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Major and Trace Elements in Rice Seeds from Kočani Field, Macedonia

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Abstract

The objective of this study was to assess the total concentrations of selected major and trace elements in rice seeds from Kočani Field impacted by heavy metals due to irrigation with riverine water affected by acid mine drainage and other mining activities of the Zletovo-Kratovo and Sasa-Toranica Pb-Zn ore districts. The analytical results obtained with the k_0-instrumental neutron-activation analysis (k_0-INAA) revealed that the contaminant concentrations of the analyzed trace elements in unpolished rice were usually lower than their limit level in food. The only exceptions were As, which in the unpolished rice from some magazines of the local farmers from Kočani Field was in the range 0.109 to 0.52 μg/g, and Cd, with a concentration of 0.21 μg/g, found only in one magazine, which mostly contained rice grown in the most polluted paddy soils in the vicinity of the Zletovska River. The results also suggested that the regular consumption of unpolished rice could pose a potential health problem from long-term As and Cd exposure if weekly dietary intakes exceeded more than 2 kg of unpolished rice with the highest concentration levels of As and/or Cd.

Keywords: Major and trace elements, rice (*Oriza sativa L.*) contamination, k_0-INAA, mining activity, Kočani Field, Macedonia

1. Introduction

Plants are an important component of ecosystems as they transfer elements from abiotic into biotic environments. The primary sources of elements from the environment to plants are air, water and soil. Plants grown in a polluted area may accumulate a much higher than normal amount of trace elements. It is well known that heavy metals in agricultural soils may influence crop yields and quality. Special attention should therefore be paid to the concentration of trace elements in agricultural soils because they can be ingested by humans and animals through the food chain as a result of their uptake by edible plants. Heavy metal contamination in agricultural soils has increased as a result of the rapid industrialization and other anthropogenic activities. In eastern Macedonia the pollution of soil with heavy metals due to irrigation with acid mine drainage and mining activities impacted riverine water is one such example. Acid mine drainage impacted riverine water as well as effluents from base metal mining and milling operations, which discharged untreated into the riverine water, may pose a serious risk to human health and animals through the food chain, when contaminated riverine water is used for the irrigation of food crops. Elevated concentrations of heavy metals were reported in rice and other food stuffs as well as in agricultural soils and stream sediments around the abandoned and active mining areas due to the discharge and dispersion of the mines´ waste materials, including tailings into nearby ecosystems. According to Jung and Thornton, the concentration of heavy metals such as Cd, Cu, Pb and Zn in rice grain grown in soil contaminated by Pb-Zn mining activity in Korea averaged 0.21, 3.0, 0.22 and 22.5 μg/g, respectively. High concentrations of heavy metals were also reported in rice and vegetables irrigated with As contaminated groundwater.

In Kočani Field previous investigations have shown that paddy soil and riverine water from Zletovska, Kočanska, Orizarska and Bregalnica River used for the irrigation of paddy soil were contaminated with heavy metals because of mining activities and acid mine drainage from the Zletovo-Kratovo and Sasa-Toranica ore district. It is therefore anticipated that food plants grown in this area cannot be free from heavy metal pollution. Therefore, the present preliminary research is conducted: (1) to investigate the major and trace element concentrations and evaluate the potentially ecotoxic pollutant element´s concentrations in rice grain influenced by mining activities, (2) to help create a database for estimating the heavy metal content in the diet of local people and (3) to assess the potential health risk to local humans as a result of ingesting the contaminated food.

2. Materials and Methods

2. 1. Site Description and Paddy Soil Characteristics

Kočani Field is located in the eastern part of Macedonia, about 32 km from the city of Štip. It is situated in the valley of the Bregalnica River between the Osogovo Mountains in the north and the Plačkovica Mountains in the south (Fig. 1). Its average length is 35 km and its width is 5 km. Paddy soil in the western part of Kočani Field has considerably elevated concentrations of heavy metals, such as As, Cd, Pb and Zn, which could represent a long term contamination due to the irrigation with acid mine drainage and mining activities impacted riverine water from the Zletovska River. The detected total concentrations in µg/g of As (48), Cd (6.8), Zn (1250) and Pb (994) are far above the threshold values considered as a phytotoxically excessive for surface soil as reported by various environmental protection agencies. The paddy soil in the vicinity of the Zletovska River which is far more polluted than the Bregalnica River, as well as Orizarska and Kočanska River, also exhibited elevated levels of Ba, Th, U, V, W, Mo, Cu, Sb, Bi, Ag, Au, Hg and Tl.

2. 2. Rice Sampling and Preparation

Rice grain samples with hulls were collected after the harvest time in November 2004 from 11 local farmer's

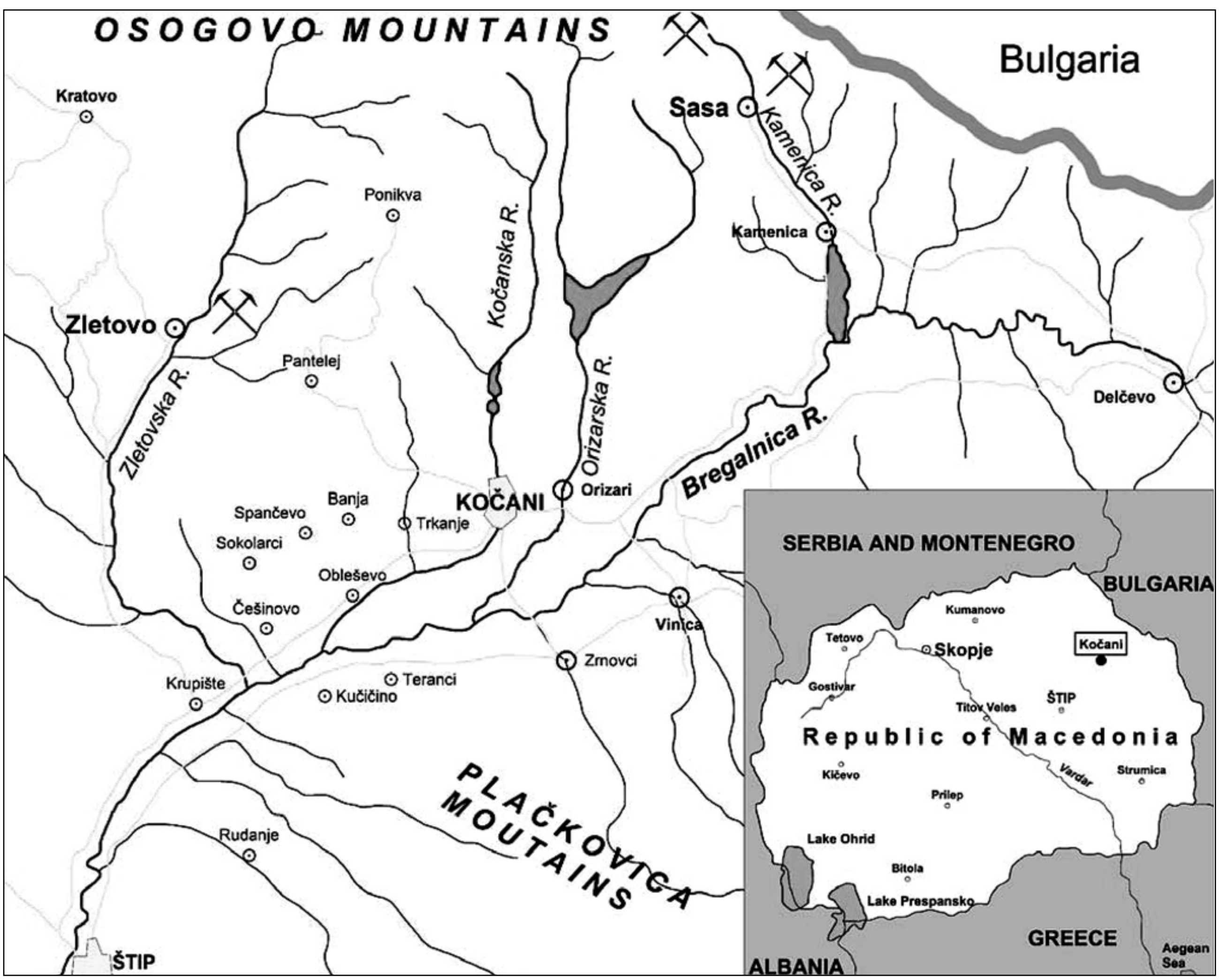

Fig. 1: Map of the study area showing the drainage system of the Bregalnica River and its tributaries.

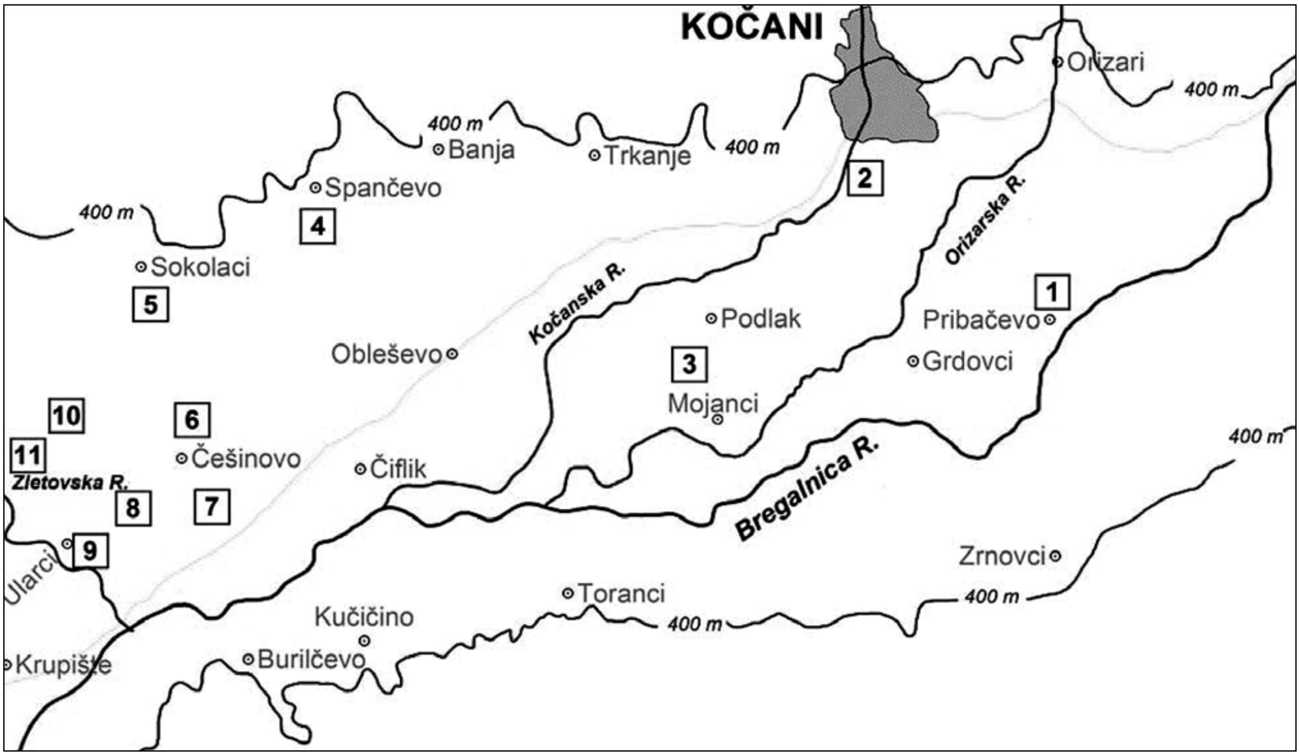

Fig. 2: Location map of the local farmers magazines on the Kočani Field from which the rice samples for the purpose of this study were collected after the harvest time in November 2004.

magazines in Kočani Field (Fig. 2). Each magazine contained approximately 12 tons of rice grain, which was reaped over an area of about 10 hectares. A composite sample taken from each magazine selected for this study weighted of about 1 kg and represented an average sample of the rice grown on the corresponding paddy fields. All the samples were collected and stored in polythene bags and brought to the laboratory for further preparation and treatment. In the laboratory the rice grains with hulls were thoroughly washed three times with deionised water to remove any soil particles and dust, and after this they were oven dried to a constant weight at 75 °C for 72 hours. The dried rice was divided into two parts: 1) one part represented grains with the hull and the other portion grains without the hull (i.e., unpolished rice). The rice was de-hulled with a ceramic pestle and mortar. The grains with hulls and the de-hulled rice were separately ground to a fine powder in an agate mortar. The powdered samples were packed in clean, dry, stoppered glass containers and stored in a refrigerator before the analysis.

2. 3. Instrumentation

To identify the major and trace element concentrations and the possible toxicological risk posed to human health resulting from exposure to heavy metals by rice ingestions the rice samples were analysed for a broad range of major and trace elements (Ag, As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hf, Hg, Ho, In, K, La, Mo, Na, Nd, Rb, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Tm, U, W, Yb, Zn and Zr) using k_0-instrumental neutron activation analysis and compared with the literature and to the store-bought Zlato polje rice. The main advantages of k_0-INAA compared to other methods are as follows: (i) a non-destructive analytical method for the measurements of inorganic components in solid matrices, because this method does not require any sample dissolution. INAA is a valuable technique particularly for elements that form or are in refractory phases that may be difficult to dissolve. In this way, the effect of the dissolution steps on the final measurement results for As, Co, Cr, Sb and Zn did not need to be investigated; (ii) it has a small or insignificant matrix effect during irradiation by reactor neutrons (neutrons are transparent for sample matrices); (iii) it is a multi-elemental technique suitable for the determination of trace elements in several matrices, covering a large range of concentration, with a low detection limit, with accuracy and precision, as shown by Jaćimović et al. The main disadvantages of k_0-INAA are: (i) a major limitation is that the great majority of the signal on the HPGe detector is usually produced from only a few (often 2 or 3: ^{24}Na, ^{82}Br, ^{32}P) elements in the gamma spectrum, and problems in trying to measure signals superimposed on a large background noise; (ii) it suffers from spectral interferences and, when plastic irradiation vials are used, volatilization losses.

In the studied matrix the concentrations of Ag, Cs, Eu, Ga, Hf, Hg, Ho, In, Nd, Ru, Sn, Ta, Te, Th, U, V, Yb and Zr were generally lower than the detection limit of the analytical method used. Therefore, these elements were not taken into consideration during this study. In order to determine their concentrations in rice samples, more sensitive analytical methods should be used.

2. 4. k0-instrumental Neutron Activation Analysis (k_0-INAA)

Powdered, well-homogenized rice samples (about 200 mg) were pressed into pellets with diameters of 10 mm. The samples and standards (Al-0.1%Au IRMM-530 disc of 6 mm in diameter and 0.2 mm high) were stacked together and fixed in a polyethylene ampoule in sandwich form and irradiated for 18 hours in the carousel facility (CF) of the 250-kW TRIGA Mark II reactor of the Jožef Stefan Institute at a thermal neutron flux of 1.1×10^{12} cm^{-2} s^{-1}.

After irradiation the samples were measured after 2, 8–10 and 30 days cooling time for k_0-INAA. Measurements were performed on two absolutely calibrated HPG-e detectors (Ortec & Canberra, USA) with 20 and 40% relative efficiencies. The measurements were performed at such distances that the dead time was kept below 10%, with negligible random coincidences. The detector with a 20% relative efficiency was connected to an EG&G ORTEC Spectrum Master high-rate multichannel analyzer, while the detector with a 40% relative efficiency was connected to a CANBERRA S100 multichannel analyzer.

For the peak-area evaluation, the HyperLab program was used. For the determination of f (thermal to epithermal flux ratio) and α (the parameter that measures the epithermal flux deviation from the ideal 1/E distribution), the "Cd-ratio" method for the multi-monitor was applied. The values $f = 28.8$ and $\alpha = -0.005$ were used to calculate the element concentrations. For the elemental concentrations and the effective solid-angle calculations a software package called KAYZERO/SOLCOI® was employed.

2. 5. Quantity Control

The accuracy of the results was checked with NIST CRM 1568 Rice Flour. The results obtained with k_0-INAA are presented in Table 3. All the concentrations in this paper were expressed on a dry weight basis.

2. 6. Statistical Analyses

The calculations for mean, medium, minimum and maximum concentration values for the analyzed elements in the rice samples together with variance and standard deviation data (S. D.) were obtained using the statistical package Statistica version 6, and the t-test was also employed to evaluate the significant differences between the hulled and de-hulled rice samples using the package. Values below the detection limits were treated for statistical analyses according to the suggestions of Gough et al., They recommend not analyzing variables with BDLs (Below Detection Limit) greater than 33%, and replacing BDLs with 0.7 for variables that have less than 33% BDLs. Consequently, for the statistical analyses, we did not analyze the BDLs for Cd, Se, Sm and Th in rice with a hull and without a hull and Ba, Cr and La in rice without a hull. Furthermore, we substituted 0.7 BDL for the BDL values for Au, Cr, La and Sb in rice with a hull as well as for Sb in rice without a hull.

3. Results

The concentrations of the analyzed elements in rice with a hull and without a hull are presented in Tables 1 and 2, respectively. The uncertainty budget of k_0-INAA for a particular element shown in Table 1 is calculated as follows: (i) the uncertainty coming from the literature ($T_{1/2}$, E_r, Q_0, k_0, the standard uncertainty of the coincidence correction factors (COI) and the Au (standard) composition in the Al-(0.1%)Au alloy); (ii) the uncertainty coming from the previously determined neutron flux parameters (f and α) using the Cd-ratio method, detector efficiency of a sample, sample and standard masses and the net peak area in the measured gamma-line. In general, the uncertainty budget of the k_0-INAA in most cases is around 4%. The main contribution to it comes from the last one (ii), especially from the net peak area in gamma-spectrum, determined by the HyperLab program. In our case it is evident for Se, Sm, Sr and Th in Table 1. In addition, Table 2 has the results for the data of the Zlato polje (ZP) store-bought rice, the maximum permitted limits of selected trace elements in plants used as food and the provisional tolerable weekly intake (PTWI) values. The results obtained with k_0-INAA for the NIST CRM 1568 Rice Flour are presented in Table 3. Table 4 shows a synthesis of the main statistical parameters (mean, median, range and standard deviation – S.D.) of the rice with a hull and the unpolished rice. The results of the t-test are summarized in Table 5.

3. 1. Major Elements

The concentrations of the major elements (Ca, Fe, K and Na) in the rice samples with hulls are much higher than the unpolished rice samples. For individual elements in the rice with a hull K had the highest concentration of the analysed elements with a median value in µg/g of 3150; this should be compared to Ca (295), Fe (22) and Na (21) (Table 4). A similar order of the major element concentrations, in µg/g, but lower median values and higher Na relative to the Fe content were found in the unpolished rice grains: K (2650) > Ca (131) > Na (15) > Fe (9.3) (Table 4), as well as in the store-bought polished rice (Zlato polje): K (950) > Ca (71) > Na (7) > Fe (2.6) (Tab-

Table 1. Results obtained with k0-INAA in rice with a hull from Kočani Field (Macedonia).

Sample No.	1	2	3	4	5	6	7	8	9	10	11	Uncert. Budget*
El.	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**
As	0.414	0.319	1.02	0.342	0.295	0.246	n.d.	0.133	0.152	0.125	0.171	4%
Au	0.00035	0.00035	0.00040	0.00041	< 0.0004	0.00043	n.d.	0.00054	0.00046	0.00038	0.00067	6%
Ba	1.78	1.70	36.6	2.06	3.04	52.3	n.d.	1.44	4.50	8.80	4.14	5%
Br	1.13	0.82	0.71	2.48	1.58	2.60	n.d.	2.20	2.21	1.34	5.67	4%
Ca	353	330	330	310	302	250	n.d.	220	278	287	277	10%
Cd	< 0.2	< 0.2	< 0.1	< 0.3	< 0.4	< 0.1	n.d.	< 0.2	0.28	< 0.1	< 0.2	12%
Co	0.019	0.019	0.010	0.028	0.042	0.020	n.d.	0.022	0.020	0.023	0.053	6%
Cr	0.081	0.076	0.109	< 0.1	0.193	0.116	n.d.	0.075	0.108	0.143	0.097	10%
Fe	18.3	19.6	19.9	23.8	75.0	27.6	n.d.	13.1	28.5	32.0	19.1	5%
K	3530	3710	2710	2990	3350	2960	n.d.	3080	3220	2870	3530	4%
La	< 0.006	0.0081	0.0076	0.0100	0.0530	0.0160	n.d.	< 0.004	0.0184	0.0195	0.0073	10%
Mo	0.15	0.37	0.24	0.30	0.25	0.20	n.d.	0.23	0.42	0.27	0.21	12%
Na	20.3	63.3	21.1	40.4	83.4	20.7	n.d.	14.1	20.3	17.6	20.1	4%
Rb	2.95	1.86	1.70	6.23	22.8	6.07	n.d.	8.55	2.82	5.89	2.77	4%
Sb	0.0027	0.0017	< 0.002	0.0023	0.0063	0.0051	n.d.	< 0.003	0.0110	0.0021	< 0.003	10%
Sc	0.0031	0.0030	0.0042	0.0051	0.0262	0.0080	n.d.	0.0017	0.0072	0.0076	0.0025	4%
Se	< 0.05	< 0.05	< 0.04	0.066	0.075	< 0.03	n.d.	< 0.05	< 0.05	< 0.05	< 0.05	15%
Sm	< 0.003	< 0.003	0.0014	< 0.003	0.0100	0.0029	n.d.	< 0.003	0.0036	0.0034	< 0.003	15%
Sr	2.25	1.20	3.19	3.85	4.13	2.52	n.d.	2.14	3.57	3.10	4.41	20%
Th	< 0.003	0.0025	0.0024	< 0.007	0.0180	0.0058	n.d.	< 0.007	0.0070	0.0073	< 0.007	15%
Zn	19.8	20.0	13.1	17.0	16.3	15.0	n.d.	16.1	25.4	16.8	19.7	4%

n.d. – no data; * uncertainty budget of the method used for the studied matrix

Table 2. Results obtained with k_0-INAA in rice without a hull (unpolished rice) from Kočani Field (Macedonia); A) maximum permitted limit of selected trace elements in plants used as food, B) Commission Regulation Directive and C) provisional tolerable weekly intake (PTWI) values (µg/kg/BW) ([a]WHO; [b]WHO; [c]JECFA)

Sample No.	1	2	3	4	5	6	7	8	9	10	11	ZP	A	B	C
El.	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**
As	0.325	0.229	0.523	0.255	0.194	0.175	0.158	0.118	0.116	0.109	0.136	0.122	0.20		15 [a]
Au	0.00057	0.00081	0.00300	0.00120	0.00660	0.00370	0.00038	0.00160	0.00090	0.00060	0.00077	< 0.001			
Ba	< 1	< 1	40.8	1.31	1.91	11.6	< 0.6	< 1	1.30	3.87	< 2	< 2			
Br	0.37	0.23	2.08	0.71	0.43	0.99	0.25	0.77	0.79	0.47	1.79	< 0.01			
Ca	133	138	159	110	131	106	63.0	92.0	117	143	131	70.9			
Cd	< 0.2	< 0.15	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.15	0.21	< 0.2	< 0.15	< 0.3	0.15	0.1	7 [b]
Co	0.011	0.010	0.017	0.013	0.017	0.043	0.0050	0.019	0.017	0.013	0.046	0.0030			
Cr	< 0.08	< 0.06	0.113	0.157	0.069	0.128	0.076	< 0.06	< 0.1	< 0.15	< 0.08	0.200			
Fe	8.18	8.86	9.55	9.28	13.1	11.8	2.92	8.39	10.4	8.06	10.3	2.59			
K	3080	2970	2270	2680	2650	2430	801	2730	2500	2620	3280	950			
La	< 0.004	< 0.004	0.0067	< 0.01	< 0.01	< 0.02	< 0.006	< 0.004	< 0.01	< 0.02	0.003	0.015			
Mo	0.24	0.21	0.28	0.33	0.34	0.23	0.14	0.28	0.38	0.37	0.30	0.35			
Na	13.0	25.6	16.7	25.8	25.6	14.8	9.80	12.5	14.0	15.1	16.2	6.74			
Rb	3.08	1.71	1.45	6.18	19.1	5.40	0.95	8.60	2.58	5.12	2.80	0.42			
Sb	0.0034	0.0021	0.0043	0.0023	0.0083	0.025	< 0.003	0.0053	0.0085	0.0023	0.0020	< 0.01			
Sc	0.00026	0.00020	0.00070	0.00030	0.0018	0.00087	0.00057	0.00013	0.00056	0.0004	0.00016	0.0390			
Se	< 0.05	< 0.05	< 0.03	0.082	0.085	< 0.03	< 0.03	< 0.05	< 0.06	< 0.06	< 0.05	< 0.05			
Sm	< 0.002	< 0.002	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.002	< 0.003	< 0.003	< 0.002	0.0030			
Sr	1.84	1.49	1.40	2.30	2.39	1.12	< 2	< 2	< 3	3.50	3.05	< 1			
Th	< 0.003	< 0.003	< 0.008	< 0.006	< 0.006	< 0.005	< 0.003	< 0.006	< 0.008	< 0.009	< 0.006	0.052			
Zn	19.0	19.3	14.4	17.5	17.2	15.4	11.7	17.3	23.7	18.3	21.8	10.8	50		300–1000 [c]

ZP – store-bought Zlato polje rice

Table 3. Results obtained with k0-INAA for NIST CRM 1568 Rice flour

El. value	µg/g	Uncert.*	Cert. value	Uncert.	Indic.
As	0.40	0.02	0.41	0.05	
Au	< 0.001				
Ba	< 1				
Br	0.78	0.03			1
Ca	147	21	140	20	
Cd	< 0.3		0.029	0.004	
Co	0.050	0.002	0.02	0.01	
Cr	< 0.2				
Fe	12.6	1.2	8.7	0.6	
K	1045	38	1120	20	
La	< 0.005				
Mo	1.80	0.10			1.6
Na	7.42	0.27	6.0	1.5	
Rb	8.19	0.31			7
Sb	0.0079	0.0006			
Sc	0.0005	0.0001			
Se	0.36	0.02	0.4	0.1	
Sm	< 0.002				
Sr	< 2				
Th	< 0.004				
Zn	19.3	0.7	19.4	1.0	

le 2). An analysis of the major elements for possible differences between the hulled and de-hulled rice using the t-test showed a statistically significant difference at $\alpha \leq 0.05$ in K, Ca and Fe content, while the concentration levels of Na were not statistically different (Table 5). According to Jung et al. the median values in µg/g of the rice produced in South Korea were of the order of K (2190) > Ca (94.7) > Na (14.0) > Fe (10.5). In addition to compiled data from the U.S. Department of Agriculture, the concentrations in µg/g of the same elements in short-grain white rice were of the total estimated uncertainty of the method order of K (760) > Fe (42.3) > Ca (30) > Na (10). In spite of the similar order of the major element concentrations in unpolished rice from different countries the absolute levels of the elements were significantly different.

3. 2. Trace Elements

For trace elements in rice with the hull, Zn had the highest concentrations, with a median level of 16.9 µg/g, followed by Rb with 4.42 µg/g. For other trace elements, the median values in µg/g of the elements were of the order of Ba (3.55) > Sr (3.15) > Br (1.89) > Cd (0.28 – only one value) > As (0.275) > Mo (0.245) > Cr (0.103) > Co (0.02) > La (0.009) > Sc (0.005) > Sb (0.0022) > Au (0.00041) (Table 4). A similar order of the median values in µg/g were also found for unpolished rice: Zn (17.5) > Rb (3.08) > Sr (1.50) > Br (0.71) > Mo (0.28) > Cd (0.21 – only one value) > As (0.18) > Co (0.017) > Sb (0.0034) > Au (0.0009) > Sc (0.0004) (Table 4).

It is interesting to note that like the major elements the trace elements also generally showed higher median concentration levels in hulled rice compared to the rice without hulls. The only exceptions were Au, Mo, Sb, and Zn, with slightly higher concentrations in the unpolished rice (Table 1 and 2). T-test indicated that only Au, Br, Sc and Sr exhibited statistically significant differences at $\alpha \leq$ 0.05between hulled and unpolished rice samples (Table 5). From the limited number of samples analysed it is not possible to suggest a reason for this. Most probably the

Table 4. Descriptive basic statistic of the element contents in rice with and without hull (unpolished rice) from Kočani Field (Macedonia).

	With a hull					Without a hull				
El.	Mean	Median	Min	Max	Std. Dev.	Mean	Median	Min	Max	Std. Dev.
As	0.322	0.275	0.130	1.020	0.264	0.215	0.180	0.109	0.520	0.1217
Au	0.00043	0.00041	0.00028	0.00067	0.00011	0.0018	0.0009	0.00038	0.0066	0.0019
Ba	11.63	3.55	1.40	52.30	17.82	n.d.	n.d.	n.d.	n.d.	n.d.
Br	2.074	1.890	0.710	5.670	1.434	0.807	0.710	0.230	2.080	0.610
Ca	293.7	294.5	220.0	353.0	40.0	120.3	131.0	63.0	159.0	26.7
Co	0.026	0.021	0.010	0.053	0.013	0.019	0.017	0.005	0.046	0.013
Cr	0.107	0.103	0.070	0.193	0.038	n.d.	n.d.	n.d.	n.d.	n.d.
Fe	27.69	21.85	13.10	75.00	17.55	9.18	9.30	2.90	13.10	2.60
K	3195	3150	2710	3710	328	2546	2650	801	3280	649
La	0.015	0.009	0.003	0.053	0.015	n.d.	n.d.	n.d.	n.d.	n.d.
Mo	0.264	0.245	0.150	0.420	0.081	0.282	0.280	0.140	0.380	0.073
Na	32.00	20.50	14.00	83.00	23.14	17.36	15.00	10.00	26.00	5.84
Rb	6.164	4.420	1.700	22.800	6.272	5.179	3.080	0.950	19.100	5.169
Sb	0.0037	0.0022	0.0014	0.0110	0.0030	0.0060	0.0034	0.0020	0.0250	0.0068
Sc	0.0069	0.0047	0.0017	0.0262	0.0072	0.0005	0.0004	0.0001	0.0018	0.0005
Sr	3.040	3.150	1.200	4.400	1.009	1.599	1.500	0.140	3.500	1.163
Zn	17.92	16.90	13.10	25.40	3.44	17.782	17.500	11.700	23.700	3.316

n.d. – no data

differences are due to the fact that the major part of the element is blocked in the husk.

4. Discussion

4. 1. Major Elements

The major elements are present in plant tissues in much higher concentrations than trace elements and are referred to as macronutrients. The observed differences in the major element concentrations between unpolished rice and rice from different countries, including the eastern Macedonia, might be due to the differences in both the physical and chemical properties of the paddy soil affected by the weathering processes of parent rocks and other growing conditions. Statistically significant differences in K, Ca and Fe concentration levels between hulled and dehulled rice samples indicated that major elements like the trace element concentrations vary for different parts of the plant. Elements that are considered essential for growth are generally mobile within the plant, while elements considered non-essential and/or toxic are usually confined to root.

Table 5. Results of the t-test to evaluate the significant differences at $\alpha \leq 0.05$ between the rice with a hull (HR) and de-hulled rice – unpolished rice (UR).

El.	Rice type	HR	UR
As	HR		–
	UR	–	
Au	HR		*
	UR	*	
Ba	HR		*
	UR	*	
Br	HR		*
	UR	*	
Ca	HR		*
	UR	*	
Co	HR		–
	UR	–	
Fe	HR		*
	UR	*	
K	HR		*
	UR	*	
Mo	HR		–
	UR	–	
Na	HR		–
	UR	–	
Rb	HR		–
	UR	–	
Sb	HR		–
	UR	–	
Sc	HR		*
	UR	*	
Sr	HR		*
	UR	*	
Zn	HR		–
	UR	–	

* significant difference at $\alpha \leq 0.05$

4. 2. Trace Elements

The uptake of trace elements by plants is a key stage in the soil-plant-animal/human pathway and is second only to intake via drinking water with regard to the link between geochemistry and human health, apart from where there is excessive ingestion of soil. The amount of metal uptake from soils is influenced by soil factors, including pH, redox potential, organic matter content, fertilizer application, the presence of Mn, Fe and Al oxides/hydroxides, cation-exchange capacity, texture and the amounts of other metals and plant factors including plant species cultivars and age. However, marked differences can occur within families and within species and plant parts.

Many studies have shown that even within species there are great genotypic differences in the effect that heavy metals have on plant growth, grain yield as well as the heavy metal concentrations in grain. The term heavy metals refers to trace metals and metalloids having densities greater than 5 g/cm^3.

Metalloid As is a constituent of most plants, but little is known about its biochemical role. It is generally accepted that the concentrations of As in edible plants grown on uncontaminated or unmineralized soils vary from 0.009 to 1.5 μg/g. The mean value for As concentrations in brown rice from Taiwan is 0.17 μg/g. Liu et al. reported that the rice grains collected in the area covered with Pb-Zn mining tailing spills showed elevated As concentrations of about 0.49 μg/g. In Poland the critical contents of As in plants used as food assessed by the Institute of Plant protection in Poznan was 0.20 μg/g. During this study As concentrations in unpolished rice were found to be in the range of 0.109 to 0.52 μg/g with a median value of 0.18 μg/g (Table 4), which were still within the normal range reported by Kabata-Pendias and Pendias. However, these values were up to 2.6 times higher than the corresponding limit level of 0.2 μg/g for food plants and up to 4.3 times higher than the As concentrations in polished Zlato polje rice and most probably indicated the possible contamination related to the mining activities of the region.

The Au concentrations in polish rice samples were in the range 0.00038 to 0.0066 μg/g, with a median value of 0.0009 μg/g (Table 4), while the Au content in the polished Zlato polje rice were below the detection limit of the analytical method. These concentrations were far below the range of Au concentration levels in barley and flax roots (from 0.014 to 0.022 μg/g) as reported by Ozoliniya and Kiunke.

Although Ba is reported to be commonly present in plants, it apparently is not an essential component of plant tissue. The Ba concentrations in cereal grains from different countries were in the range of 4.2 to 6.6 μg/g with a mean value of 5.5 µg/g. In this study, Ba concentrations in unpolished rice sampled were in the range < 1 to 40.8 µg/g (Table 2). The Ba content in polished Zlato polje rice was below the detection limit. Although the Ba concentrations in samples from magazines No. 1, 2, 7, 8 and 11 were also below the detection limit of the analytical method, in two magazines, No. 3 and 6, however, they were found to be as high as 40.8 and 11.6 µg/g (Table 2), which indicated the possible anthropogenic contamination of the unpolished rice.

Br is reported to occur in all plant tissues although it is not yet known whether it is essential for plant growth. The natural Br content of plants seems not to exceed about 40 µg/g, and some higher values could apparently be related to pollution. The Br concentrations in analysed de-hulled rice samples, which were in the range 0.23 to 2.08 µg/g (Table 4), suggested that Br is not a contaminant element in the rice of Kočani Field.

Cd is considered to be one of the most environmentally hazardous trace metals. It is mobile in the soil-plant system and easily transfers along the food chain. The background levels of Cd in cereal grains were in general in the range 0.013 to 0.22 µg/g. According to Jung the Cd concentrations in rice grown in various countries were in the range of 0.01 to 0.05 µg/g, while the average level of Cd in rice reported by Al-Saleh and Shinwari was 0.02 µg/g. Brown rice from the Cd contaminated paddy soils in Japan contained 1 µg/g Cd or more. Very high concentrations of Cd (5.9 µg/g) were also found in brown rice grown in contaminated soils in Taiwan. Extremely high concentrations of Cd (6.99 µg/g) were measured in rice affected by the Chenzhou Pb-Zn mine spill in China, while an average Cd concentration level of 0.24 µg/g in unpolished rice contaminated due to irrigation with untreated mining water from the paddy field around the Lechang Pb-Zn mine (southern China) was reported by Yang et al.

In this study Cd concentrations above the detection limit of 0.1 µg/g were measured only in the rice with a hull and in the polished rice samples from the magazine No. 9, which contained rice mostly from the paddy fields close to the Zletovska River (Tables 1 and 2). The measured value of 0.21 µg/g in the polished rice was in the upper part of the range for cereal grains reported by Kabata-Pendias and Pendias. However, it was slightly higher than the internationally recognized maximum level (ML) for Cd in rice grain of 0.2 µg/g and 2.1 times higher than the maximum permitted levels of 0.1 µg/g for food suggested by the Commission Regulation Directive. The ML is based on both a safe lifetime consumption of rice and the free movement of rice in international trade. From a health perspective, the Joint FAO/WHO Expert Committee of Food perspective agreed to maintain the provisional tolerable weekly intake (PTWI) of Cd at 7 µg/g Cd per kg body weight (BW) per week. This PTWI value is established to prevent a potential Cd-induced detrimental health impact via dietary Cd intake and is based on a rice grain Cd of < 0.2 µg/g. However, in Japan the maximum permissible level of Cd in unpolished rice is 1.0 µg/g. In Taiwan, it is 0.5 µg/g, while in mainland China it is 0.4 µg/g. Although the measured concentrations in the unpolished rice from the magazine No. 9 were still below the permissible levels for the unpolished rice from most Asian governments they undoubtedly suggested the heavy metal contamination related to the mining activities in the Zletovo-Kratovo ore district.

The maximum Co and Cr concentrations in the unpolished rice of Kočani Field (0.046 and 0.157 µg/g) (Table 2) were in the range from around 0.004 to 0.080 µg/g and of 0.02 to 0.2 µg/g reported for the Co and Cr contents in cereal grains and/or plant material. In this range were also the concentrations of Co and Cr measured in polished Zlato polje rice (0.003 and 0.2 µg/g) (Table 2). Recently, Jung et al. reported the median content of Co and Cr in unpolished rice from South Korea to be 0.006 and 0.093 µg/g. These values are lower than those of unpolished Kočani rice and suggested that our samples would be contaminated to some extent with these two elements. For example, in rice from the contaminated area of Asembagus (East Java, Indonesia) due to irrigation by contaminated water impacted with effluent from the hyperacid Ijen Crater Lake the Co concentrations were of about 0.027 µg/g.

Rare-earth elements (REEs) in plants follow their occurrence in soil. The order of REEs content in plants decrease with the increase in the atomic number. In the analysed rice samples their concentrations were mostly below the detection limit of the analytical method. The only exceptions were La and Sm in some hulled rice samples and La in unpolished rice and in Zlato polje rice grains, with concentrations close to the detection limit (Table 2).

Mo is an essential micronutrient, but the physiological requirement for this element is relatively low. Mo median concentrations of 0.28 µg/g and its maximum concentration level (0.38 µg/g) in unpolished rice (Table 4) as well as the Mo content of 0.35 µg in polished Zlato polje rice (Table 2) measured in this study were in the range of 0.12 to 1.14 µg/g, as reported by Adriano for cereal grains. The Mo concentrations in rice grown in the polluted soil of Asembagus (East Java, Indonesia) were reported to be 0.102 µg/g and were even lower than that of 0.325 µg/g measured in rice grains from the reference uncontaminated locations of the same area. This is probably because of the low soil pH, which is in contrast with many other metals, negatively correlated with the bioavaibility of Mo.

Rb is apparently easily taken up by plants, where it may partly substitute for K sites as their properties are similar, but it cannot substitute for the metabolic role of K. The mean concentrations of Rb in cereal grains were reported to be 4 µg/g. The Rb content in the range from 0.95 to 19.1 µg/g and a median value of 3.08 µg/g were measured in unpolished rice during this study (Table 4). The polished Zlato polje rice was, however, depleted in Rb content and exhibited Rb concentrations of about 0.42 µg/g (Table 2), which was lower than the reported mean for cereal grains. However, the highest concentrations of Rb were still below the range 20 to 70 µg/g found for most of the higher plant species.

In general very little is known about plant uptake of Sb and its phytoxicity. Adriano reported that the normal levels in most terrestrial plants should be around < 0.1 µg/g. In the present study the Sb concentrations of all rice samples were also below that value (Table 2).

There is a paucity of data on the Sc distribution in plants. The Sc content seemed to be higher in older leaves than in younger leaves, and its highest concentrations in the range of 0.014 to 0.026 µg/g were reported for flax plants, while in lettuce leaves Sc ranged from 0.007 to 0.012 µg/g. The medium value of 0.0004 µg/g and the maximum concentrations of 0.0018 µg/g for Sc in unpolished rice samples on the Kočani paddy fields (Table 4) were considerably lower, relative to that range and also as compared to the extremely elevated Sb concentrations of 0.039 measured in polished Zlato polje rice (Table 2).

The Se content in crops receives popular attention because of its importance in the food chain. Usually, vegetables are mostly low in Se content (0.010 µg/g) and grain and cereal products contain < 0.010 to 0.670 µg/g Se. The variation of Se concentrations in staple foods such as rice, wheat and corn is mainly due to the variation of geochemistry, the conditions and the types of plants. The normal Se content in rice grain ranged from 0.04 to 0.07 µg/g. Se concentrations in rice produced in the Yangtze River Delta ranged from 0.020 to 0.036 µg/g, with an average of 0.029 µg/g. In this study the Se contents in the sampled rice and polished Zlato polje rice were mostly below the detection limit of 0.05 µg/g. However, the only exception was the rice sampled at magazine No. 4 and 5 with detectable concentrations in the hulled grain of 0.082 and 0.085 µg/g (Table 2) and slightly lower contents in the grain with a hull (0.066 and 0.075 µg/g) (Table 1). These values are only slightly higher than the upper limit of the Se range in normal rice grain reported by Zhen and Li.

The Sr concentrations in plants are highly variable and are reported to range from < 1 to 10.000 µg/g. In wheat grains the Sr content ranged from 0.48 to 2.3 µg/g. A slightly higher content of Sr with a median value of 1.5 µg/g and a range from < 1 to 3.5 µg/g (Table 4) were found in the unpolished rice sampled from Kočani Field. In polished Zlato polje rice the Sr content was also found to be below the detection limit of 1 µg/g (Table 2).

Bowen reported a range of contents of Th in land plants of < 0.008 to 1.3 µg/g, while Laul et al. found Th concentrations in vegetables in the range between < 0.005 and 0.020 µg/g. In the present study Th content at detectable concentrations in the similar range of < 0.0024 to 0.018 µg/g were measured only in the rice with a hull from some magazines of the local farmers (Table 1). The polished Zlato polje rice was, however, considerably enriched, with a Th content of 0.052 µg/g (Table 2), which was, however, still in the reported range for land plants.

Zinc is one of the essential nutrients for both plants and animals. In high concentrations it can be toxic to living organisms. It is assumed that Zn concentrations in plants vary considerably, reflecting different factors of the various ecosystems and genotypes. However, the Zn contents in certain foodstuffs, cereal grains and pasture herbage from different countries do not differ widely. In edible plants from uncontaminated soils the content usually ranges from 1.2 to 73 µg/g. There are two limits proposed for Zn concentrations in crops: 50 µg/g in crops grown for food and 100 µg/g in crops grown for forage. According to Nriagu and Liu the average for Zn in rice sold in the United States was 23 µg/g, while the median value for Zn in wild rice from northern Wisconsin, USA, was 43.9 µg/g. Zn concentrations in unpolished rice samples were in the range 11.7 to 23.7 µg/g, with a median value of 17.5 µg/g (Table 4), while in polished Zlato polje rice it attained only 10.8 µg/g (Table 2). The median value of 17.5 µg/g for Zn was similar to median values of 16.9 µg/g for rice grain reported by Jung et al. as well as to an average Zn content of 16.4 µg/g for unpolished rice from 22 countries. These values were much lower than the concentration level of Zn (43.19 µg/g) in rice from the Chenzhou mine (Southern China) impacted area. Compared to the Zn concentrations in cereal grains grown around a lead smelter in the Upper Silesia Region (Poland), which were in the range from 30.3 to 111.7 µg/g, the Zn contents in unpolished rice measured in this study were much lower than that in the Upper Silesia Region. It is interesting to note that the highest concentrations of Zn (23.7 µg/g) were measured in rice from magazine No. 9, which also exhibited the highest Cd concentration level (0.21 µg/g) and Mo concentration of 0.38 µg/g (Table 2). Such elevated levels of the above- mentioned trace elements indicated the heavy metal pollution related to the mining activities and acid mine drainage impacted riverine water used for the irrigation of the paddy fields from which the rice was reaped. The highest Zn concentrations in unpolished rice from Kočani Field were similar to the average Zn content of 22.5 µg/g in rice grain from soils in Korea impacted by Pb-Zn mining activities.

4. 3. Dietary Risk Assessment

This study was also attempted to estimate the possible dietary exposure to the levels of some heavy metals such as As, Cd and Zn in the Macedonian rice of Kočani

Field. From the data obtained on heavy metal concentrations in unpolished rice it is possible to estimate the daily and/or weekly safe intake of heavy metal via rice consumption as well as the safe weekly rice intake in kg. The calculation was made according to the equation:

$$WI = WXdi / BW$$

Where WXdi is the weekly intake of heavy metal X (X = As, Cd, Zn). The weekly intake of the heavy metal X is the daily rice intake in kg x 7 x rice grain heavy metal X concentrations (μg/g) and BW is the body weight in kg. Assuming a provisional tolerable weekly intake (PTWI) in μg/kg/BW of inorganic As (15 μg) and Cd (7 μg) and a provisional maximum tolerable daily intake for Zn of 300 to 1000 μg/kg/BW the estimated weekly intake of unpolished rice of Kočani Field (in kg) containing the maximum concentration level in μg/g of As (0.52), Cd (0.21) and Zn (23.7) were calculated to be 2.0 and 2.3 kg for As and Zn and in the range from 6.2 and 20.7 kg for Zn (for an adult of 70 kg BW) (Table 6).

Table 6. The estimated safe weekly intake of unpolished rice (in kg) from Kočani paddy field containing the maximum concentration levels of As, Cd and Zn for adults of 70 kg BW.

El.	PTWI (μg/kg/BW)	Maximum concentrations (μg/g)	PTWI for 70 kg BW adult (μg)	Safe weekly rice intake (kg)
As	15	0.52	1050	2.0
Cd	7	0.21	490	2.3
Zn	2100	23.7	147	6.2
Zn	7000	23.7	490	20.7

The results indicated that a regular consumption only of rice with the highest concentrations of As and Cd in weekly amounts greater than those presented in Table 6 could pose a potential health problem from long-term As and Cd exposure. In the broader area of Kočani Field the expected major contribution of the daily intake of heavy metal is not only from rice but also from other consumed edible plants, in the proportion of contaminated food in the whole diet and the intake of heavy metals from other sources, such as drinking water, atmosphere, regular farming activities in paddy fields and everything in the environment. For further discussion more detailed studies on heavy metal concentrations in agricultural soils, irrigation and drinking water, rice and other edible plants are essential and such future studies are planned.

5. Conclusions

The contamination of riverine water used for the irrigation of the Kočani paddy soil due to the mining activities and acid mine drainage from the Zletovo-Kratovo and Sasa-Toranica Pb-Zn ore district has caused increased concentrations of various trace elements in the rice of that area.

The unpolished rice analysed during this study by k_0-instrumental neutron activation analysis had the normal levels of the major elements (Ca, Fe, K and Na), and these elements were distributed within the rice grain as expected. The concentration levels of heavy metals such as Au, Br, Co, Cr, REE, Mo, Sb, Sc and Zn were generally within the normal limits published for edible plants and cereals consumed in other parts of the world, while those of Ba, Rb, Se and Sr in rice collected in some magazines slightly exceeded their normal content in cereal grains as reported from different countries.

However, the amount of As measured in unpolished rice from magazines No. 1 to 4 and that of Cd found only in magazine No. 9, which mostly contained the rice grown in the most polluted paddy fields in the vicinity of Zletovska River substantially exceeded some national standards and international recommendations. Thus, an urgent and more systematic study of the heavy metal concentrations in rice and other foodstuffs as well as of agricultural soils and irrigation water is recommended, since the long-term dietary heavy metal intake could pose a serious threat to human health.

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Povzetek

S k_0 nevtronsko aktivacijsko analizo smo raziskali vsebnost nekateri glavnih in slednih prvin v oluščenem in neoluščenem rižu iz 10 različnih skladišč na območju Kočanskega polja v Makedoniji. Raziskava je pokazala, da vsebnost toksičnih prvin v oluščenem rižu večinoma ne presega mejnih vrednosti za prehrambene izdelke. Izjema sta le As, katerega vsebnosti v oluščenem rižu iz nekaterih skladišč so v intervalu 0,23–0,52 μg/g, kar je več od dovoljene vsebnosti v hrani (0,2 μg/g), in Cd iz skladišča, v katerem je bil riž v glavnem požet v neposredni bližini Zletovske reke. Tu so tla zaradi navodnavanja z rečno vodo, v katero se izlivajo tako rudniške odplake iz Pb-Zn rudišča Zletovo kot meteorska voda, ki drenira haldo in flotacijsko deponijo, močno onesnažena s težkimi kovinami. Vsebnost Cd v rižu iz tega območja je 0,2 μg/g, kar je dvakrat več, kot je dovoljena vsebnost (0,1 μg/g) v hrani. Redno konzumiranje riža z najvišjo vsebnostjo As in Cd v količini, večji od 2 kg tedensko, lahko na daljši rok vodi do zdravstvenih problemov.