.00	0.001	0.010	0.005

4. Conclusions

Many studies try to understand how plants acquire and accumulate Se, mainly in terms of appropriate dietary Se intakes for animals and humans. Such studies are particularly useful in the case of remediation of land contaminated with Se. This study showed that home-grown vegetables, and wild plants and figs from the Raša town area were highly enriched in Se, U, Mo, and V. This is a consequence of leaching of Raša coal that is also enriched in the four PTEs. The Raša coal deposits are hosted by karst rocks, the groundwater reserves of which are highly vulnerable to pollution. They are characterized by complex hydrological circulation patterns that contribute to dispersion of Se from Raša coal to food chain. The calculated Se EDI values should be taken with caution as they are based on a limited number of vegetable samples, and an approximate measure of daily food consumption. Therefore, future research should include onsite questionnaires of the dietary habits of the Raša town residents. Also, further studies should provide more insight into biochemical mechanisms of native plants inhabiting Se-enriched soil in the Raša Bay region. Herewith, the most polluted locations could be cleaned up by employing selenium hyperaccumulator plants as a viable green option.

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SAŽETAK

Povišene vrijednosti selenija u povrću te samoniklom bilju i voću pod utjecajem kemizma vode iz Raških ugljenokopa

Selenij (Se), mikronutrijent toksičan za ljude i životinje izložene njegovim povišenim vrijednostima, sveprisutan je u ugljenu. Raški ugljen, iznimno obogaćen sumporom (S), selenijem, uranom (U), vanadijem (V) i molibdenom (Mo), stoljećima je pridobivan i korišten u industriji na području Raškog zaljeva, smještenog u Istri (sjeverni Jadran, Hrvatska). Postoji bojazan da voda iz Raških ugljenokopa onečišćuje okolno tlo, vodu i nasade. Cilj ovog istraživanja praćenja stanja okoliša bio je utvrditi razine Se i odabranih potencijalno toksičnih elemenata u tragovima (As, Cd, Cu, Cr, Mo, Pb, U, V i Zn) te onih sporednih (Fe i Mn) u vodi iz Raških ugljenokopa, površinskoj vodi te okolnom povrću, voću i samoniklom bilju. Vrijednosti Se u vodi iz ugljenokopa (do 12 μg/L) premašile su dozvoljenu vrijednost Se za vodu u okolišu (10 μg/L). U usporedbi s prosječnim vrijednostima Se u tlu u EU (1,15 mg/kg), Se u povrtnom tlu u Raši bio je peterostruko povišen. U usporedbi s vrijednostima Se u hrvatskom i grčkom povrću (niske do normalne), Se u raškom povrću je povišen 20 odnosno 50 puta. U radu je približno procijenjeno da je dnevni unos (EDI) Se ispitivanim domaćim povrćem (broj uzoraka 21) vjerojatno povišen (0,055 mg/dan). Naime, preporučeni dnevni unosi (RDA) Se za žene i muškarce iznose 0,055 odnosno 0,070 mg/dan. Vrijednosti EDI analiziranog povrća pridonijele su prosječnim razinama RDA kako slijedi: češnjak (183%), repa (154%), peršin (147%), luk i tikva (76%), zelena salata (74%), kelj (62%), radič (51%) te krumpir (20%). Premda izračunata EDI vrijednost analiziranog povrća iz Raše predstavlja tek 1/8 toksične doze (>0,4 mg/dan), rezultati ovog rada trebali bi potaknuti daljnja istraživanja o prehrambenim navikama i prehrambenom statusu dotičnog stanovništva u smislu unosa selenija.

Ključne riječi: Raški ugljen, voda, povrće, selenij, procijenjeni dnevni unos

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Authors contribution

Gordana Medunić (Full Professor, PhD, Earth Sciences) participated in sampling campaigns, and drafted the manuscript. **Nina Bilandžić** and **Marija Sedak** (Senior scientists, PhD, Veterinary Sciences) conducted chemical analyses of soil, vegetable, fruit, and wild plant samples. **Željka Fiket** (Senior scientist, PhD, Earth Sciences) conducted chemical analyses of water samples. **Andreja Prevendar Crnić** (Full Professor, PhD, Veterinary Toxicology) provided financial funds for the field work, and calculated and interpreted dietary data values. **Vanja Geng** (Geology MSc student) participated in a sampling campaign.