Subject Area 7.2: Evaluation of the impacts and interactions of chemicals in the laboratory or real environments, and their fate in biota, including animals and humans

Research Article

U and Th in Some Brown Coals of Serbia and Montenegro and Their Environmental Impact*

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Abstract

Goal, Scope and Background. The objective of this paper is to determine and compare the concentrations of U and Th in soft to hard brown (lignite to sub-bituminous) coals of Serbia and Montenegro. It also presents comparison of the obtained data on U and Th concentrations with the published data on coals located in some other countries of the world. Almost the whole coal production of Serbia and Montenegro is used as feed coals for combustion in thermal power plants.

Methods. Channel samples from open pit and underground mines and core samples were collected for hard and soft brown coals. For the analysis the samples were decomposed using microwave technique. Obtained solutions containing U and Th were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) using NIST standards.

Results. Concentration of U from the investigated basins and the corresponding mine fields ranges within 0.60–70.10 mg/kg, 0.65–3.20 mg/kg, 0.95–6.59 mg/kg, 1.20–6.05 mg/kg, 0.80–6.66 mg/kg, 0.18–89.90 mg/kg, 0.19–4.14 mg/kg, and 0.28–3.52 mg/kg for the Kostolac, Kolubara, Krepoljin, Sjenica, Soko Banja, Bogovina East field, Senje-Resavica and Pljevlja basins, respectively. Concentration of Th ranges within 0.20–2.60 mg/kg, 0.84–6.57 mg/kg, 1.48–6.48 mg/kg, 0.12–2.71 mg/kg, 0.13–4.95 mg/kg, 0.14–3.48 mg/kg, 0.29–3.56 mg/kg, and 0.17–1.89 mg/kg for the Kostolac, Kolubara, Krepoljin, Sjenica, Soko Banja, Bogovina East field, Senje-Resavica and Pljevlja basins, respectively.

Discussion. Brown coal from Senje-Resavica, Kolubara, Kostolac and Pljevlja is characterized by low U concentration. Coals form the Krepoljin, Soko Banja and Sjenica basins have slightly higher U concentrations than the mentioned group. The highest concentration of U is characteristic for the coal from the Bogovina East field. Concentration of Th in coals from Serbia and Montenegro has proved to be low. Out of all investigated coal basins, only the coal from the Krepoljin and Kolubara basins has high concentration of Th. The hydrothermally altered rocks of the Timok dacite-andesite complex, representing the basement of the Bogovina basin, could be a potential source of U, especially at the bottom part of the Lower seam of the Bogovina East field.

Conclusions. This study shows that brown coals in Serbia and Montenegro (soft to hard brown coals or lignite to sub-bituminous) contain low levels of U (5.30 mg/kg, average value and 2.10 mg/kg geometric mean value) and Th (1.80 mg/kg, average value and 1.12 mg/kg geometric mean value). There are some obvious differences in concentration of U and Th in coals from different basins in Serbia and Montenegro. The approximate value for U and Th release mainly from power plants was 644.33 t and 983.46 t, respectively within the period 1965–2000 for the studied mines in Serbia, and 23.76 t and 15.05 t for the Potrlica mine (Montenegro) within the period 1965–1997.

Recommendations. The coals in Serbia and Montenegro show no identifiable unfavourable impact on the surrounding environment, due to low natural radioactive concentration of U and Th, but further investigations concerning human health should be performed.

Perspectives. Preliminary research revealed that in some Serbian coals (and, particularly, parts of the coal seam) U and Th content are rather high. Such coals should be carefully studied, as well as U and Th concentrations in ash, fly ash, waste disposals, nearby soil and ground water. Further studies should include determination of the radioactivity of all these products, and estimation of possible health impact.

Keywords: Brown coals; ICP-MS analysis; radioactivity; radionuclides; Serbia and Montenegro; Th; U

Introduction

Brown coals, particularly soft brown coals (lignite), represent the major source of energy production in Serbia and Montenegro. All other better quality coals are used both in other industries and for domestic heating. Brown coals of Serbia occur in 33 coal basins, of which only 11 are in exploitation – six underground mines, four opencast mines, and one at the Danube riverbed. Brown coals in Montenegro occur in fourteen coal basins, out of which only two mines, one opencast and one underground are in exploitation. Geological reserves of brown coal in Serbia are estimated to 22.6 billion tons, and mineable reserves to 8.9 billion tons (Vujić & Janković 1999). Economically mineable reserves of brown coals in Serbia have not yet been proved, but those in Montenegro are estimated at 189 x 10^6 t (Bulajić 2001).

Soft brown coals (%Ro.ran=0.26–0.30; Ercegovac 1998) in Serbia are used for combustion in thermal power plants. Hard brown coals (%Ro.ran=0.31–0.50; Ercegovac 1998) of Serbia are of less economic importance. Brown coal in Serbia amounts to over 95% of total coal production in the

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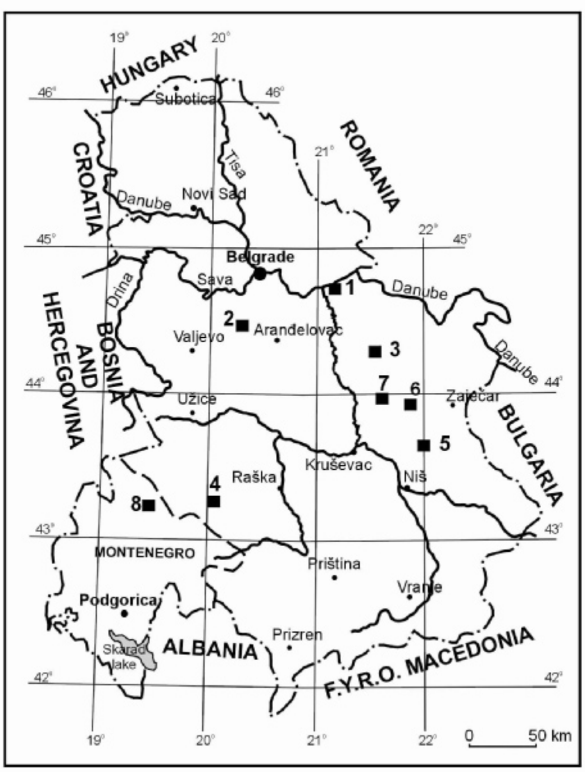
last decade of the 20th century; out of which soft brown coal takes 98.79% (577,468,564 t) of production, and hard brown coal 1.21% (7,100,900 t) according to data from statistical yearbooks. Over 90% of soft brown coal production is used in power plants, especially in the Kolubara, Kostolac and Kosovo basins. In Montenegro, only brown coals are produced, and in the last decade the total coal production amounted to 14,130,000 t (Živanović et al. 2003). The studied brown coal basins in Serbia and Montenegro are shown in **Fig. 1**.

The information on concentration, distribution and occurrence of potentially hazardous trace elements in coals are of paramount importance, especially when they are used as feed coals for combustion in thermal power plants (Finkelman 1994). These data are most urgently required in coal utilization and environmental assessment. Radioactive elements, mainly U and Th as well as their decay products are of special concern. These elements are less chemically toxic (Zielinski and Finkelman 1997) than As, Se and Hg, but when accumulated in ash they increase radioactivity and possible radiation hazards and they pose health risks not associated with As, Se, Hg etc.

Prior to this study accurate and systematic data on the concentration of natural radioactive elements (U & Th) in brown coals of Serbia were not available. Sound conclusions regarding U and Th impact on the surrounding environment can be made only on the basis of precise data for concentrations (this study) in combination with other observations such as mode of occurrence and leachability of U and Th.



■ 1. Kostolac basin; 2. Kolubara basin; 3. Krepoljin basin; 4. Sjenica basin; 5. Soko Banja basin; 6. Bogovina basin (East field); 7. Senje-Resavica basin; 8. Pljevlja basin

Fig. 1: Location of the studied coal basins in Serbia and Montenegro

The studied brown coal basins were formed in the period from Lower to Upper Miocene. Most of the coal-bearing basins in Serbia originated as a result of strong tectonic movements (faulting) in Upper Oligocene and the subsequent formation of the Pannonian basin, and in numerous intermontane depressions in the 'Balkan land'.

Coal from the Senje-Resavica was formed in Lower Miocene limnic basins on the 'Balkan land'. Bogovina East Field coal was probably formed in the uppermost part of Lower Miocene on the 'Balkan land', in which limnic and marine facies alternated. In both these basins coal originated in sedimentary environment with predominantly marly clays and marlstones. Geological reserves of Senje-Resavica basin are estimated to 14 Mt and of Bogovina East Field at 2.5 Mt (Simeunović et. al. 2003), but with the very complicated geological settings and exploitation conditions.

Coals from the Soko Banja and Krepoljin basins were most probably formed in Lower Miocene limnic basins on the 'Balkan land', and Sjenica basin on 'Dinaric land'. The Pljevlja basin is reported to be of Lower to Middle Miocene age (Mirković 1981). In all of these basins coal was formed in predominantly marly-clayey sediments and marlstones. Coals from the Soko Banja, Krepoljin and Sjenica basins have relatively large geological reserves of around 260 Mt (in all basins) and are also of economic importance, but the conditions of their exploitation are complicated due to the complex geological settings. Geological reserves of coal from the Pljevlja basin are estimated at 230 Mt with favourable exploitation conditions (Gomilanović 1999).

Coals from the Kostolac and Kolubara basins were formed during Upper Miocene in limnic clastic depositional environment along the southern border of the Pannonian basin. Geological reserves can be estimated at more than 1 billion tons with favourable exploitation conditions.

1 Materials and Methods

Channel samples were collected from fresh, working faces in mines from five coal basins: Soko (Soko Banja basin), Jasenovac (Krepoljin basin), Bogovina East field (Bogovina basin), Senje mine, Strmosten mine and Jelovac mine (Senje-Resavica basin), Štavalj (Sjenica basin) and one open pit from the Potrlica mine (Pljevlja basin) in the northeastern part of Montenegro. Core samples of soft brown coals were collected from two boreholes: the Drmno field (Kostolac basin) and the 'D' field (Kolubara basin). The thickness of each sample interval was determined as per the changes in macroscopic lithology of coal. In total, 95 samples were collected from eight brown coal basins in Serbia and Montenegro (see Table 1).

For the requirement of microwave treatment, about 200 mg samples (<40 µm) are weighed in the PTFE vessels and 2 ml of HF (50%) + 5 ml of HNO_3 (65%) + 2 ml of H_2O_2 (30%) added. The vessels are kept inside the microwave for 1 h at the temperature of 210°C. Samples are allowed to cool overnight and the treated liquid evaporates at 90°C in vacuum within 1 h. The residue is dissolved with 1ml of HCl (32%) + 8ml of deionised water + 1 ml of HNO_3 (65%). Such a solution, poured into 125 ml FEP bottles that are diluted to 100 ml with deionised water, is prepared for ICP-MS analysis.

In this study, U and Th were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) using NIST standards at Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) laboratories in Hanover following the procedure outlined by Meier et al. (1996). All studied samples were also checked by the XRF analyzer.

2 Results

U and Th concentrations in brown coals from the eight most important coal basins in Serbia and Montenegro are presented in **Table 1** and the statistical parameters (for coal

Table 1: Concentrations of U and Th (dry mass) in eight brown coal basins and mines in Serbia and Montenegro (individual measurements)

Basin	Coalfield/ mine	Sample mark	Rock type	Thick-ness (m)	Concentration (mg/kg)		Basin	Coalfield/ mine	Sample mark	Rock type	Thick-ness (m)	Concentration (mg/kg)	
					U	Th						U	Th
Kostolac	Drmno field II seam	P-17/9	Coal	0.20	2.81	2.04	Soko Banja	Soko mine	Soko 1	Coal	0.86	0.97	0.27
		P-17/10	Coal	0.50	5.81	1.65			Soko 2	Coal	0.84	5.32	0.13
		P-17/11	Coal	0.03	0.97	0.59			Soko 3	Coal	1.10	4.13	3.06
		P-17/13	Coal	0.10	70.10	0.52			Soko 4	Coal	1.20	6.66	4.95
	Drmno field III seam	P-17/15	Coal	0.40	0.24	0.48			Soko 5	Coal	0.89	4.22	0.99
		P-17/22	Coal	0.80	0.25	0.67			Soko 6	Coal	0.75	2.88	2.78
		P-17/25	Coal	0.10	0.93	1.44			Soko 7/1	Coal	0.53	3.45	0.55
		P-17/29	Coal	0.20	0.06	0.20			Soko 7/2	Coal	0.35	1.27	0.39
		P-17/35	Coal	0.60	0.33	1.04			Soko 11	Coal	0.88	0.80	2.06
		P-17/39	Coal	0.20	1.61	2.00			Soko 10/2	Clay	0.35	3.03	5.40
		P-17/40	Coal	2.70	0.38	1.11			Soko 10/1	Clay	0.50	2.76	0.62
		P-17/42	Coal	2.30	1.66	2.60			Soko 8	Coal	0.50	2.74	0.61
Kolubara	'D' field	Dg-29/03-1	Coal	0.30	2.29	6.57	Bogovina East field	Upper seam	Bogo 2	Coal	0.02	13.60	0.26
		Dg-29/03-2	Coal	0.38	3.22	5.99			Bogo 4	Coal	0.23	4.87	0.45
		Dg-29/03-3	Coal	1.25	1.26	0.84			Bogo 5	Coal	0.01	1.63	3.48
		Dg-29/03-4	Coal	0.90	0.86	1.43			Bogo 6	Coal	0.05	2.77	1.06
		Dg-29/03-5	Coal	0.54	2.00	3.73			Bogo 7	Coal	0.03	1.93	0.21
		Dg-29/03-6	Coal	3.30	2.08	1.70			Bogo 10	Coal	0.02	0.77	0.47
		Dg-29/03-7	Coal	2.80	1.38	3.08			Bogo 12	Coal	0.80	0.18	0.48
		Dg-29/03-8	Coal	0.60	1.68	3.34		Lower seam	Bogo 16	Coal	0.35	23.30	0.34
		Dg-29/03-9	Coal	2.30	0.65	1.89			Bogo 18	Coal	0.02	13.50	0.17
		Dg-29/03-10	Coal	2.60	2.61	4.55			Bogo 20	Coal	0.11	15.70	0.31
		Dg-29/03-11	Coal	0.60	2.79	1.74			Bogo 21	Coal	0.03	20.60	0.24
		Dg-29/03-12	Coal	1.00	2.29	4.34			Bogo 22	Coal	0.03	14.40	0.14
		Dg-29/03-13	Coal	0.70	1.41	2.62			Bogo 24	Coal	0.50	16.80	0.24
		Dg-29/03-14	Coal	0.50	1.33	3.28			Bogo 26	Coal	1.20	89.90	3.03
		Dg-29/03-15	Clay	2.20	7.83	2.38		Underlying sediments	Bogo 25	Clay	0.25	4.13	6.58
		Bg-4a/97	Clay	0.50	–	–			BJ-1/02	Clay	1.20	1.92	6.26
Krepoljin	Jasenovac Central field	Jas 2	Clay	0.20	2.01	1.39	Senje-Resavica	Senje mine	SENJ 1	Coal	0.80	0.19	0.44
		Jas 1	Coal	0.58	3.80	5.79			SENJ 2	Coal	0.30	0.99	1.69
		Jas 3	Coal	0.50	1.53	5.28			SENJ 7	Coal	0.30	0.27	0.75
		Jas4	Coal	0.20	2.21	1.48			SENJ 9	Coal	0.85	1.20	1.57
		Jas 5A	Clay	0.10	10.60	3.30		Jelovac mine	JEL 1	Coal	0.58	3.30	1.71
		Jas 5	Coal	0.30	6.59	2.21			JEL 2	Coal	1.20	4.14	3.56
		Jas 6	Coal	0.50	6.58	6.30			JEL 4	Coal	0.70	2.44	1.56
		Jas 7	Coal	1.20	3.77	2.39			JEL 6	Coal	0.88	1.49	0.87
		Jas 8	Coal	0.67	3.78	4.90		Strmosten mine	STRM 1	Coal	1.05	2.73	0.80
		Jas 9	Coal	0.43	1.85	2.21			STRM 6	Coal	0.34	3.20	0.93
		Jas 10	Coal	0.88	0.95	6.48			STRM 9	Coal	0.10	0.34	0.29
		Jas 11	Coal	1.11	1.11	1.57			STRM 15	Coal	0.60	0.27	0.46
		Jas 12	Clay	0.20	2.61	1.35	Pljevlja	Potrlica field	Potrlica 1	Coal	0.50	0.28	0.17
Sjenica	Štavalj mine	Št 1	Coal	0.92	6.05	2.71			Potrlica 2	Coal	0.50	1.02	1.33
		Št 2	Coal	0.21	2.95	0.12			Potrlica 3	Coal	0.50	1.86	0.77
		Št 4	Coal	0.37	2.07	0.39			Potrlica 4	Coal	0.50	1.06	0.79
		Št 5	Coal	0.56	4.20	1.18			Potrlica 5	Coal	0.50	1.53	0.72
		Št 6	Coal	0.58	1.20	1.37			Potrlica 6	Coal	0.50	3.52	1.89
		Št 7	Coal	0.70	5.34	1.60							
		Št 8	Coal	0.88	3.11	0.68							

Table 2: Statistical parameters of U (mg/kg) and Th (mg/kg) concentrations from eight brown coal basins in Serbia and Montenegro (calculated on the basis of the coal samples data given in Table 1); min-max: minimum and maximum of concentrations; AM: arithmetic mean value; GM: geometric mean; MD: median values; SD: standard deviations

Basin	Coal Seam	U					Th				
		min-max	AM	GM	MD	SD	min-max	AM	GM	MD	SD
Kostolac	Whole basin	0.06–70.10	7.10	1.02	0.95	19.91	0.20–2.60	1.20	0.95	1.08	0.75
	II seam	0.97–70.10	19.92	5.77	4.31	33.51	0.52–2.04	1.20	1.01	1.12	0.76
	III seam	0.06–1.66	0.68	0.43	0.35	0.64	0.20–2.60	1.19	0.93	1.07	0.80
Kolubara	Main seam	0.65–3.20	1.85	1.69	1.84	0.75	0.84–6.57	3.22	2.79	3.18	1.70
Krepoljin	Main seam	0.95–6.59	3.22	2.62	2.99	2.08	1.48–6.48	3.86	3.33	3.65	2.06
Sjenica	Main seam	1.20–6.05	3.56	3.15	3.11	1.74	0.12–2.71	1.15	0.81	1.18	0.87
Soko Banja	Main seam	0.80–6.66	3.24	2.64	3.17	1.92	0.13–4.95	1.58	0.91	0.80	1.59
Bogovina East field	Whole basin	0.18–89.90	15.71	6.36	13.55	22.76	0.14–3.48	0.78	0.44	0.33	1.08
	Upper seam	0.18–13.60	3.68	1.87	1.93	4.63	0.21–3.48	0.92	0.57	0.47	1.16
	Lower seam	13.50–89.90	27.74	21.63	16.80	27.63	0.14–3.03	0.64	0.33	0.24	1.06
Senje-Resavica	Main seam	0.19–4.14	1.71	1.08	1.35	1.39	0.29–3.56	1.22	0.97	0.90	0.90
Pljevlja	Main seam	0.28–3.52	1.55	1.20	1.30	1.11	0.17–1.89	0.95	0.76	0.78	0.59

samples only) in **Table 2**. Although arithmetic mean values (AM), geometric mean values (GM), median values (MD) and standard deviation value (SD) are presented in Table 2, only geometric mean values and median values are reasonably considered from the statistical point of view (Dixon & Massey 1983). Arithmetic mean value and standard deviation value are statistical parameters, relevant only for analytical measurement sets with normal (Gaussian) distribution. Since all our measurement sets for different basins have skewed distributions, geometric mean values and median values are the only remaining statistical parameters that give meaningful average concentrations, appropriate for the data sets as used.

As there are only four analyses of U and Th from the II coal seam with very variable results, further studies are necessary for the explanation of U and Th behavior in this coal seam. As concerning the III coal seam in this basin, both U and Th concentrations are rather low and very uniform. Concentration of U in the **Kolubara basin** is low, while Th concentration is higher than in the Kostolac basin. The highest concentration of U is evidenced in the underlying clay (see Table 1). It is also obvious that the upper part of the coal seam from the Kolubara basin is characterized by a higher concentration of Th.

The coal from the **Krepoljin basin** is characterized by a higher Th than U concentration, and the highest Th content of all studied coals. Concentrations of both U and Th in coal from the **Sjenica and Soko Banja basins** are low. The highest concentration of Th in Soko Banja basin was determined in interbedded carbonaceous marly clay, while the highest concentration of U was detected in the upper part of the seam.

The coal from the **Senje-Resavica basin** is characterized by low concentrations of U and Th. The coal from the Jelovac mine has the highest U and Th concentrations within the basin. Coal from the **Pljevlja basin** (Montenegro) shows very low U and Th concentrations.

The situation in the **Bogovina East field** differs in a certain way. Vertical variations of U within the Lower coal seam indicate the highest concentration of the same in the samples taken from the lower part of seam (89.90 mg/kg), while in the Upper coal seam the concentration of U mainly decreases following the same direction. Concentration of Th is low in both seams. A relatively high concentration of Th, compared to coals in the Lower seam, was found in bottom clays as a result of weathering enrichment.

There are some obvious differences in concentrations of U and Th characteristic for coal basins in Serbia and Montenegro, as numerous factors control coal enrichment in U and Th, but this is not the subject of this article.

3 Discussion

U is highly dispersed throughout the Earth's crust and has an average crustal abundance of 2.8 mg/kg (Guide to the Nuclear Wallchart 2004), that is greater than that of Hg, Sb, Ag or Cd and is almost similar to Mo or As. The average crustal concentration of Th is about three times that of U (10.7 mg/kg) and almost equal to that of Pb or Mo (Lide 1997–98).

In the majority of USA coals, the concentration of U, covering approximately 2000 coal samples from the West United States and 300 coals from the Illinois Basin, falls within the range from slightly below 1 to 4 mg/kg (Zielinski and Finkelman 1997). Coals containing U in excess of 20 mg/kg are rare in the United States. Th concentrations in USA coals fall within a similar 1–4 mg/kg range, compared to an average crustal abundance of approximately 10 mg/kg. Coals containing more than 20 mg/kg of Th are extremely rare in the United States.

Extremely intense exploration works covering U in coals in Germany after the Second World War, revealed the presence of this element in many coals. Generally speaking, U fails to occur as a separate mineral, but is bound to organic constituents. The U_3O_8 content is usually very low; less than 0.1% in average, mostly even less than 0.05%. Therefore, the extraction of the same has never been economic; not even after combustion when exposed to enrichment. Occurrences of coal – Freital in Saxony, Slovenia and Croatia are certain exceptions. The hard brown coal deposit in the Rotliegend formation of the Döhlen basin near Freital in Saxony underwent mining from 1947 to 1953 due to high U concentration, but detailed information, considered a military secret, has never been reported. According to certain individual data, the ash there contained 1% of U_3O_8 (Ziehr 1961). In West Germany, somewhat higher U contents are found in brown coals of Bavaria, i.e. in Wackersdorf lignite (20–2000 mg/kg, single samples up to 12,000 mg/kg) and in subbituminous coals of Hausham (25–40 mg/kg) and Peiting (12–125 mg/kg). U was probably extracted from the crystalline rocks situated in the wider vicinity of the mentioned deposits. In subbituminous coals, U occurs within all seams; its formations considers to be synsedimentary, whereas in the Wackersdorf lignite there are several U-rich layers, discordantly crossing coal and barren rock. Here, U was formed epigenetically, i.e. discharged subsequently (Ziehr 1961).

It is known that brown coals from the Drama (Foscolos et al. 1998), Ioannina (Gentzis et al. 1997), and Plakias basins (Gentzis et al. 1996) in Greece are characteristic for higher U concentration.

Also, the coal from the Kangal basin, Turkey (Karayigit et al. 2001), disposes of high U concentration ranging between 5.5 and 131 mg/kg, but the coal from the Sorguni basin (Karayigit et al. 2000) disposes of higher Th (1.4–69 mg/kg) compared to U (<0.7–11 mg/kg) concentration. The highest possible concentration of U in Turkish coals (140 mg/kg) was detected in the deposit within the Aegean Region (Palmer et al. 2004).

When comparing the arithmetic mean values of U and Th in brown coals from the Sofia basin, Bulgaria (Kortenski and Sotirov 2002) to some Canadian brown coals (Goodarzi & Van der Klier-Keller 1988, Grieve & Goodarzi 1993, Potter et al. 1991), it was noticed that brown coals from Kostolac, Krepoljin, Sjenica, Soko Banja and Bogovina basins have higher U concentrations; only the coal from the Krepoljin basin has a somewhat higher Th concentration.

Comprehensive analyses of radioactive elements in coals of Australia (ACARP 1996, Dale et al. 1991) show that the average concentration of U is 1.3 mg/kg, ranging from 0.3 to 2.1 mg/kg, while the average concentration for Th is 3.5 mg/kg, ranging from 1.5 to 6.0 mg/kg.

The comparison made between geometric mean values of U concentration in lignite from 31 different worldwide countries (Bouška and Pešek 1999) and the coals from Serbia and Montenegro, has shown 4 times higher U concentration in the Bogovina East field than is the mean world concentration, as well as 2 times higher U concentration in the Sjenica basin. Concentration of U in other basins in Serbia and Montenegro is either slightly higher (Krepoljin, Soko Banja and Kolubara basin) or lower (Pljevlja, Senje-Resavica and Kostolac basin) than it is in world lignites. Compared to geometric mean value of Th concentration in world lignite, the coals from Serbia and Montenegro show low concentration. Only the coal from the Krepoljin and Kolubara basin shows slightly higher concentration than the world lignite.

During coal combustion non-volatile elements, such as Th and U, are almost entirely retained in solid combustion wastes. The average ash yield value of brown coals from Serbia and Montenegro ranges between 12.51% and 21.89% as received basis (**Table 3**). Therefore, the concentration of most radioactive elements in solid combustion wastes will be approximately five times the concentration of the original coal. It certainly would be very useful to make some estimation of these elements effects on environment, based on coal production, ash concentration and release of U and Th during combustion.

Table 3: Approximate total release of U and Th from investigated mines in the period from 1965 to 2000

	Kostolac Drmno	Kolubara 'D' field	Krepoljin Jasenovac	Sjenica Štavalj	Soko Banja Soko	Bogovina East field	Senje-Resavica	Pljevlja Potrlica
Total coal production (t) 1965–2000	43,662,135	327,969,926	1,525,338	2,158,987	5,148,239	4,899,008	14,576,544	19,797,349 (1965–1997)
Ash (%, ar)	15.72 [a]	12.51 [b]	17.12 [b]	12.78 [b]	19.85 [b]	18.35 [b]	12.54 [b]	15.86 [c]
Total ash production (t) 1965–2000	6,863,688	41,029,038	261,138	275,919	1,021,925	898,968	1,827,899	3,139,860
U (GM), (mg/kg)	0.43	1.69	2.62	3.15	2.64	6.36	1.08	1.20
Th (GM), (mg/kg)	0.93	2.79	3.33	0.81	0.91	0.44	0.97	0.76
Total U production (t)	18.77	554.27	4.00	6.80	13.59	31.16	15.74	23.76
Total Th production (t)	40.61	915.04	5.08	1.75	4.68	2.16	14.14	15.05
Total U production (kg/year)	522	15.5	111	189	378	865	437	720
Total Th production (kg/year)	1,128	26.1	141	49	130	60	393	456

[a] after Životić (2001); [b] after Ercegovac (1998); [c] after Životić (1998)

Table 4: The activity concentration (Bq/kg) of some natural radionuclides in coal, ash, fly ash and slag from the Kolubara and Kostolac thermal power plant (after Todorovi et al. 2005 and Todorovi 2005)

	Kolubara thermal power plant			Kostolac thermal power plant		
	^{232}Th	^{238}U	^{235}U	^{232}Th	^{238}U	^{235}U
Coal	14–22	27–71	1.7–2.6	14 ± 2	33 ± 12	1.3 ± 0.2
Ash (active depository)	66–81	71–143	5.3–8.6	38 ± 4	55 ± 13	4.2 ± 0.5
Fly ash	94–104	100–174	4.8–12.0	34 ± 4	75 ± 16	2.7 ± 0.4
Slag	24–65	26–118	2.0–6.6	14 ± 2	51 ± 15	1.7 ± 0.2

In the period from 1965 to 2000, soft brown coal mines in Serbia (Kostolac and Kolubara basins) had total coal production exceeding 371.63 Mt (see Table 3). Combustion of the same resulted in production of approximately 47.89 Mt of coal ash (see Table 3) disposed in the vicinity of thermal power plants (TPP). Within the same period, hard brown coal mines (Jasenovac, Štavalj, Soko, Bogovina-East field, Jelovac, Strmosten and Senje mine) in Serbia had total coal production exceeding 28.39 Mt yielding 4.28 Mt of coal ash. From 1965 to 1997, brown coal mines in Montenegro had total coal production exceeding 17.79 Mt, the combustion of which resulted in approximately 3.13 Mt of coal ash, disposed in the vicinity of thermal power plants.

Based on the data obtained during this study on coal production in Serbia and Montenegro (Živanović et al. 2003, Gagić 1998, Simeunović et al. 2003, Gomilanović 1999) as well as on the geometric mean values of U and Th concentration, the estimated quantities of U and Th stored in fly ash within the period 1965–2000 (see Table 3) are 644.33 t for U and 983.46 t for Th. The approximate total stored U and Th in fly ash (within 1965–1997 period) from the Potrlica mine (Montenegro) was 23.76 t and 15.05 t, respectively.

For possible human health risk assessment, whenever radioactive elements are in question, activity is more useful than concentration, so the activity of some natural radionuclides is always valuable information. As Kolubara basin produces most of the feed coal for the thermal power plants in Serbia (see Table 3), the data on activity concentration of U and Th in coal, ash, fly ash and slag from the Kolubara thermal power plant (Todorović et al. 2005) and Kostolac thermal power plant (Todorović 2005), are shown in **Table 4**. The obtained values are within the usual limits cited in literature (IAEA 2003), although Serbian low sets no limits for natural radionuclides in coals, ash and excavation residues.

When estimating the U and Th emission, the geometric mean value was used, as it seems to be more reliable than the arithmetic one. In calculating the release value of U and Th originating from the Kostolac basin, only the values for the coal seam III were used, as the coal seam II has never been exploited in the Drmno field.

During coal combustion, the majority of U and Th are released from the original coal matrix and, in form of solid phase, distributed between the gas phase, as particulate matter (fly ash), and ordinary solid combustion products (ash). Consequently, the evidence of U and Th release may be found in the vicinity of combustion facilities, at dumps, in soil and water. Furthermore some interesting literature data (WNA 2004) confirmed the previous. Namely, the major part of U and Th from coal, leaving power station in form of light fly ash, is fused and chemically stable. Some 99% of fly ash, normally retained and collected by electrofilters built in modern power stations (90% is some old ones) is deposited at ash dumps. The amounts of radionuclides involved are noteworthy. In Victoria, USA, approximately 65 Mt of brown coal per year undergoes combustion for the purpose of electric power production. This tonnage contains about 1.6 mg/kg of U and 3.0–3.5 mg/kg of Th, and thus about 100 t of U and 200 t of Th are buried in landfill every year in the Latrobe Valley. Australia exports 88 Mt/y of steam coal, containing approximately 1.1 mg/kg of U and 3.5 mg/kg of Th, and thus 100 t of U and 300 t of Th would be concentrated in form of ash in importer countries.

4 Conclusion

This study shows that brown coals in Serbia and Montenegro (soft to hard brown coals or lignite to subbituminous) generally contain low levels of U. Higher concentrations of U were recorded in the bottom part of the II seam of the Kostolac basin, and in the complete Lower seam of the Bogovina East field. Concentrations of Th in coals from Serbia and Montenegro have proved to be low as well. Elevated U concentrations are typical for coal seams associated to magmatic rocks and crystalline schist. It is assumed that hydrothermally altered granite and schist from such regions could be the source of U what explains the high concentration of this element in the coal seam II of the Kostolac basin. Also, the hydrothermally altered rocks of the Timok dacite-andesite complex, representing the basement of the Bogovina basin, is assumed to be the potential source of U, especially at the bottom part of the Lower seam of the Bogovina East field.

According to obtained results release of U and Th from brown coals in Serbia and Montenegro has proved not to be dangerous. In general, high concentration of U and Th may cause certain health problems (ATSDR 2003) due to radioactive effects, but contamination effects resulting from coal combustion and certain products of combustion in Serbia and Montenegro are not related to U and Th but to heavy metals. Environmental impact of heavy metals has still been insufficiently known due to incomplete studies that should be completed or performed. Zielinski and Finkelman (1997) have concluded that in comparison of radioactive elements in coals, fly ash and ash to other chemically toxic and hazardous air pollutants like As, Se, Hg, Be, Cd, Cr, Mn, Ni, Pb and Sb, have less harmful effects on health, as coal and fly ash are usually not significantly enriched in radioactive elements or associated radioactivity. For example, extremely high concentrations of U in brown coal were detected in Wackersdorf lignite (Germany) 2000 mg/kg (single samples up to 12,000 mg/kg), but hazardous radioactive effects of coal combustion and the resulting products of combustion on human health have not been reported.

5 Recommendations and Perspectives

U and Th from the coals in Serbia and Montenegro show no identifiable unfavourable impact on the surrounding environment, due to their low natural concentrations, but investigations concerning human health should be performed.

Our investigations revealed that in some Serbian coals (particularly, parts of the coal seams) U and Th contents are rather high. Such coals should be carefully studied particularly for U and Th concentrations in ash, fly ash and waste disposals together with land and soil nearby and ground water. Further studies should include determination of the radioactivity of all these products, and estimation of eventual health impact.

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