GEOLOGICA BALCANICA, 42. 1 – 3, Dec. 2013, p. 49-57.

Trace elements in some biomass collected from areas associated with the lignite mining and power producing enterprise Maritsa East, Bulgaria

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(Accepted in revised form: November 2013)

Abstract. The contents and concentration trends of 53 elements in four vegetation species and their parts have been investigated. The studied samples include culture plants (wheat and sunflower) taken from the areas of Maritsa East-2 and Maritsa East-3 TEPSs as well as wild plants (*Hypericum perforatum* and *Typha*) collected from the Troyanovo-3 mine of Maritsa East lignite basin. According to the number of elements that exceed the lower limit of average values of terrestrial vegetation , the analyzed vegetation species could be arranged as follows: *Hypericum perforatum* > sunflower > *Typha* ≥ wheat. It has been found that in wheat and sunflower the elements with coefficient of concentration (CC) ≥3 exceeding the average values of terrestrial vegetation are Au and Cr, and Au and Sr, respectively. Most of the trace elements concentrate in wheat and sunflower stem+leaves while in *Hypericum perforatum* trace elements accumulate in blossoms. It has also been identified that the accumulated trace elements in *Typha* are equally distributed in all parts of the plant.

Yossifova, M.G., Dimitrova, D.A. 2013. Trace elements in some biomass collected from areas associated with the lignite mining and power producing enterprise Maritsa East, Bulgaria. *Geologica Balcanica* 42 (1 – 3), 49-57.

Key words: biomass, trace elements, concentration trend, Bulgaria.

INTRODUCTION

Mankind has been using biomass as energy resource for centuries. Even today, biomass is not only used in everyday way of life, but also as addition to other feed fuels for burning in thermo-electric power stations (TEPSs). Waste residues from food, wine and tobacco industries, agriculture and wood-processing are commonly used for such purposes. The increasing of bioenergy production at present caused an expansion in cultivation of different cultures that could be used for such a process. Recently, some extended overviews of: 1) chemical composition of biomass (Vassilev et al., 2010, Vassilev et al., 2014a,b); 2) organic and inorganic phase composition of biomass (Vassilev et al., 2012); 3) phase–mineral and chemical composition and classification of biomass ash (Vassilev et al., 2013a); and 4) potential application of biomass ash (Vassilev et al., 2013b) have been published to emphasize the importance of such topics for the future utilization of biofuels and their combustion products.

Biomass is not used presently as feed fuel for burning in the main thermo-electric power stations in Bulgaria such as Bobov Dol, Republika, Maritsa East–1, 2, 3, and Brikel TEPSs. They are processing only coals as feed fuel but there are some future perspectives for their possible co-firing with biomass. The aim of this study is to characterize the inorganic chemical composition of certain cultural and wild vegetation associated with the Maritsa East coal region.

GEOLOGICAL SETTING

The Maritsa East lignite basin is a part of the Zagore Depression of the Upper Thracian tectonic trough and has a complex geological structure (Valćeva et al., 2000). Three main geological bodies have been divided, namely: basement, coal-bearing formation and superstructure (Nedyialkov, 1979). The basement consists of granites, metamorphic and sedimentary rocks of different ages (from Late Cambrian to Late Cretaceous) and degrees of alteration. The Miocene coal-bearing formation is well developed with a sandy–clayey level at the bottom (Nedyialkov, 1985) and Maritsa (Troyanovo) coal level (Panov, 1982). The coal-bearing strata consist of three lignite seams interbedded by grayish-black thinly layered clays. The second seam of maximum thickness of 24 m bears the main coal reserves. The superstructure, namely the Gledachevo Formation (Nedyialkov and Kojumdgieva, 1983) covers the Maritsa coal-bearing sediments. It lies conformably over the Maritsa Formation and is covered, on its turn, by Quaternary sediments. The lithology of Gledachevo Formation consists of clays, sands, and limestones. The clays are the dominant rocks in the sedimentary sequence. They are gray to bluish-green or light green, and rust-yellowish in colour, layered, dense, and with variable quantity of sand. The sands and sandstones form lenses or wedging intercalations between the clayey layers, mostly in the uppermost parts of the sediments covering the coal complex (Valćeva et al., 2000).

The mining and power producing enterprise Maritsa East (Fig. 1) is the biggest unit for lignite mining and thermo-electric power generation in Bulgaria. It includes three large open-pit mines and four thermo-electric power stations (TEPSs). The total area of the coal and power-producing enterprise includes more than 200 km^2.

The region is located in the Thracian Plain, the second largest area in Bulgaria used in cultivation and production of grain cultures.

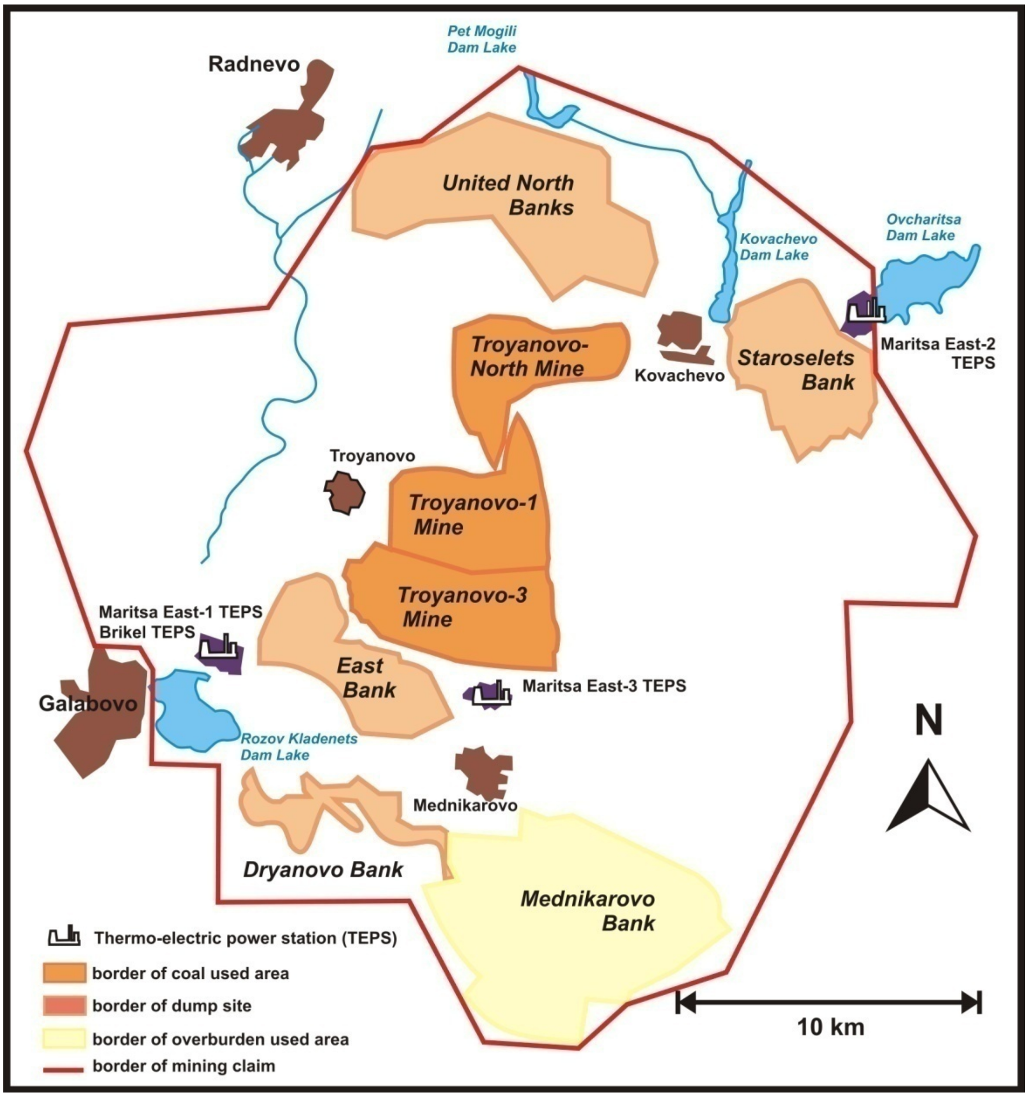

Fig. 1. Sketch map of Maritsa East lignite thermo-electric power enterprise unit, modified after Ganchev and Bossev (1988).

MATERIALS AND METHODS

The studied samples are listed in Table 1. They include composite samples of wild and cultural vegetation growing in the area of Troyanovo-3 mine and Maritsa East 2 and 3 TEPSs. Plant samples were water washed, cut in parts (blossoms, sunflower heads, wheat-ears and stems+leaves) and dried in furnace at 50°C. Then, the dried vegetation was milled, macerated to 1 mm and digested with aqua regia for further analysis using ICP-MS. Analyses were made in Acme Laboratories Ltd. (Canada).

RESULTS AND DISCUSSION

The concentrations of 53 elements have been determined in the studied vegetation (dry basis) and compared to the average values of terrestrial vegetation (AVTV) (Kabata-Pendias, Pendias, 1979). The results are shown in Tables 2 and 3. Element concentration ratios (*ECR*) of wheat stems+leaves to wheat-ears, sunflower stems+leaves to sunflower heads and stems+leaves to blossoms have been used to determine the concentration trend of elements in different part of plants (Table 4).

Wheat

Wheat-ears show concentrations of 13 elements exceeding AVTV (Al (?), K, Mo, P, Sc, Ti, V (?), Cr, Zn, Te (?), Bi, and Au). Some of them have coefficient of concentration (CC), even above the upper limit of AVTV such as $V_{(<2.9)}$, $Sc_{2.0}$, $Au_{1.3}$, and $Cr_{1.1}$.

Aluminum (?), K, Sr, Mo, Ba, S, Sc, Ti, V(?), Cr, Ni, Te(?), Pb, Bi, and Au have over AVTV concentrations in wheat stems+leaves, as those with values above the upper AVTV limit are: $Au_{23.0}$, $Cr_{3.2}$, $V_{<2.9}$(?), $Sc_{2.0}$, $Pb_{1.7}$, $Sr_{1.4}$, $(Mo, Ni)_{1.1}$.

A half of the measured elements show trend of concentration in stems+leaves, as the following elements have concentrations twice as higher than the wheat-ears: Pb, Au, Hg, Ag, Ba, Bi, Ca, K, Sr, Li, Y, Cr, Ni, Na, Zr, and La.

Only 6 elements tend to accumulate in the wheat-ears and have *ECR*>2: P, Ti, and Zn. The other 17 elements are equally distributed in all parts of the plant.

Sunflower

In the sunflower head samples, namely sunflower-I and sunflower-II, the elements exceeding AVTV are 21 and 22, respectively: Al, Mg, K, Ca, Rb, Sr, Mo, Ba, B, P, S, Sc, Ti, V (?), Cr, Co, Ni, Cu, Zn, Se, Te (?), Bi, and Au. The only difference between their chemical patterns is the presence of Sr and Co in sample sunflower-I and Ba and Rb in sample sunflower-II. The elements having CC exceeding the upper AVTV limit in sunflower-I heads are: $Au_{4.0}$, $V_{<2.9}$(?), $(Sr, Se)_{2.0}$, $Sc_{1.5}$, $K_{1.4}$, $P_{1.2}$, $Mg_{1.1}$, and respectively $V_{<2.9}$(?), $Sr_{2.6}$, $Au_{2.0}$, $(K, P)_{1.6}$, $(Sc, Se)_{1.5}$, and $Cu_{1.1}$ in sunflower-II heads.

A similar trend is observed in the stems+leaves samples. In the samples sunflower-I and sunflower-II, a total of 23 and 25 elements, respectively, exceed AVTV concentration. Generally, these groups comprise the following elements: Li, Mg, Al, K, Ca, Rb, Sr, Mo, Ba, La, B, P, S, Sc, Ti, V (?), Cr, Fe, Co, Cu, Zn, As, Se, Te (?), Bi, U, and Au. Unlike the sunflower-I sample, where As and U were determined, the sunflower-II sample is enriched in Rb, Ba, Co, and Zn. The elements having CC above the upper AVTV values are: 1) $Au_{6.8}$, $Sr_{3.4}$, $V_{<2.9}$(?), $(K, La)_{1.9}$, $Mg_{1.8}$, $(Sc, As, Se)_{1.5}$, $Li_{1.4}$, and $U_{1.1}$ in sunflower-I; and 2) $Au_{6.0}$, $Sr_{3.7}$, $K_{2.9}$, $V_{<2.9}$(?), $Se_{2.0}$, $Sc_{1.5}$, $Cu_{1.4}$, $La_{1.3}$, $(Ca, Rb, P)_{1.2}$, $(Li, Mg)_{1.1}$ in sunflower-II.

More than a half of the analyzed elements accumulate in stem+leaves samples (29 in sunflower-I and 31 in sunflower-II). Yttrium, La, Li, Ce, Fe, Al, U, Th, Na, Cr, Mo, Ba, Zr, Cs, Mg, Sr, Au, Cd, Hf, Mn, K, and Ca in the two stem+leave samples have concentrations higher than those determined in sunflower head samples. The *ECR* of Y is more than 85 and 95 (Table 4).

The concentrations of the rest elements vary among the samples. Some of them have higher concentrations in the two samples of sunflower heads (Ni, P, and B), others are accumulated either in sunflower-I sample (Hg, Ge, Zn, Se, Co, Cu, Pb, and Ag) or in sunflower-II sample (Re and Bi). Rubidium, S, Sc, Ti, Sb, Be, W, V, Ga, Sn, In, Te, Pt, Nb, Ta, As, Tl, and Pd are equally distributed in all parts of the sunflower plant.

This study shows that the lithophile metals are dominant in the stem+leaves sunflower samples.

Table 1
List of studied samples

Sample	Location	Sampling place	Date
Sunflower-I Wheat	42°16,421' and 025°07,821'	~5 km away from Maritsa East-2 TEPS ~7 km away from Maritsa East-2 TEPS	June, 2012
Sunflower-II	42°09,377' and 025°57,773'	~3 km away from Maritsa East-3 TEPS	June, 2012
Hypericum perforatum *Typha*	42°07,825' and 026 °01,220' 42°08,388' and 026 °01,071'	Troyanovo-3 mine, close to Maritsa East -3 TEPS	June, 2012

Table 2

Element concentration in culture plants, ppm

Element[1]	*AVTV*[2]	Wheat				Sunflower (I)				Sunflower (II)			
		Ears	*CC*[7]	Stems+Leaves	*CC*[7]	Heads	*CC*[7]	Stems+Leaves	*CC*[7]	Heads	*CC*[7]	Stems+Leaves	*CC*[7]
Lithophilic metals													
Li	*0.1*	0.02		0.06		0.02		0.14	*1.4*	<0.01		0.11	*1.1*
Be	*0.1*	<0.1		<0.1		<0.1		<0.1		<0.1		<0.1	
Na	*0.03-0.1%*	20.0		50.0		20.0		60		10		30	
Mg	*0.1-0.3%*	1010	*1.0*	1050	*1.0*	3350	*1.1-3.4*	5530	*1.8-5.5*	2840	*2.8*	3430	*1.1-3.4*
Al	*6-1400*	<100	*<16.7*	<100	*<16.7*	<100	*<16.7*	400	*66.7*	<100	*<16.7*	100	*16.7*
K	*0.2-1.8%*	4500	*2.3*	16100	*8.1*	25900	*1.4-13.0*	34100	*1.9-17.1*	28200	*1.6-14.1*	44500	*2.5-22.3*
Ca	*0.3-1.8%*	800.0		2900	*~1.0*	13900	*4.6*	16800	*5.6*	13600	*4.5*	21400	*1.2-7.1*
Rb	*20*	3.3		6.4		19.6	*~1.0*	18.2		24	*1.2*	23.8	*1.2*
Sr	*15-25*	10.2		34.9	*1.4-2.3*	50.5	*2.0-3.4*	84.4	*3.4-5.6*	64.0	*2.6-4.3*	93.1	*3.7-6.2*
Y	*<0.6*[3]	0.012		0.036		0.001		0.094		<0.001		0.085	
Zr	*0.2-0.6*	0.02		0.05		0.09		0.19	*~1.0*	0.03		0.11	
Nb	*0.3*	<0.01		<0.01		<0.01		0.02		<0.01		<0.01	
Mo	*0.1-0.9*	0.59	*5.9*	1.01	*1.1-10*	0.34	*3.4*	0.75	*7.5*	0.19	*1.9*	0.49	*4.9*
Cs	*0.2*	<0.005		0.007		0.031		0.065		0.009		0.027	
Ba	*10-150*	8.1		42.2	*4.2*	3.5		7.8		16.8	*1.7*	27.4	*2.7*
La	*0.085*[3]	0.02		0.05		0.02		0.16	*1.9*	0.01		0.11	*1.3*
Ce	*30*	0.05		0.10		0.07		0.31	*1.0*	0.01		0.23	
Hf	*1.2*[4]	<0.001		<0.001		0.006		0.009		<0.001		0.002	
Ta	*0.26*[4]	<0.001		<0.001		<0.001		0.003		<0.001		<0.001	
W	*0.07*	<0.1		<0.1		<0.1		<0.1		<0.1		<0.1	
Re	*0.06*[5]	<0.001		<0.001		0.002		0.006		0.007		0.004	
Non-metals													
B	*20-80*	2.0		3.0		62	*3.1*	33	*1.7*	52	*2.6*	43	*2.2*
P	*0.04-0.3%*	2130	*5.3*	200		3680	*1.2-9.2*	2450	*6.1*	4700	*1.6-11.8*	3590	*1.2-9.0*
S	*0.1-0.8%*	1200	*1.2*	2100	*2.1*	2900	*2.9*	3000	*3.0*	2600	*2.6*	3900	*3.9*
Siderophilic metals													
Sc	*0.008-0.2*	0.4	*2-50*	0.4	*2-50*	0.3	*1.5-37.5*	0.3	*1.5-37.5*	0.3	*1.5-37.5*	0.3	*1.5-37.5*
Ti	*1-65*	11.0	*11.0*	3.0	*3.0*	17	*17*	18.0	*18*	19	*19*	19	*19*
V	*0.1-0.7*	<2	*<2.9-20*	<2	*<2.9-20*	<2	*<2.9-20*	<2	*<2.9-20*	<2	*<2.9-20*	<2	*<2.9-20*
Cr	*0.15-2*	2.2	*1.1-14.7*	6.3	*3.2-42*	0.8	*5.3*	1.9	*12.7*	1.0	*6.7*	1.6	*10.7*
Mn	*250-630*	40.0		36.0		33.0		45.0		32		57	
Fe	*130-1200*	60.0		100		90.0		460	*3.5*	60.0		260	*2.0*
Co	*0.2-0.8*	0.05		0.08		0.23	*1.2*	0.20	*1.0*	0.15		0.35	*1.8*
Ni	*1.5-2.7*	1.1		3.0	*1.1-2.0*	1.6	*1.1*	1.4		2.0	*1.3*	0.9	

Table 2 (continued)

Element[1]	*AVTV*[2]	Wheat				Sunflower (I)				Sunflower (II)			
		Ears	*CC*[7]	Stems+Leaves	*CC*[7]	Heads	*CC*[7]	Stems+Leaves	*CC*[7]	Heads	*CC*[7]	Stems+Leaves	*CC*[7]
Chalcophilic metals and metalloid non-metals													
Cu	*7-15*	4.73		2.4		15.3	*1.0-2.2*	13.6	*1.9*	17.2	*1.1-2.5*	21.7	*1.4-3.1*
Zn	*25-160*	32.0	*1.3*	11.2		37.8	*1.5*	24.3	*~1.0*	44.8	*1.8*	42.6	*1.7*
Ga	*0.05-0.25*	<0.1		<0.1		<0.1		<0.1		<0.1		<0.1	
Ge	*2.0*[4]	<0.1		0.04		0.11		0.05		0.03		0.02	
As	*0.2*	<0.1		<0.1		<0.1		0.3	*1.5*	<0.1		<0.1	
Se	*0.2*	0.2	*1.0*	0.2	*1.0*	0.4	*2.0*	0.3	*1.5*	0.3	*1.5*	0.4	*2.0*
Cd	*0.1-0.6*	0.01		0.01		0.05		0.08		0.08		0.11	*1.1*
In	*0.021*[4]	<0.02		<0.02		<0.02		<0.02		<0.02		<0.02	
Sn	*0.2-0.3*	0.03		0.04		0.03		0.03		0.02		0.04	
Sb	*0.06*	<0.02		0.03		0.03		0.04		0.03		0.03	
Te	*0.01-0.05*[6]	<0.02		<0.02	*<2.0*	<0.02	*<2.0*	<0.02	*<2.0*	<0.02	*<2.0*	<0.02	*<2.0*
Hg	*0.15*	<0.001		0.008		0.005		<0.001		<0.001		0.007	
Tl	*0.68*[4]	<0.02		<0.02		<0.02		0.04		<0.02		<0.02	
Pb	*1.8-3.3*	0.30		5.70	*1.7-3.2*	0.26		0.29		0.18		0.43	
Bi	*<0.01-<1*	<0.02	*2.0*	0.08	*8.0*	0.05	*5.0*	0.07	*0.7*	0.04	*4.0*	0.03	*3.0*
Radioactive elements													
Th	*3.3*[4]	<0.01		0.01		<0.01		0.03		<0.01		0.02	
U	*0.038*[3]	<0.01		<0.01		<0.01		0.04	*1.1*	<0.01		0.03	
Noble metals													
Pd	*0.013*[4]	<0.002		<0.002		0.002		0.002		<0.002		<0.002	
Ag	*<0.1-0.2*	0.005		0.037		0.026		0.024		0.014		0.064	
Pt	*0.065*[4]	0.001		<0.001		<0.001		<0.001		<0.001		<0.001	
Au	*0.0004*	0.0005	*1.3*	0.0092	*23.0*	0.0016	*4.0*	0.0027	*6.8*	0.0008	*2.0*	0.0024	*6.0*

[1]Mineralogical classification of the elements (Solodov et al., 1987).
[2] Average values for terrestrial vegetation (dry basis) (Kabata-Pendias, Pendias, 1979).
[3] Average values for angiosperm plants (Bowen, 1966).
[4] Average value for brown coal (Ketris, Yudovich, 2009).
[5] Background content of Re in coals (Shpirt et al., 1990).
[6] Supposed content of Te in coals (Yudovich, Ketris, 2006).
[7] Coefficient of concentration (CC), ratio of element content in plant to average value according to published data.

Table 3
Element concentration in wild plants, ppm

Element[1]	AVTV[2]	*Hypericum perforatum*				*Typha*			
		Blossoms	CC[7]	Stems+ Leaves	CC[7]	Blossoms	CC[7]	Stems+ Leaves	CC[7]
Lithophilic metals									
Li	*0.1*	0.52	*5.2*	0.23	*2.3*	0.01		0.27	*2.7*
Be	*0.1*	<0.1		<0.1		<0.1		<0.1	
Na	*0.03-0.1%*	60	*2.0*	40	*1.3*	61		89	
Mg	*0.1-0.3%*	2670	*2.7*	1310	*1.3*	2020	*2.0*	1150	*1.2*
Al	*6-1400*	700	*1170*	200	*33.3*	<0.01		<0.01	
K	*0.2-1.8%*	14300	*7.2*	7300	*3.7*	15200	*7.6*	19400	*1.1-9.7*
Ca	*0.3-1.8%*	11400	*3.8*	5700	*1.9*	6200	*2.1*	5700	*1.9*
Rb	*20*	4.9		1.7		1.6		1.2	
Sr	*15-25*	53.9	*2.2-3.6*	37.5	*1.5-2.5*	43.1	*1.7-2.9*	41.6	*1.7-2.8*
Y	*<0.6*[3]	0.315		0.098		0.011		0.005	
Zr	*0.2-0.6*	0.23	*1.2*	0.14		0.03		0.04	
Nb	*0.3*	0.05		0.02		<0.01		<0.01	
Mo	*0.1-0.9*	3.64	*4.0-36.4*	1,26	*1.4-12.6*	0.62	*6.2*	0.35	*3.5*
Cs	*0.2*	0.067		0.025		<0.005		<0.005	
Ba	*10-150*	15.8	*1.6*	17.5	*1.8*	1.9		2.2	
La	*0.085*[3]	0.57	*6.7*	0.18	*2.1*	0.03		0.03	
Ce	*30*	1.35		0.48		0.06		0.06	
Hf	*1.2*[4]	0.007		<0.001		<0.001		0.004	
Ta	*0.26*[4]	<0.001		<0.001		<0.001		<0.001	
W	*0.07*	<0.1		<0.1		<0.1		<0.1	
Re	*0.06*[5]	0.02		0.014		<0.001		0.001	
Non-metals									
B	*20-80*	65	*3.3*	27	*1.4*	27	*1.4*	12	
P	*0.04-0.3%*	4580	*1.5-11.5*	1640	*4.1*	3000	*1.0-7.5*	1820	*4.6*
S	*0.1-0.8%*	7300	*7.3*	2600	*2.6*	1000	*1.0*	1200	*1.2*
Siderophilic metals									
Sc	*0.008-0.2*	0.4	*2.0-50*	0.4	*2.0-50*	0.2	*1.0-25*	0.4	*2.0-50*
Ti	*1-65*	33	*33.0*	11	*11.0*	13	*13.0*	7	*7.0*
V	*0.1-0.7*	<2	*<2.9-20*	<2	*<2.9-20*	<2	*<2.9-20*	<2	*<2.9-20*
Cr	*0.15-2*	2.6	*1.3-17.3*	5.7	*2.9-38.0*	1.2	*8.0*	0.8	*5.3*
Mn	*250-630*	52		22		54		108	
Fe	*130-1200*	850	*3.4*	290	*2.2*	70		70	
Co	*0.2-0.8*	0.50	*2.5*	0.19		0.04		0.03	
Ni	*1.5-2.7*	1.7	*1.1*	2.6	*1.0-1.7*	1.0		0.4	
Chalcophilic metals and metalloid non-metals									
Cu	*7-15*	14.67	*1.0-2.1*	11.19	*1.6*	4.44		2.33	
Zn	*25-160*	50.3	*2.0*	17.4		15.8		10.1	
Ga	*0.05-0.25*	0.2	*4.0*	0.1	*2.0*	<0.1		<0.1	
Ge	*2.0*[4]	0.03		0.04		<0.01		<0.01	
As	*0.2*	0.5	*2.5*	<0.1		<0.1		<0.1	
Se	*0.2*	0.8	*4.0*	0.4	*2.0*	0.3	*1.5*	0.4	*2.0*
Cd	*0.1-0.6*	0.12	*1.2*	0.15	*1.5*	<0.1		0.02	
In	*0.021*[4]	<0.02		<0.02		<0.02		<0.02	
Sn	*0.2-0.3*	0.05		0.07		0.03		0.03	
Sb	*0.06*	0.05		0.04		0.03		0.02	
Te	*0.01-0.05*[6]	<0.02		<0.02		<0.02		<0.02	
Hg	*0.15*	0.004		<0.001		0.001		0.003	
Tl	*0.68*[4]	<0.02		<0.02		<0.02		<0.02	
Pb	*1.8-3.3*	0.90		0.51		0.34		0.76	
Bi	*<0.01-<1*	0.05	*5.0*	0.08	*8.0*	0.06	*6.0*	0.06	*6.0*
Radioactive elements									
Th	*3.3*[4]	0.10		0.05		<0.1		<0.1	
U	*0.038*[3]	0.13	*3.4*	0.07	*1.8*	<0.1		<0.1	
Noble metals									
Pd	*0.013*[4]	<0.002		<0.002		<0.002		<0.002	
Ag	*<0.1-0.2*	0.056		0.050		0.022		0.023	
Pt	*0.065*[4]	<0.001		0.001		0.001		<0.001	
Au	*0.0004*	0.0047	*11.8*	0.015	*37.5*	0.0084	*21.0*	0.0063	*15.8*

←

[1]Mineralogical classification of the elements (Solodov et al., 1987).
[2] Average values for terrestrial vegetation (dry basis) (Kabata-Pendias, Pendias, 1979).
[3] Average values for angiosperm plants (Bowen, 1966).
[4] Average value for brown coal (Ketris, Yudovich, 2009).
[5] Background content of Re in coals (Shpirt et al., 1990).
[6] Supposed content of Te in coals (Yudovich, Ketris, 2006).
[7] Coefficient of concentration (CC), ratio of element content in plant to average value according to published data.

Hypericum perforatum

A total of 30 elements determined in blossoms and 26 in stem+leaves sample have over AVTV. Elements with CC exceeding the upper limit of AVTV in blossoms are: $Au_{11.8}$, $La_{6.7}$, $Li_{5.2}$, $(Mo, Se)_{4.0}$, $U_{3.4}$, $V_{<2.9}$(?), $As_{2.5}$, $Sr_{2.2}$, $Sc_{2.0}$, $P_{1.5}$, $Cr_{1.3}$. The stem+leaves samples contain the same group of elements, but with different CC values such as: $Au_{37.5}$, $Cr_{2.9}$, $V_{<2.9}$(?), $Li_{2.3}$, $La_{2.1}$, $(Sc, Se)_{2.0}$, $U_{1.8}$, $Sr_{1.5}$, and $Mo_{1.4}$.

A specific feature of this plant species is that most elements (35) accumulate in blossoms while 9 elements concentrate in stem+leaves (Au, Cr, Bi, Ni, Sn, Ge, Cd, Ba, and Pt), and 9 elements show equal distribution in the whole plant (Sc, Pd, Be, Ta, W, V, In, Te, Tl). Elements having *ECR*>2 in blossoms compared to stem+leaves are: K, Hf, Co, As, Hg, Al, Y, La, Ti, Rb, Mo, Fe, Zn, Ce, P, S, Cs, Nb, B, Mn, Li, and Mg.

Typha

In both samples, namely blossoms and stem+leaves, a total of 14 and 15 elements, respectively, have over AVTV. Elements which have concentrations exceeding the upper limit of AVTV in blossoms are $Au_{21.0}$, $V_{<2.9}$(?), $Sr_{1.7}$, and $Se_{1.5}$, while these elements for stem+leaves are $Au_{15.8}$, $V_{<2.9}$(?), $Li_{2.7}$, $(Sc, Se)_{2.0}$, $Sr_{1.7}$, and $K_{1.1}$.

Almost all elements (23) are equally accumulated in blossoms and stem+leaves. Elements such as Hg, Ni, Y, Mo, Mg, P, Zn, K, Co, Se, Au, Ba, Ca, and Pt were concentrated in blossoms. On the other hand, elements such as Li, Cd, Hf, Sc, B, Pb, Mn, Ti, Cu, Na, Cr, Sb, Zr, S, and Re were determined in stem+leaves. It should be stated that Li demonstrates a trend of high concentration in stem+leaves (*ECR*=27).

DISCUSSION

The studied culture vegetation (wheat and sunflower) is used for co-firing with coal in many countries worldwide. Currently, it could also be used for burning in TEPSs in Bulgaria. According to the number of elements that exceed the lower limit of AVTV, the analyzed vegetation species could be arranged as follows: *Hypericum perforatum* > sunflower > *Typha* ≥ wheat.

Hypericum perforatum is characterized by the following elements having CC≥3 (based upon the upper limit of AVTV): Au, La, Li, Mo, Se, and U. In wheat and sunflower the elements with CC≥3 are Au and Cr, and Au and Sr, respectively. Most of the elements determined in wheat and sunflower have concentrations close to the upper limit of AVTV. On the other hand, some elements tend to accumulate in different parts of the plant. For example, Y, Ce, La, Li, Fe, Al, U, Th, Na, Cr, Mo, Ba, Zr, Cs, Mh, Sr, Au, Cd, Hf, Mn, K, and Ca, concentrate mainly in sunflower stem+leaves and less in sunflower heads. Some elements have even *ECR* > 10 (Y and Ce).

Typha is also used for co-firing with coal. Present study has confirmed its capability to accumulate trace elements showing equal distribution of almost all studied elements in the plant.

It can be suggested that most of the trace elements determined in plants may emit in the atmosphere during burning. Hence, special attention should be paid on the following potentially toxic elements: Pb, Hg, Bi, Sr, Cr, Ni, U, Th, As, Cd, Sb, Be, Mn, and others. Since a trend of accumulation of trace elements in different parts of the vegetation has been determined, this can be used as a basis for determination which vegetation parts are suitable for burning, in order to diminish possible pollution. On the other hand, plant ash can be used as bio fertilizer containing K, Na, Mg, P, Ca, Se, Mo, Cu, Au, and Zn in agriculture.

CONCLUSION

This study is a part of a project that aims at tracing possible mobilization and transport of hazardous elements from waste facilities in coal mining and power producing stations and their accumulation in soils and vegetation. Based on the preliminary results obtained we have made the following conclusions:

1. Different plant species show preference in trace element accumulation as well as element concentration in certain parts of the plant. These results confirm previous statements regarding this subject.

2. Compared to AVTV the concentrations of lithophile (Li, Na, Mg, K, Ca, Sr, Al, Mo, Ba, La), non-metals (B, P, S), siderophile (Sc, Ti, V(?), Cr, Fe, Co, Ni), chalcophile (Cu, Zn, Ga, Pb, Se, As, Bi),

Table 4
Concentration trend of elements in different parts of studied plants

Wheat, *ECR*[1]	
Ears	$P_{11.0}$, $Ti_{3.7}$, $Zn_{2.9}$, $Cu_{1.8}$, $Mn_{1.1}$, $Pt_{>1.0}$
Stems+leaves	$Pb_{19.0}$, $Au_{18.4}$, $Hg_{>8.0}$, $Ag_{7.4}$, $Ba_{5.2}$, $Bi_{4.0}$, $(Ca, K)_{3.6}$, $Sr_{3.4}$, $(Li, Y)_{3.1}$, $Cr_{2.9}$, $Ni_{2.7}$, $(Na, Zr, La)_{2.5}$, $Ce_{2.0}$, $Rb_{1.9}$, $S_{1.8}$, $(Mo, Fe)_{1.7}$, $Co_{1.6}$, $Sb_{>1.5}$, $Cs_{>1.4}$, $Sn_{1.3}$, $B_{1.2}$, $Th_{>1.0}$
Equally in both parts	$(Mg, Sc, Se, Cd)_{1.0}$, $(Be, Al, Nb, Hf, Ta, W, Re, V, In, Te, Tl, U, Pd)_{(?)}$
Sunflower-I, *ECR*[1]	
Heads	$Hg_{>5.0}$, $Ge_{2.2}$, $B_{1.9}$, $Zn_{1.6}$, $P_{1.5}$, $Se_{1.3}$, $Co_{1.2}$, $(Ni, Cu, Pb, Ag)_{1.1}$,
Stems+leaves	$Y_{(94.0)}$, $La_{8.0}$, $Li_{7.0}$, $(Ce, Fe)_{4.4}$, $(Al, U)_{>4.0}$, $(Ta, As, Th)_{>3.0}$, $(Na, Re)_{3.0}$, $Cr_{2.4}$, $(Mo, Ba)_{2.2}$, $(Zr, Cs)_{2.1}$, $(Nb, Tl)_{>2.0}$, $(Mg, Sr, Au)_{1.7}$, $Cd_{1.6}$, $Hf_{1.5}$, $(Mn, Bi)_{1.4}$, $(K, Sb)_{1.3}$, $Ca_{1.2}$,
Equally in both parts	$(Rb, S, Sc, Ti, Sn, Pd)_{1.0}$, $(Be, W, V, Ga, In, Te, Pt)_{(?)}$,
Sunflower-II, *ECR*[1]	
Heads	$Ni_{2.2}$, $Re_{1.8}$, $(P, Bi)_{1.3}$, $B_{1.2}$,
Stems+leaves	$Y_{>85.0}$, $Ce_{23.0}$, $Li_{>11.0}$, $La_{11.0}$, $Hg_{<7.0}$, $Ag_{4.6}$, $Fe_{4.3}$, $Zr_{3.7}$, $U_{>3.0}$, $(Na, Cs, Au)_{3.0}$, $Mo_{2.6}$, $Pb_{2.4}$, $Co_{2.3}$, $(Hf, Th)_{>2.0}$, $Sn_{2.0}$, $Mn_{1.8}$, $(K, Ca, Ba, Cr)_{1.6}$, $(Sr, S, Ge)_{1.5}$, $Cd_{1.4}$, $(Cu, Se)_{1.3}$, $Mg_{1.2}$, $Al_{>1.0}$,
Equally in both parts	$(Rb, Sc, Ti, Zn, Sb,)_{1.0}$, $(Be, Nb, Ta, W, V, Ga, As, In, Te, Tl, Pd, Pt)_{(?)}$
Hypericum perforatum, ECR[1]	
Blossoms	$K_{19.6}$, $Hf_{7.0}$, $Co_{5.6}$, $As_{>5.0}$, $Hg_{>4.0}$, $Al_{3.5}$, $(Y, La)_{3.2}$, $Ti_{3.0}$, $(Rb, Mo, Fe, Zn)_{2.9}$, $(Ce, P, S)_{2.8}$, $Cs_{2.7}$, $Nb_{2.5}$, $(B, Mn)_{2.4}$, $Li_{2.3}$, $Mg_{2.1}$, $(Ca, Ga, Se, Th)_{2.0}$, $U_{1.9}$, $Pb_{1.8}$, $Zr_{1.6}$, $Na_{1.5}$, $(Sr, Re)_{1.4}$, $(Cu, Sb)_{1.3}$, $Ag_{1.1}$
Stems+leaves	$Au_{3.2}$, $Cr_{2.2}$, $Bi_{1.6}$, $Ni_{1.5}$, $Sn_{1.4}$, $(Ge, Cd)_{1.3}$, $Ba_{1.1}$, $Pt_{>1.0}$
Equally in both parts	$(Sc, Pd)_{1.0}$, $(Be, Ta, W, V, In, Te, Tl)_{(?)}$
Typha, ECR[1]	
Blossoms	$Hg_{3.0}$, $Ni_{2.5}$, $Y_{2.2}$, $Mo_{1.8}$, $Mg_{1.7}$, $(P, Zn)_{1.6}$, $(K, Co, Se, Au)_{1.3}$, $Ba_{1.2}$, $Ca_{1.1}$, $Pt_{>1.0}$
Stems+leaves	$Li_{27.0}$, $Cd_{>5.0}$, $Hf_{>4.0}$, $Sc_{4.0}$, $B_{2.3}$, $Pb_{2.2}$, $Mn_{2.0}$, $(Ti, Cu)_{1.9}$, $(Na, Cr, Sb)_{1.5}$, $Zr_{1.3}$, $S_{1.2}$, $Re_{>1.0}$,
Equally in both parts	$(Sr, La, Ce, Fe, Sn, Bi, Th, U, Pd, Ag)_{1.0}$, $(Be, Al, Nb, Cs, Ta, W, V, Ga, Ge, As, In, Te, Tl)_{(?)}$

[1]*ECR*- enrichment concentration ratio, ratio of element content between both parts of plant.

radioactive (U) and noble elements (Au) in the studied plants are increased by CC>1,5.

3. This study reports concentrations for Te, Ta nd Re about which the information in the literature is scarce.

4. Possible emission of hazardous elements (Pb, Hg, Bi, Sr, Cr, Ni, U, Th, As, Cd, Sb, Be, Mn) in the atmosphere during burning of stubbles and co-firing of biomass in TEPs has been suggested.

5. Some elements could migrate in food chain through grain fodder used in stock-breeding or directly from wheat grains and sunflower seeds used in food producing industry.

At present there are no established regulations concerning limit values for most trace elements in vegetation regarding pollution, thus reliable assessment of the environmental impact could not be carried out.

Acknowledgements

This study is financially supported by DNTS China 1/07 grant of the Bulgarian Science Fund.

REFERENCES

Bowen, H. 1966. *Trace elements in biochemistry*. New York-London, Academic Press, 241 pp.

Ganchev, G., Bossev, G. 1988. 120 MW new and replacing powers in „Maritza-East“ up to 2010. *Minno Delo and Geology* 5-6, 24-27 (in Bulgarian).

Kabata-Pendias, A., Pendias, H. 1979. *Trace Elements in the Biological Environment*. Wydawnictwa Geologiczne, Warszawa, 299 pp. (in Polish).

Ketris, M., Yudovich, Y. 2009. Estimation of Clarkes for Carbonaceous biolithes: world averages for trace element contents in black shales and coals. *International Journal of Coal Geology* 78, 135-148.

Nedyialkov, N. 1979. Maritza East lignite basin–mining and geological conditions, qualitative characteristics and features of the deposit. *Coal* 9, 8-12 (in Bulgarian).

Nedyialkov, N. 1985. *Geological structure of the Maritza East basin and landslide phenomenon.* PhD Thesis Summary, Bulgarian Academy of Science, Sofia, 32 pp. (in Bulgarian).

Nedyialkov, N., Kojumdgieva E. 1983. Stratigraphy of over coal-bearing sediments in Maritza East basin. *Review of the Bulgarian Geological Society* 44, 239-264 (in Bulgarian).

Panov, G. 1982. *The Tertiary coal-bearing sedimentation in upper Thracian graben*. PhD Thesis Summary, Bulgarian Academy of Science, 32 pp. (in Bulgarian).

Shpirt, M., Ruban, V., Itkin, U. 1990. *Rational using of waste from coal mining and reparation*. Nedra, Moskow, 233 pp. (in Russian).

Solodov, N., Semenov, E., Burkov, V. 1987. *Geological handbook on heavy lithophilic trace metals*. Nedra, Moskow, 438 pp. (in Russian).

Valćeva, S., Djourova, E., Stanimirova, T., Dimitrova, D., Aleksieva, L. 2000. Mineralo-geochemical features of Gledachevska formation sediments in the Maritza East lignite basin and in the technogeneous soils of the recultivated terrains. *Annuaire de L'Universite de Sofia, Livre 1 - Geologie* 92, 203-212.

Vassilev, S., Baxter, D., Andersen, L., Vassileva, C. 2010. An overview of the chemical composition of biomass. *Fuel* 89, 913-933.

Vassilev, S., Baxter, D., Andersen, L., Vassileva, C., Morgan, T. 2012. An overview of the organic and inorganic phase composition of biomass. *Fuel* 94, 1-33.

Vassilev, S., Baxter, D., Andersen, L., Vassileva, C. 2013a. An overview of the composition and application of biomass ash. Part I. Phase-mineral and chemical composition and classification. *Fuel* 105, 40-73.

Vassilev, S., Baxter, D., Andersen, L., Vassileva, C. 2013b. An overview of the composition and application of biomass ash. Part II. Potential utilisation, technological and ecological advantages and challenges. *Fuel* 105, 19-39.

Vassilev, S., Baxter, D., Vassileva, C. 2014a. An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types. *Fuel* 117, 152-183.

Vassilev, S., Vassileva, C., Baxter, D. 2014b. Trace element concentrations and associations in some biomass ashes. *Fuel* 129, 292-313.

Yudovich, Y., Ketris, M. 2006. *Valuable trace elements in coal*. Ekaterinburg, 538 pp. (in Russian).

Printed 2014