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TRACE ELEMENT CONTENT OF SEVERAL WEED SEEDS

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Abstract: Although there is a potential contamination of cereal grains by weed seeds, an evaluation of microelement and potentially toxic element content of weed seeds concerning the potential contribution to the culture plant grains is still lacking. In our study, 30 seed samples from different weed families were analysed for some potentially toxic elements (Al, Cr, Hg, Pb) and microelements (Fe, Mn, B, Zn, Cu, Ni, Co, Se). Taking consideration the fact that even at low level of weed seed contamination of the cereal grains (1 % m/m)) increased significantly the toxic element concentrations of that, Al and the Sr can be regarded as potentially harmful elements concerning to the food chain. There is a significant increase of Al concentration at 5 % contamination level; the concentration was nearly two-fold comparing to the ingenious concentration, while for Sr the final concentration of the grain+weed seed mixture is higher by 166.7 % than the initial concentration. In case of microelements, the modifying effect of the weed seeds on it was more moderately. There was 1.9-21.2 % increase for Cu, 0.2-47.9 % for Mn and 0.5-7.8 % for Zn.

Keywords: trace element, toxic element, micronutrient, weed, seed, wheat, maize

1. INTRODUCTION

The food chain might be polluted by toxic elements, aromatic compounds etc. through the simultaneous harvesting of weeds and crops (Liener, 1969; Crawford & Friedman, 1990). The contamination of grains by weeds and weed seeds represents approximately 1 to 5% of the grains delivered to customers (Harrold & Nalewaja, 1977). Weeds and their seeds are considered as potentially harmful materials contaminated by toxic elements (Cd, Hg, Cr, Pb etc.). Also, seeds can contain microelements (Fe, Mn, B, Zn, Cu, Ni, Co, Se) that are useful of any living creatures. The investigations of the toxic element and microelement contents of weeds are important to improve our knowledge of this field.

To date, in most research, the main task is the evaluation of the phytoremeditation potential of the given weed plant. A systematic assessment of the nutrient and toxic element concentrations in the weed seed based on the weed families is still lacking. The uptake and accumulation of nutrients or toxic elements in plants depend on their genetic properties and so, on the species and the family (Singh et al., 2003). Consequently, it would be worth clarifying how weed families affect the nutrient and potentially toxic element accumulation and also revealing the differences in the rates of accumulation between families.

For this reason, our objectives are (i) to measure the potentially toxic element (Al, As, Cr, Hg, Ni, Pb) and microelement contents (B, Co, Cu, Fe, Mn, Mo, Se, Zn) in 30 weed seeds from 12 weed families, (ii) to evaluate the risk of the contamination of toxic elements in wheat and maize by the seed of weeds, and we want (iii) to estimate the influence of the weed family on the element contents.

2. MATERIALS AND METHOD

2.1 Study area

The survey area was a cultivated area of Hungary with an average annual precipitation of 678±134 mm. The soil type is Eutric Cambisol according to FAO classification (FAO, 1998). The pH of the top 30 cm of soil is 6.79 in KCl solution, organic matter content is 1.9 %, $CaCO_3$ content is 0.4 %. The texture of the soil is sandy silt. The most common cereals are wheat, rye and barley. The cereals are combine-harvested in July.

2.2 Plant sampling procedure

Weed samples were taken in July of 2011 by sampling the mature weed plants on an area of 2 m × 2 m. In the laboratory, weeds were trashed and their seeds were manually separated. The 30 weed species are listed in table 1.

2.3 Chemical analysis

Determination of the weed seed concentrations for Al, B, Co, Cr, Cu, Fe, Mn, Zn, As, Mo, Ni, Pb, Se was carried out with ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) method after microwave Teflon bomb digestion with cc. HNO_3 + H_2O_2 (Kovács et al, 1996). For ICP-MS analysis, each sample was analyzed in triplicate and quantified using external standards analysis. BCR (Community Bureau of Reference) CRM (certified reference materials) (No. 189) was analyzed by the proposed methodology to assure the accuracy of the whole analytical procedure (Table 2).

Table 2. Results of the analysis of certificated samples

Element	Certified value	Measured value
Cd (µg·kg^{-1})	71.3±3.0	69.2±14
Pb (µg·kg^{-1})	379±12	382±20
Se (µg·kg^{-1})	132±10	135±15
Cu (mg·kg^{-1})	6.4±0.2	6.42±3.12
Zn (mg·kg^{-1})	56.5±1.7	57.3±1.12
Fe (mg·kg^{-1})	68.3±1.9	69.2±2.53
Mn (mg·kg^{-1})	63.3±1.6	61.5±3.52

[a] mean±standard deviation

2.4 Calculation of the risk of toxic element contamination

To calculate the final concentration of toxic elements in the grain-weed seed mixture weeds were selected according to prevalence of that on wheat and corn fields (Novák et al., 2009; Table 1).

Table 1. Weeds investigated

	Name	Family	Raunkiær's life form*	Typical plant associated with weed
1	*Abutilon theophrasti*	Malvaceae	Th	maize
2	*Amaranthus albus*	Amaranthaceae	Th	
3	*Amaranthus retroflexus*	Amaranthaceae	Th	maize
4	*Ambrosia artemisiifolia*	Asteraceae	Th	wheat/maize
5	*Asclepias syriaca*	Apocynaceae	H	
6	*Bilderdykia convolvulus*	Polygonaceae	Th	
7	*Calystegia sepium*	Convolvulaceae	H	
8	*Chenopodium album*	Amaranthaceae	Th	wheat/maize
9	*Chenopodium hybridum*	Amaranthaceae	Th	maize
10	*Cirsium arvense*	Asteraceae	G	wheat/maize
11	*Consolida regalis*	Ranunculaceae	Th	wheat
12	*Convolvulus arvensis*	Convolvulaceae	H/G	wheat/maize
13	*Conyza canadensis*	Asteraceae	Th/TH	
14	*Cynodon dactylon*	Poaceae	G(H)	maize
15	*Datura stramonium*	Solanaceae	Th	maize
16	*Echinochloa crus-galli*	Poaceae	Th	maize
17	*Galinsoga parviflora*	Asteraceae	Th	
18	*Matricaria inodora*	Asteraceae	TH/H	
19	*Panicum miliaceum*	Poaceae	Th	maize
20	*Persicaria lapathifolia*	Polygonaceae	H	maize
21	*Polygonum aviculare*	Polygonaceae	Th	wheat
22	*Polygonum persicara*	Polygonaceae	Th	
23	*Senecio vulgaris*	Asteraceae	Th/TH	
24	*Sinapsis arvensis*	Brassicaceae	Th	
25	*Solanum nigrum*	Solanaceae	Th	
26	*Sorghum halepense*	Poaceae	G(H)	maize
27	*Stellaria media*	Caryophyllaceae	Th/TH	wheat
28	*Veronica hederiflora*	Plantaginaceae	Th	wheat
29	*Xanthium spinosum*	Asteraceae	Th	
30	*Xanthium strumarium*	Asteraceae	Th	

*Th: therophyta; H: hemikryptophyta; G: kryptophyta; TH: hemitherophyta (Raunkiær, 1934).

The average concentration of the selected weed seeds for the given plant (wheat or maize) was used for the following calculation. When two sources of differing composition are mixed, the resulting mixture represents an average of the two sources weighted for the amount of toxic element contributed by each source. Binary mixing model was used to calculate the toxic element concentrations of the harvested grain contaminated weed seeds. A mixing parameter (f) was defined that describes the proportions of end-members:

$$f_w = \frac{W_w}{W_w + W_{cp}}$$

$$f_{cp} = 1 - f_w$$

where f_w, f_{cp}, W_w and W_{cp} are the mixing parameter and weights of the weed and the culture plant grain in a given mixture.

The concentrations of toxic element in a mixture of the weed seeds and grain are calculated as a weighted average:

$$c_f = c_w \cdot f_w + c_{cp} \cdot (1 - f_w)$$

where c_f, c_w and c_{cp} are the concentration of the harvested grain, weed seed and the culture plant.

Two scenarios were set; one of them is the calculation the amount of the weed seed at 1 % (m/m), while the other one is the same calculation at 5 % (m/m).

2.5 Statistical methods

Analysis of variance (ANOVA) of data concerning the element concentrations in the different weed families was carried out by using a SPSS 16.0 software. To evaluate the ranking order of trace element contents in the weed families, we carried out a pot hoc test according to Duncan at $p<0.05$ with only families that have more than one species.

3. RESULTS AND DISCUSSIONS

3.1 Potentially toxic elements and microelement concentrations in 30 weed seeds

In this study, seeds of 30 weed samples were analysed for potentially toxic elements and microelement concentrations (Table 3). Al, As, Ba, Cd, Mn, Pb and Sr showed high variability which was indicated by the huge differences between the minimum and the maximum values.

Very limited information is available on the toxic element contents of weed seeds. Fatima et al., (2013) applied neutron activation analysis to characterize As, Ba, Br, Ce, Cl, Co, Cr, Cs, Eu, Fe, Hg, K, Mn, Na, Rb, Sb, Se and Zn, and Sc in seeds of *Anethum graveolens*, *Sisymbrium irio Linn*. and *Vernonia anthelmintica*. If we compare their results to ours, in our study the average Ba content in the weed seeds is 3.4 mg·kg^{-1}, while in Fatima's study the contents ranged from 20 to 40 mg·kg^{-1}. Also, as regards Hg, there is a marked difference between the 0.88 mg·kg^{-1} concentration measured in 30 weeds and the three weeds investigated by Fatima (0.01-0.045 mg·kg^{-1}).

Selected microelement contents (Cu, Zn, Fe, Mn) were determined for 15 weed seeds (Harrold & Nalewaja, 1977), and turned out that the compositions of weed seeds are comparable to our own results with the exception of Fe, for which very high concentrations were determined by Harrold & Nalewaja (1977) (615-1671 mg·kg^{-1}), while our highest value was 193 mg·kg^{-1} for *Cynodon dactylon*.

3.2 Evaluation of the risk of toxic element contamination of the food chain by weed seeds

Relevant questions can be asked about the toxic element contents of weed seeds by comparing these values to the toxic element concentrations of small grain crops, e.g. wheat, barley, oat, estimating the potential risks weed seeds may pose for the food chain. The changes in concentration of toxic and microelements of wheat and maize grain were calculated after weed seeds contamination at two different levels, namely at 1 % (m/m) and at 5 % (m/m). These contamination scenarios are adequate to evaluate the risk of toxic element contamination because the weed coverage in arable land is about 20-30 % (Novák et al., 2009), consequently the 5 % (m/m) percentage of contamination is possible.

Maize and wheat data (Győri, 2009) was used to make the calculations because these data are from similar environmental conditions to weed plants (Keszthely, Hungary).

Considerable increments were found for all elements investigated; both for toxic elements (Al, Sr) and for microelements (Cu, Mn, Zn) there was significant effect of the weed seeds on the element content of the harvested grain concentrations (Table 4).

In case of wheat, there is a significant increase of Al concentration at 5 % contamination level; the concentration was nearly two-fold comparing to the ingenious concentration. The highest increment was recorded for Sr, where the final concentration of the grain+weed seed mixture is higher by 166.7 % than the initial concentration.

Table 3. Trace element content of the weed seeds investigated.

	Al	**As**	**B**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Mo**	**Ni**	**Pb**	**Se[2]**	**Sr**	**Zn**
	mg·kg⁻¹															
1[1]	6.2	0.09	31.3	0.64	0.06	0.41	0.82	13.0	39.8	21.1	0.43	1.7	*BDL*	*BDL*	5.8	57.1
2	172	0.17	8.5	6.2	0.10	0.44	0.95	5.6	132	40.4	0.32	0.66	0.11	*BDL*	5.0	43.4
3	26.1	0.43	12.3	2.6	0.13	0.50	0.74	5.5	110	35.6	1.1	1.7	4.2	45.9	7.9	40.1
4	29.8	0.52	26.4	2.1	0.08	0.49	0.71	30.3	85.3	33.7	1.6	4.3	2.9	115	16.7	52.0
5	9.3	0.52	25.3	0.67	0.16	0.38	0.74	18.4	66.5	49.0	2.2	3.8	1.7	218	7.8	58.3
6	32.2	0.17	19.0	1.5	0.04	0.50	0.55	4.7	64.2	20.0	0.19	0.82	1.7	*BDL*	11.6	19.8
7	14.1	0.04	12.5	1.8	0.00	0.38	0.56	16.8	65.8	31.1	0.65	0.48	*BDL*	80.6	5.3	31.3
8	18.6	0.06	15.1	0.82	0.05	0.33	0.58	8.6	53.2	80.4	0.23	0.71	*BDL*	*BDL*	4.9	25.9
9	18.3	0.03	10.3	0.47	0.04	0.26	0.40	11.2	50.2	17.6	0.80	0.58	*BDL*	*BDL*	2.8	33.5
10	51.4	0.26	21.8	2.3	0.10	0.41	0.50	19.2	55.4	24.0	0.46	1.6	6.3	38.1	14.0	42.9
11	25.4	0.46	28.8	3.5	0.34	0.37	0.54	14.5	71.3	17.3	2.4	0.80	*BDL*	*BDL*	30.1	67.2
12	5.9	0.09	14.9	2.4	0.06	0.44	0.57	16.6	55.6	47.9	0.52	0.76	*BDL*	*BDL*	2.6	29.3
13	293	0.62	29.7	5.8	0.23	0.85	1.1	38.5	86.2	69.7	1.1	2.5	1.0	91.9	28.0	89.2
14	547	0.44	13.8	12.7	0.10	0.79	1.9	7.0	193	124	0.72	1.7	5.6	44.7	9.1	49.1
15	29.2	0.04	19.2	0.74	0.09	0.39	0.72	12.4	74.6	22.5	0.87	0.47	*BDL*	*BDL*	2.0	34.3
16	17.1	0.07	4.8	0.26	0.05	0.37	0.70	8.9	42.4	60.4	0.40	2.9	*BDL*	*BDL*	4.6	36.0
17	21.8	0.22	10.0	18.1	0.03	0.35	0.58	7.0	40.0	18.2	0.69	1.2	*BDL*	*BDL*	22.5	33.6
18	13.2	0.13	23.7	0.31	0.10	0.37	0.54	12.6	44.6	40.3	2.3	2.5	6.5	*BDL*	7.8	43.7
19	1.6	*BDL*	3.8	0.26	0.01	0.28	0.24	9.2	51.7	13.3	0.35	2.0	*BDL*	*BDL*	1.1	18.2
20	64.4	0.03	6.7	2.2	0.03	0.30	0.50	6.6	71.1	14.7	0.32	1.8	*BDL*	40.6	5.9	29.3
21	634	1.2	12.1	9.8	0.09	0.68	1.1	9.4	102	67.5	0.25	2.1	4.6	32.4	25.1	38.8
22	12.9	*BDL*	13.1	4.2	0.01	0.41	0.55	10.3	34.1	201	0.16	0.77	*BDL*	*BDL*	13.0	36.1
23	71.8	0.20	29.2	2.8	0.05	0.92	0.36	15.8	148	42.5	1.3	2.6	*BDL*	*BDL*	10.3	44.8
24	6.7	0.19	10.9	1.8	0.13	0.52	0.83	6.3	59.5	21.5	0.66	0.52	*BDL*	71.6	27.5	51.7
25	7.1	0.02	7.3	0.53	0.10	0.57	0.88	13.3	78.7	40.4	0.96	0.59	*BDL*	24.9	3.4	50.9
26	9.4	*BDL*	5.5	0.79	0.00	0.20	0.36	6.1	59.8	32.8	0.30	0.62	*BDL*	*BDL*	2.7	29.9
27	118	0.14	9.0	4.4	0.08	0.56	0.71	10.1	40.2	61.3	2.8	0.62	1.2	*BDL*	4.8	61.0
28	34.3	0.07	7.2	9.4	0.01	0.28	0.33	6.6	80.9	14.2	0.52	0.47	*BDL*	*BDL*	7.6	25.0
29	70.8	0.11	20.1	1.7	0.13	0.21	0.39	8.4	95.5	11.9	0.77	0.70	*BDL*	69.6	13.0	24.1
30	63.6	0.04	18.8	0.60	*BDL*	0.37	0.67	13.5	45.5	17.3	0.32	0.55	*BDL*	*BDL*	4.8	30.6

BDL: below detection limit; [1]Weed plants are listed in Table 1; [2] µg kg-1

Table 4. Changes in the concentration of the toxic and microelement of wheat and maize by samples of weed seeds (mg kg^{-1})

	Wheat				
Element	**Al**	**Cu**	**Mn**	**Sr**	**Zn**
Ingenious concentration of grains[1]	5.7	4.9	36.2	3.6	28.5
Changes in concentration by weed contamination at 1% (m/m) level	+1.1 (19.3)[2]	+0.09 (1.9)	+0.07 (0.2)	+0.10 (2.7)	+0.14 (0.5)
Changes in concentration by weed contamination at 5 % (m/m) level	+5.4 (96.3)	+0.47 (9.5)	+0.35 (1.0)	+0.48 (13.5)	+0.71 (2.5)
	Maize				
Element	**Al**	**Cu**	**Mn**	**Sr**	**Zn**
Ingenious concentration of grains[1]	-	2.3	3.8	0.18	14.4
Changes in concentration by weed contamination at 1 % (m/m) level	-	+0.10 (4.2)	+0.37 (9.6)	+0.06 (33.3)	+0.22 (1.6)
Changes in concentration by weed contamination at 5 % (m/m) level	-	+0.48 (21.2)	+1.8 (47.9)	+0.30 (166.7)	+1.1 (7.8)

[1]Data from Győri, 2009. [2] Changes in concentration expressed by %.

In case of microelements, the modifying effect of the weed seeds was more moderately. There was 1.9-21.2 % increase for Cu, 0.2-47.9 % for Mn and 0.5-7.8 % for Zn.

These data indicate that in some cases the seed of weeds might be a risk to the food chain by contaminating small grain crops during the harvest and the industrial processing of food. Taking consideration the fact that even the low level of weed seed contamination of the cereal grains increased significantly the toxic element concentrations of that, Al and the Sr can be regarded as potentially harmful elements concerning to the food chain.

Calculation presented in table 4 shows moderate increase in Zn concentrations, while in case of Cu and Mn considerable increment was seen. It indicates that contamination of cereal grains by weed seeds may cause improvement in nutritional status.

Wheat and maize data of trace elements from literature from sites with different environmental sites clearly confirm the calculations presented above. Without any calculation – not to calculate exact effects because of the different sites characteristic – the main conclusions can be drawn from the data of table 5. The Al, As, B, Co and Cu concentrations in weed seeds were found to be significantly higher than those in cereal grains. In other studies, data for several toxic element concentrations in cereal seeds presented in Table 5, similar values were found regarding Cd and Pb. Similarly, the average Cr contents in seeds of weeds show similarity in the ranges of values to crop seeds.

For microelements, such as Se, Zn or Fe, on the average, there are not any advantages for weed seeds in contrast with cereal seeds, but Se contents in weeds were significantly higher than in wheat.

3.3 Differences in the element contents between weed seeds of different families

There were significant differences in the microelement concentrations and, in some cases, in the toxic element contents of the weed seeds belonging to different weed families. We found significant differences for B and Sr (Fig. 1).

In the case of B, the *Astereceae* family has the highest B value, followed by *Convolvulaceae* = *Solanaceae* > *Amaranthaceae* = *Poaceae* = *Polygonaceae*. The following order of Sr content was identified: *Astereceae* = *Polygonaceae* > *Amaranthaceae* = *Convolvulaceae* = *Poaceae* > *Solanaceae.*

Table 5. Statistical data of trace elements contents for 30 samples of weed seeds comparing to cereal grain concentrations (mg kg^{-1})

	WS[1]	**Zhao et al., (2013); wheat**	**Shtangeeva et al., (2011); wheat**	**Marwa et al., (2012); maize**	**Lavado et al., (2007), maize**	**Lavado et al., (2007), wheat**
Al	80.8±151.2[2]		17.9±7.5			
As	0.24±0.27		0.005±0.003	-0.01		
B	15.7±8.2		1.1±0.4		2.1±1.9	
Ba	3.4±4.2		5.6±1.1			
Cd	0.08±0.07	0.01-0.41	0.058±0.040		0.02±0.03	0.11±0.00
Co	0.44±0.17	0.005-0.02	0.016±0.007		0.25±0.00	
Cr	0.67±0.32	3.4-6.5	0.20±0.10	0.10-0.12	0.42±0.29	0.33±0.08
Cu	12.2±7.3	3.4-7.4	6.5±1.3		3.9±2.1	4.1±2.3
Fe	73.2±35.4	7.0-39.8	53.6±13.8			
Mn	43.0±38.8	22.9-46.7	34.4±11.2		9.2±2.9	
Mo	0.86±0.72		0.34±0.06			
Ni	1.4±1.0			0.52-3.23	0.65±0.57	0.28±0.08
Pb	3.2±2.3	0.046-0.699	0.10±0.09	0.01-0.02	4.1±3.3	1.4±0.1
Se	0.073±0.002	0.001-0.027				
Sr	10.3±8.4	3.52-10.4	4.8±1.8			
Zn	40.9±15.5	20.0-44.1	56.5±24.8		23.4±4.0	37.1±5.0

[1] weed seed; [2] Mean±standard deviation

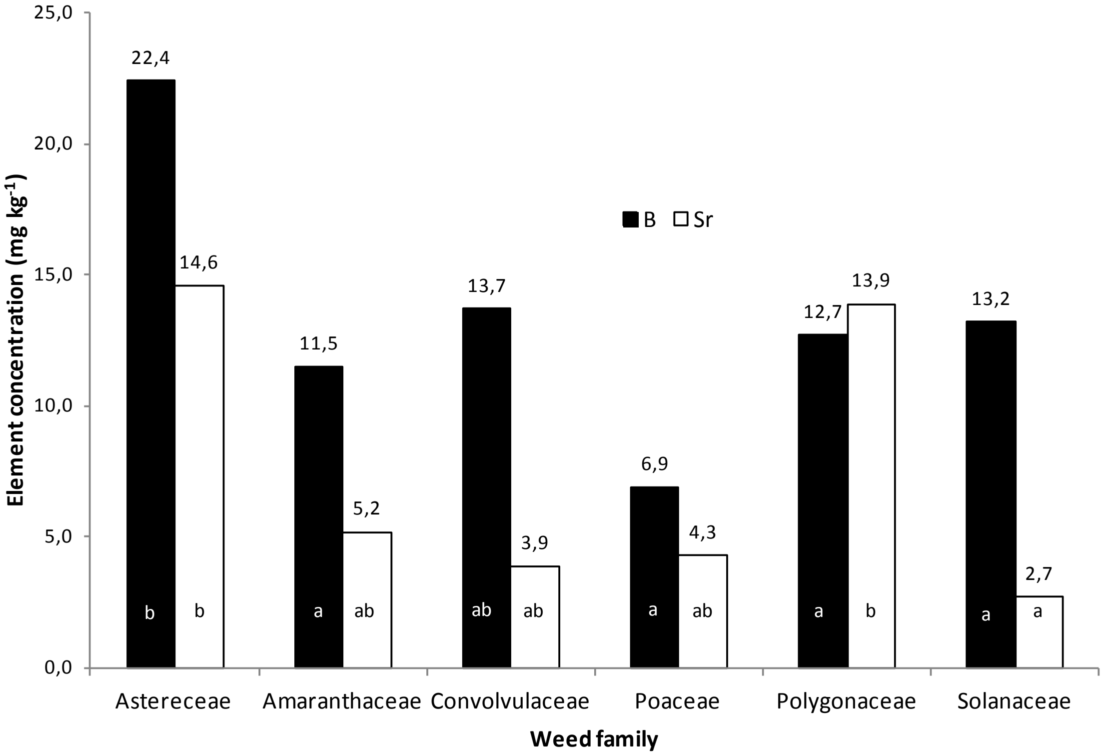

Figure 1. Boron and strontium concentrations in six different weed families (a–c) indicate significant differences within each column at the 5% level of probability according to Duncan's test).

Published experimental data on the family effect on element concentrations in weed seeds (Tanji & Elgharous, 1998) showed significant differences in most cases. These days it is a well-known paradigm that different genotypes may differ in their demands for mineral element supplies, capacities in their element uptake and transport in plants (Ramage & Williams, 2002; Lovkova et al., 2008; White & Brown, 2010).

Plant nutrient requirements are believed to be the main factors affecting the concentrations of different elements in a plant rather than concentrations of the nutrients in the soil (Markert, 1989). It was confirmed by surveys, which show different concentrations of trace and macro-elements even if different plants were grown in the same place (Løbersli & Steinnes, 1988; Willey et al., 2005).

Because of these considerations it has been assumed that the significant differences in the concentrations of element in the weed seeds investigated were mainly caused by the genetic variations between the weed species originating in different weed families.

4. CONCLUSIONS

In spite of the fact that relatively small quantities get into the food chain through the "contamination" of weed seeds, it may pose a real risk or on the contrary may become a nutrient source for humans and animals

As regards trace elements, being so called toxic or not, there may be a risk of contamination of the food chain, especially in respect of Al, As, Pb, Co, Cd, Ni and Sr. As shown in a comparison with the grain concentrations in cereal crops, these and other toxic elements may accumulate in to a great extent in the weed seeds in special conditions and this tenet might pose a risk to the food chain by contaminating small grain crops during the harvest and the industrial processing of food.

Differences in the element contents of seeds belonging to different weed families were found in case of B and Sr. These differences were mainly caused by the genetic variations in the weed species originating in different weed families.

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