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High arsenic (As) content in the Upper Miocene coal matter from TER-1/03 borehole (Terbegovci – Sveti Jurij ob Ščavnici, NE Slovenia)

Visoka vsebnost arzena (As) v drobcih zgornjemiocenskega premoga iz vrtine TER-1/03 (Terbegovci – Sveti Jurij ob Ščavnici, SV Slovenija)

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Abstract

A composite sample of coal cuttings (depth: 141.0–155.5 m) from the TER-1/03 water supply well in north-eastern (NE) Slovenia (Slovenske gorice; locality Terbegovci – Sveti Jurij ob Ščavnici) was analysed for its coal quality (proximate analysis – percent moisture, volatile matter, fixed carbon, ash), calorific value, and major (C, H, O, N, S)-, minor (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, Mn – as oxides)- and trace-elemental (43 elements) chemical composition. The coal was classified as a "normal" humic, high-grade metalignite, similar to coals in the Mura Formation of the Mura-Zala Basin. Unusually high arsenic (As) content of more than 100 μg/g was determined in the investigated coal matter, whereas the Clarke value for the world coals is between 5 and 10 μg/g, as cited by different authors. Besides As, also Sb, V, Mo, U, and W have been found to be enriched in the studied coal.

Izvleček

V članku predstavljamo rezultate osnovne (delež vlage, hlapnih snovi, vezanega ogljika in pepela), kalorimetrične (kurilna vrednost) in elementne analize kompozitnega vzorca drobcev premoga iz globine 141,0–155,5 m iz vrtine TER-1/03 – območje Terbegovci pri Svetem Juriju ob Ščavnici v Slovenskih goricah, severovzhodna (SV) Slovenija. V okviru kemično elementne analize je bila določena sestava glavnih prvin (C, H, O, N, S), sestava podrejenih prvin (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, Mn – v oksidni obliki) in sestava 43 slednih prvin. Ugotovili smo, da je preiskana premoška snov huminitni metalignit (premog nizke stopnje karbonizacije), da je glede na nizko pepelnost (pod 10 %) premog visoke kakovosti in je podoben premogom v Murski formaciji Mursko-Zalskega bazena, da pa vsebuje izstopajoče visoko koncentracijo arzena (As) in sicer več kot 100 μg/g. Po različnih virih znaša vsebnost As v premogih sveta med 5 in 10 μg/g. Kot povišane glede na povprečne vsebnosti premogov sveta so se v preiskanem premogu pokazale tudi vsebnosti Sb, V, Mo, U in W.

Introduction

Borehole TER-1/03 was designed and drilled as a water supply well in 2003 in the area of Terbegovci near Sveti Jurij ob Ščavnici in NE Slovenia, which is geologically positioned within the Mura-Zala Basin belonging to the W part of the Pannonian Basin System (Fig. 1). TER-1/03 was drilled vertically from the surface (at a location with coordinates GKX = 5 156 311.6, GKY = 5 578 506.0, Z = +219.5 m; OGK 1:100.000 – List Čakovec (Mioč & Marković, 1998a) (Fig. 2), and reached a depth of 190 m. It penetrated prevailingly clayey-silty sediments with occasional up to a few metres thick sandy-gravely sequences (Fig. 3) and with sporadic thin coal layers. Coal cuttings were sampled in the depth interval 141.0 – 155.5 m. According to the well master log, the borehole lithology is typical for the "Pontian Beds" as traditionally termed in Slovenia. The "Pontian Beds" correspond mainly to the Mura Formation as called in Slovenia (Mioč & Marković, 1998b) or the Ujfalu Formation (as named in Hungary).

During the TER-1/03 drilling campaign, we had a chance to collect coal cuttings from the borehole washout and analyse them with standard coal geochemical methods. The sampled coal cuttings proved valuable because no other coal samples were known from NE Slovenia to be geochemically investigated except for coal in the Mura Formation from the well explored Lendava (Slovenia) – Mursko Središće (Croatia)

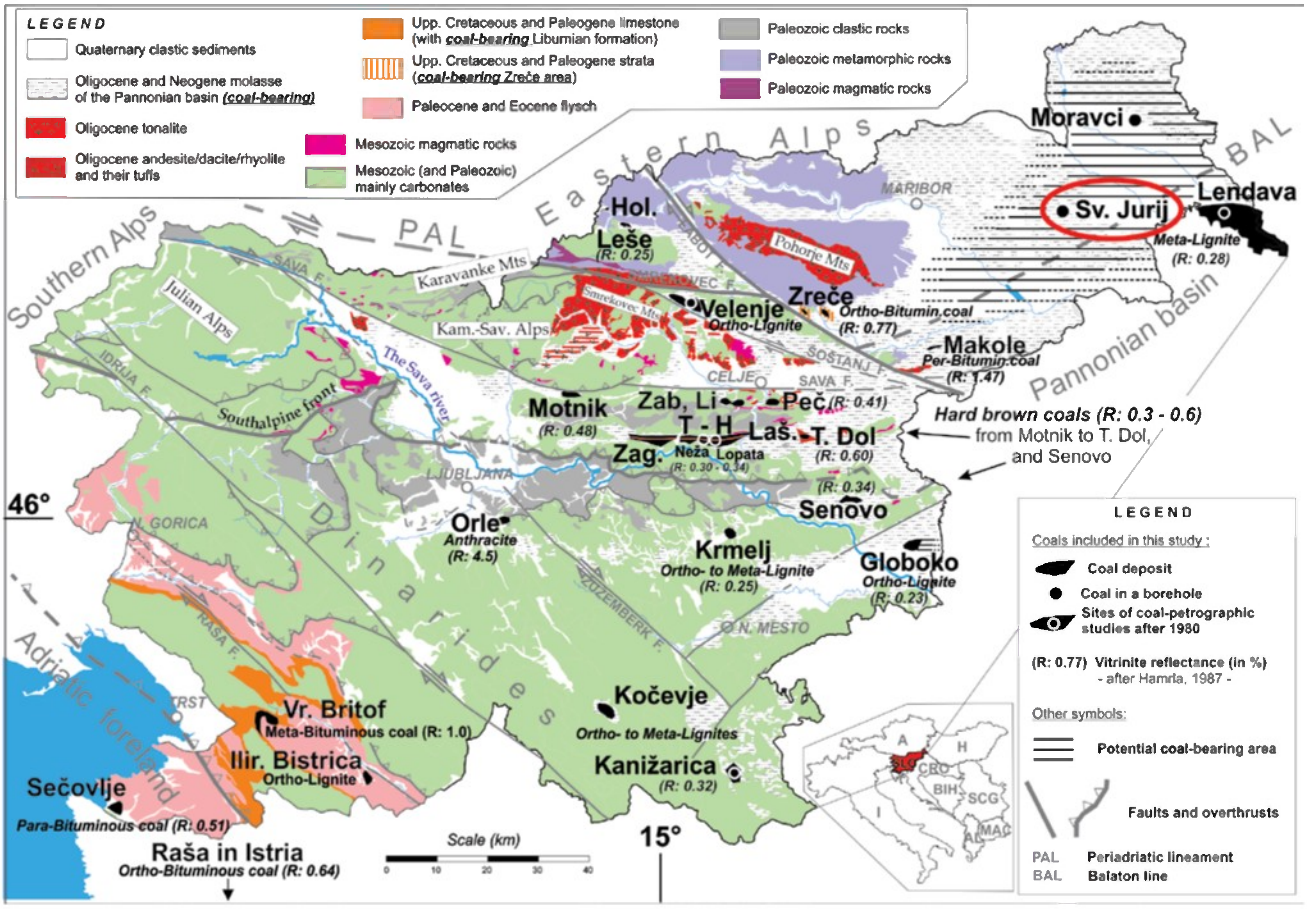

Fig. 1. Location of the TER-1/03 borehole on a simplified geological map of Slovenia compiled from 23 sheets of the Basic Geological Map of Yugoslavia (1:100.000), with general tectonics from PLACER (1998). Main coal deposits are shown on the map using coal rank terms after the ECE-UN (1998) classification (from: MARKIČ et al., 2007).

Sl. 1. Lokacija vrtine TER-1/03 na poenostavljeni geološki karti Slovenije, izdelani na podlagi 23 listov OGK Jugoslavije (1:100.000). Tektonika je povzeta po PLACER-ju (1998). Na karti so prikazana pomembnejša nahajališča premogov (iz: MARKIČ et al., 2007).

area (MARKIČ et al., 2011) (Fig. 1). However, in the 1980s, analyses of the Lendava coal were restricted mainly to coal-quality analyses involving calorific value, moisture, ash and sulphur contents. Occasionally, analyses of major (C, H, O, N, S) and minor (Si, Al, Fe, Ca, Mg, K, Na Ti, P, Mn, Cr – as oxides) coal-forming elements were done on some samples. The only trace element study of coals performed on coal ashes, including the Lendava coal, was carried out by PIRC & ŽUŽA (1989). Arsenic (As) content of the Lendava coal was unfortunately not analysed, but it was analysed for the Globoko lignite in the Krško Basin, which is also a part of the Pannonian Basin System. The Globoko lignite is well comparable to the Lendava coal, although somewhat lower in coalification rank than the Lendava coal (HAMRLA, 1987; MARKIČ et al., 2007). Both are paralic Pontian coals of the Pannonian Basin System, deposited as numerous (up to 20) but thin (up to 2.2 m) coal beds within clayey, silty, marly and sandy sediments subordinately inter-bedded by mostly fine gravels (STEVANOVIČ & ŠKERLJ, 1985; MARKIČ & ROKAVEC, 2002; MARKIČ et al., 2011). Whole sequences of the coal-bearing strata are several tens of metres thick. In comparison to other "non-Pontian" (and non-paralic) coals it is remarkable that it is the Globoko lignite, which is considerably As enriched (based on data from PIRC & ŽUŽA, 1989). Arsenic (As) content in the Globoko lignite ash is reported to be 260 µg/g, whereas of other coal ashes (Velenje, Kanižarica, Senovo, Trbovlje) it does not exceed 50 µg/g (PIRC & ŽUŽA, 1989). A similar value, within a range of 20–33 µg/g As, was obtained also for the Trbovlje coal ash from the Trbovlje Thermal Power Plant (KOČEVAR, 2000). All the data are representing "normal" high-temperature ashes.

When As in coal is reported as the As in coal ash it should be taken into account that at temperatures of ca. 750 to 950 °C, at which combustion of coal is mostly carried out, As is a readily volatile element. Other well-known easily volatile elements are Hg, I, Se, B, Br, Ge, Mo (e.g. HUGGINS, 2002; KETRIS & YUDOVICH, 2009). An alternative method to avoid the loss of trace elements is performing low-temperature ashing at 380 °C, or oxygen plasma ashing at 150–200 °C (as summarized in DIESSEL, 1992, p.158). However, these methods of low-temperature "combustion" (oxidation) of the coal's organic matter to obtain the mineral residue (ash) are not practiced routinely and the majority of comparable world data are based on high-temperature ashes.

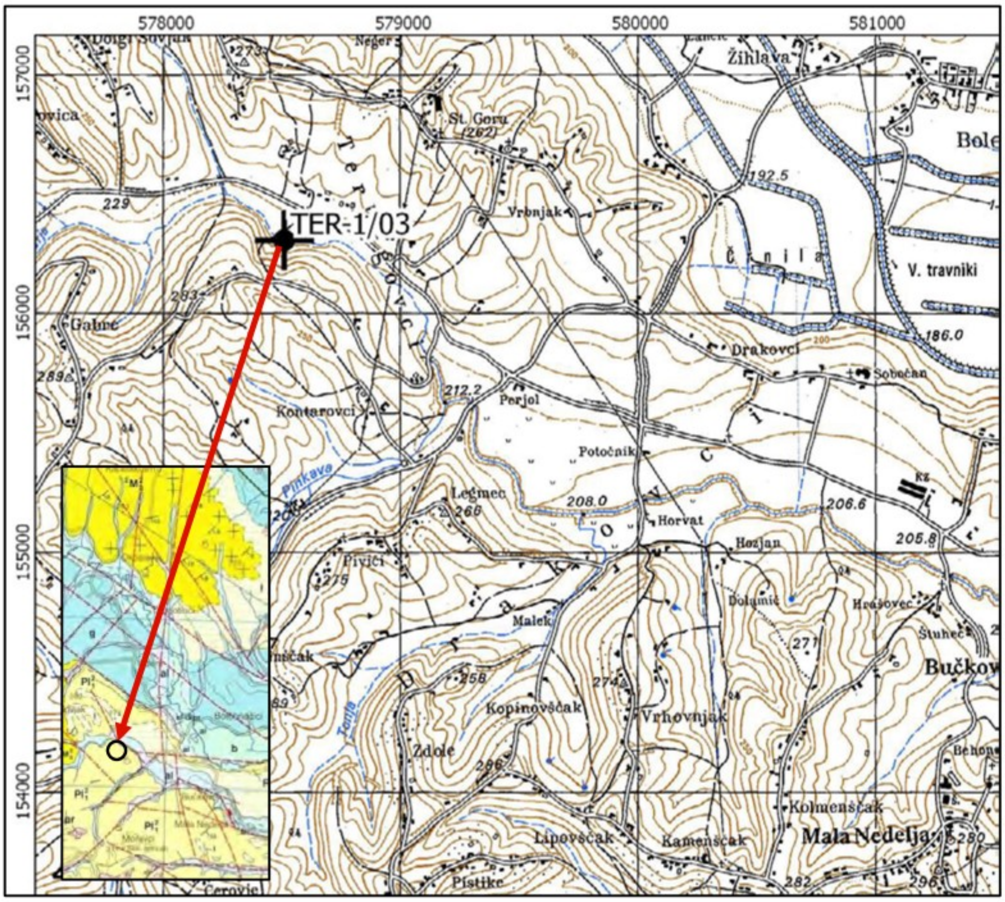

Fig. 2. Location of TER-1/03 on the basic topographic map (coordinate lines are 1 km apart). An inlet from the Basic Geological Map 1:100.000 – Sheet Čakovec (Mioč & Marković 1998a) with position of TER-1/03 is added in the left bottom corner.

Sl. 2. Lokacija vrtine TER-1/03 na osnovni državni topografski karti (razdalja med dvema koordinatnima linijama je 1 km). V spodnjem levem kotu je izrez iz OGK – List Čakovec 1 : 100.000 (Mioč & Marković, 1998a) s prikazom vrtine TER-1/03.

Šlejkovec & Kanduč (2005) studied As compounds in low-rank coals from Velenje (Pliocene) and Trbovlje (Oligocene) in Slovenia, and from the Sokolov Basin (Oligocene and Miocene) in the Czech Republic, altogether 9 samples (3 from Sokolov, 5 from Velenje and 1 from Trbovlje) were analysed. They found As contents for most of the samples below 10 µg/g, for one sample 14 µg/g, and for one exceptional sample – representing the Josef coal seam from the Sokolov Basin – as high as 142 µg/g. By extraction of As from coal samples they also ascertained that As in the Trbovlje and Sokolov coals occurs in inorganic compounds, whereas in the Velenje lignite it occurs both inorganically and organically bound.

In the Velenje lignite (Pliocene), As content was analysed in a suite of 30 lignite samples taken from the bottom of the seam (high-ash lignite) to the top of the seam (low-ash lignite) in a representative P–9k/92 borehole situated in the centre of the Velenje Basin (Markič, 2006). In addition, 6 samples from the floor and 3 samples from the roof of the lignite seam were analysed. Results of the analyses show that mineral matter of the lignite (analysed as the ash content, expressed at the dry basis) gradually decreases from 20–30 % at the bottom, to 10–15 % at the top of the seam. Correspondingly, the As content decreases from 13–25 µg/g at the bottom to 3–7 µg/g at the top of the seam. In the floor sediments, it is 10–20 µg/g, and in the roof sediments, it is 5–8 µg/g. Since the difference in As contents between inorganic sediments of the floor (mudstones), the roof (marls), and the lignite is not substantial – as in prevailing cases of other trace elements, which are mostly depleted in lignite – Markič (2006) concluded that As is probably, at least partly, organically bound. Organic bonding, even more substantial than for As, was interpreted for U and Mo, partially also for Ba and Sr, whereas other trace elements are significantly depleted in the lignite versus inorganic sediments (Markič, 2006; Markič & Sachsenhofer, 2010).

World averages for trace element contents in coals and black shales were published recently by Ketris & Yudovich (2009), and before them by Swaine (1990), Valković (1983), and Bowen (1979). For As in coals ("whole rock" basis), authors report the following averages and ranges, respectively:

- 7.6 ± 1.3 µg/g – for world brown coals (Ketris & Yudovich, 2009, p.145)

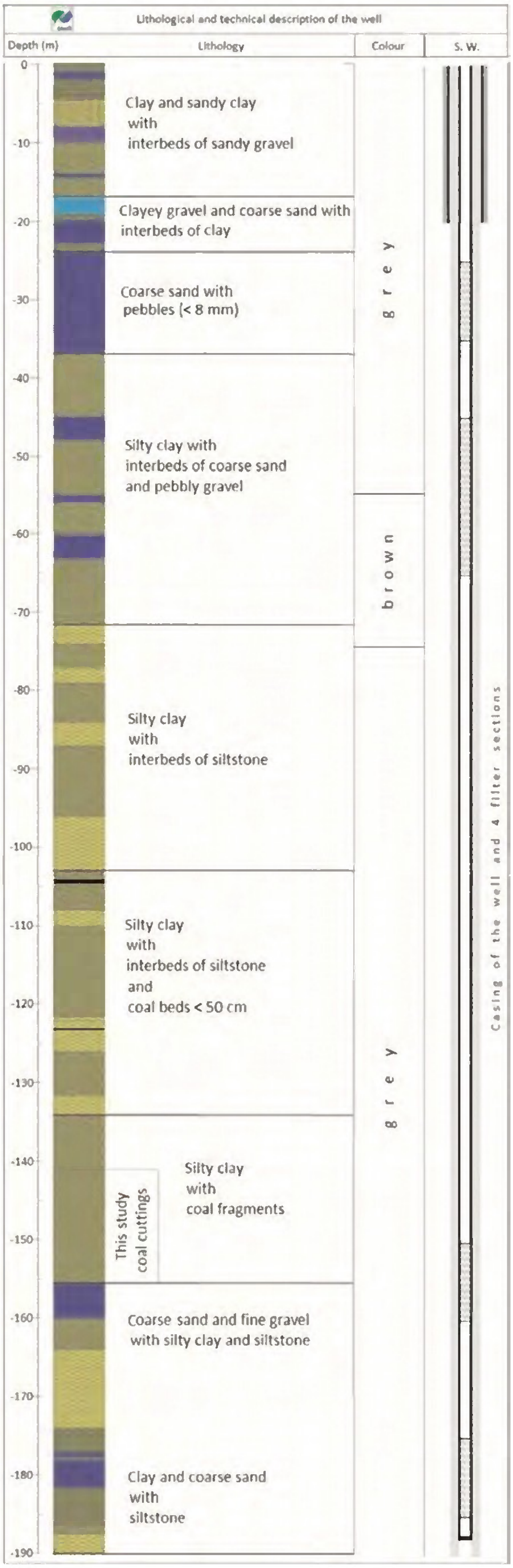

Fig. 3. Lithologic column of the TER-1/03 borehole (by T. Matoz). The sampled coal material (coal cuttings) is from the depth interval 141.0-155.5 m.

Sl. 3. Litološki stolpec vrtine TER-1/03 (obdelal T. Matoz, 2004). Vzorčeni drobci premoga so iz globine 141.0-155.5 m.

- 9.0 ± 0.7 µg/g – for world hard coals (Ketris & Yudovich, 2009, p.145)
- 8.3 µg/g – for all world coals (Ketris & Yudovich, 2009, p.145)
- 0.5–80 µg/g – for world coals (Swaine, 1990 and Bowen, 1979; cf. Taylor et al., 1998, p. 272)
- 5 µg/g – for world coals (Valković, 1983)

Comparatively, As content of the world soils is cited to be in a "normal" range of 1–50 µg/g, (Swaine, 1990, and Bowen, 1979; from Taylor et al., 1998, p. 272). To the same authors, an average As content of the world shales is 13 µg/g, whereas of the world sedimentary rocks (Ketris & Yudovich, 2009), it is 7.6 µg/g (same as for world brown coals). After Andjelov (1993), the average As content (arithmetic mean) of soils in Slovenia is 8.17 µg/g, with a minimum value of 4 µg/g and a maximum of 131 µg/g. After Šajn (2003), the median As value for soils in Slovenia is 15 µg/g, with the minimum–maximum range of 6–37 µg/g. Median As contents of soils in areas of historical long-lasting mining and metallurgic activities are slightly higher, 20–22 µg/g, and do not exceed 105 µg/g in maximum, with an exception of Mežica with a maximum content of 387 µg/g As (Šajn & Gosar, 2004; Gosar & Šajn, 2005).

For an extended insight into the geochemistry of As in coals worldwide, the reader is referred to a multi-aspect review of As in coal written by Yudovich & Ketris (2005). They report that As in coals does not occur only in very variable contents (from some µg/g to several hundreds and even above 3000 µg/g, and in coal ashes about 6–8 times these values) but also in different modes of occurrence (organic and inorganic bonding) and is of different origins (authigenic, syngenetic, epigenetic). It is generally considered that As content in a coal exceeding 100–300 µg/g may be hazardous to environment and health, but this again depends on the mode of occurrence of As in coal (risk is present especially when finely dispersed mineral As and organically bound As are present, even in relatively low contents) and on the procedures of coal processing (coal preparation, combustion technologies, fly ash treatment, etc.).

In Slovenia, As contents in soils exceeding 55 µg/g (with no regard to As forms of occurrence) are considered critical (Šajn & Gosar, 2004; tab.1 – after Official Gazette of Republic of Slovenia 68/96) – meaning that in such areas soils are not suitable for agriculture.

The aim of our study was to qualitatively characterise coal matter from the TER-1/03 well simply because it was a chance to do that. To get such material from a well is not an every-day event and may therefore represent an extraordinary challenge to widen an existing knowledge on coal grade, type, rank and chemical composition, as well as its geological occurrence and genesis in the area of the study.

Methods for characterisation of the sampled coal

Sampling

Sampled coal cuttings from the TER-1/03 borehole (depth 141.0–155.5 m) (Fig. 3) were of centimetre dimensions and were received in a mass of 200 grams. The sampled material – 1 sample – was carefully cleaned and washed with distilled water, and dried at 50 °C for 24 hours. Sampling of coal can be considered representative as it consists of randomly gathered coal cuttings from a 14.5 m long drilling interval.

Analytical methods

The "whole coal" material was investigated by the following standard coal-characterisation analyses (Thomas, 1992; ASTM, 1997; Finkelman et al., 1999):

1. Proximate coal analysis (moisture, volatile matter, fixed carbon, ash),
2. Calorific value
3. Ultimate (major element) analysis (C, H, O, N, S)
4. Minor element analysis (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, Mn, and Cr - as oxides, and Ba, Ni, Sc as elements)
5. Analysis of loss on ignition (LOI), total sulphur content (S_{tot}) and of total and organic carbon (C_{tot} and C_{org})
6. Trace element analysis (a suite of 43 elements)

The proximate and ultimate coal analyses, and determination of the calorific value were carried out in the Chemical Laboratory of RTCZ (Regionalni tehnološki center Zasavje – Regional Technological Centre of Zasavje) in Trbovlje (Slovenia) using the SIST ISO Methods N° 5068, 1171, 351, 351/C1, 157-3,4,5 for the proximate analysis parameters, SIST ISO Methods N° 625, 351, and 333 for the ultimate analysis parameters, and SIST ISO Method N° 928 for determination of the calorific value (Tab. 1). Minor coal-forming elements, LOI, C_{org}, and a suite of 43 trace elements were analysed in the Acme Analytical Laboratories (Vancouver, Canada). S_{tot} and C_{tot} were analysed in both laboratories. For the proximate and ultimate analysis in the Trbovlje Lab, a major share (185 g) of the sampled material was used, whereas about 12 g of the sample was delivered in an ampoule to the Acme Lab. In the Acme Lab (Acme, 2012a) abundances of the minor elements (expressed as oxides) were analysed by the ICP-AES emission spectrometry following a Lithium metaborate/tetraborate fusion and dilute nitric digestion. LOI was expressed by weight difference after ignition at 1000 °C. A part of trace elements (earth elements and refractory elements) was digested by the same method as the minor elements, and a part (precious and base metals) was digested by Aqua Regia. ICP-MS was then used to analyse abundances of trace elements. S_{tot}, C_{tot} and C_{org} were analysed by the Leco analysis (Acme, 2012b).

Accuracy and precision (repeatability) of trace element analytics

For accuracy of the results for the contents of As as well as for all other elements the reader is referred to a paper about geochemical characterisation of the Velenje lignite based on 39 samples from the 100 m thick lignite seam and its direct floor and roof sediments (Markič, 2006). Coal from the TER-1/03 borehole was added as the fortieth sample (signed as sample 5 CK) to the suite of samples from Velenje. For precision (repeatability) estimation, 4 homogenized lignite samples were split each into 3 sub-samples, which were then analysed by the same ICP procedures as the main suite of samples. The results of the three reruns of four samples (at As contents between 3 and 6 µg/g) showed that differences between the averages and minima and the averages and maxima do not exceed 4 % of the average contents. These results show high repeatability. High precision was also ascertained by the Acme self-testing with the standard material DS4 – both values coinciding at 22.8 µg/g As. However, the comparison between the reference value for As content in the CRM 180 standard material (a standard material by European Commission – Joint Research Centre – IRMM – representing bituminous coal with 76 % C, but referencing only 10 trace elements) and the As content in the same reference material as analysed by Acme revealed a drastic difference – the reference value being 4.23 µg/g, and the Acme's as high as 9 µg/g. A similar low accuracy was found for Cd and Pb. The highest accuracy was found for Ba and Th (<10 % difference), and a reliable one for Zn, V, Ni, La and Cu (<40 % difference). The CRM 180 reference contents of individual elements were higher than those analysed by Acme in all cases, except for As and Cd. Unfortunately, the well known NBS coal and coal ash standards were not used because they were not available at the time of the analyses. Due to very high content in our sample we consider the resultant As content significant in spite of the fact that the content can be lower.

Results and discussion

Grade, type and coalification rank

The results of proximate analysis (moisture and ash content, S contents in different forms, and calorific value), and of ultimate analysis (contents of C, H, S, O and N which compose combustible matter) are given in Table 1 (upper part) at the "as received basis"*(arb)*, "dry basis"*(db)* and at the "dry, ash-free basis"*(dafb)*.

Characterisation of coal on the "as received basis" *(arb)* is mostly reported when a raw quality of coal (e.g."coal as mined", "run-of-mine coal" or "coal-pile coal for combustion") is under consideration. When grade of coal (e.g. market coal) is in question, mostly ash content at the "dry basis" *(db)* (coal without moisture) is taken into account. On the "dry basis" *(db)*, designations such as "high grade", "medium grade" and "low grade" coal are differentiated according to the Ece-Un Classification (1998). "Dry, ash-free basis" *(dafb)* of coal relates to pure organic matter, and its calorific value is one of the coalification rank parameters which classify coals as lignite, subbituminous coal, bituminous coal etc. An overview of rank and grade of coals in Slovenia based on pre-existing data is reported in Markič et al. (2007).

As seen from Table 1, at the *arb*, both moisture content and ash content of the sampled coal are low (moisture 9.61 %, and ash 8.48 %). Moisture content is not very realistic due to a sample disposal (no-intact sampling conditions), but realistic is low ash content below 10 % at the "dry basis", which classifies the investigated coal according to the Ece Un Clasiffication (1998) into a "high grade coal".

Atomic ratios H/C (1.030) and O/C (0.277) (Tab. 1) clearly classify the investigated coal into a normal "humic type of coal", consistent with petrographic maceral/microlithotype characterisation of the Lendava coal (Markič, 1983).

Calorific value of 21.8 MJ/kg at the *arb* is a realistic bulk coal quality datum, but is not a coalification rank one. The most reliable coalification-rank designation of the treated coal is by its calorific value at the dry, ash-free basis (CV*dafb*). The calorific value of 26.91 MJ/kg as cited in Table 1 is the net or lower CV*dafb*, whereas a real coalification rank parameter is the gross or the higher CV. Gross CV*dafb* is calculated from the following equation (from Thomas, 1992, p.33):

Table 1. Proximate and ultimate chemical analyses of the TER-1/03 coal matter, H/C versus O/C characterisation, and coalification rank by Gross Calorific Value at the dry, ash free basis (*dafb*).

Tabela 1. Osnovna in elementna kemična analiza drobcev premoga iz vrtine TER-1/03 ter opredelitvi s H/C proti O/C razmerjem in s stopnjo karbonizacije na podlagi zgornje kurilne vrednosti na suho stanje, brez pepela (*dafb*).

		Parameter	***Method SIST ISO***	**Results at different bases**		
				As-received *arb*	**Dry at 105 °C *db***	**Dry, ash-free *dafb***
Source analytical data	**Proximate analysis**	Total moisture (%)	*5068*	9.61		
		Ash (%)	*1171*	8.48	**9.38**	
		Combust. matt. (%)	*351*	81.91	90.62	100.00
		S total (%)	*351/C1*	1.66	1.84	
		S sulphide form (%)	*157-4*	0.76	0.84	
		S sulphate form (%)	*157-3*	0.02	0.02	
		S organic form (%)	*157-5*	0.88	0.97	
		Calorific value (MJ/kg)	*1928*	21.801	24.386	26.910
	Ultim. anal.	**Carbon (%)**	*625*	55.41	61.30	**67.65**
		Hydrogen (%)	*625*	4.79	5.30	5.85
		Sulphur (%)	*351*	0.92	1.01	1.12
		Oxygen (%)	*calculated*	20.47	22.65	24.99
		Nitrogen (%)	*333*	0.32	0.35	0.39
Type by H/C-O/C		**Atomic H/C** = (%H × a.w.C) / (%C × a.w.H) = (5.85 × 12.011) / (67.65 × 1.008) = **1.030**				
		Atomic O/C = (%O × a.w.C) / (%C × a.w.O) = (24.99 × 12.011) / (67.65 × 15.999) = **0.277**				
Coalif. Rank by Gross CV*dafb*	Eq. 1	Gross CV*arb* = Net CV*arb*+0.212H+0.024M = 21.801+(0.212×4.79)+(0.024×9.61) = 23.047 MJ/kg				
		Gross CV*dafb* = (Gross CV*arb* / Combust. matt.) × 100 = (23.047 / 81.91)×100 = **28.137 MJ/kg**				
	Eq. 2	$\text{Gross CV}_{dafb}(\text{ccal/kg}) = \frac{[\text{Net CV}_{ar}(\text{ccal/kg}) + M_{ar}(\%)\times 6]\times 100}{OM_{ar}(\%)} + H_{daf}(\%)\times 54\,\text{ccal/kg}$				
		$\text{Gross CV}_{dafb}(\text{ccal/kg}) = \frac{[(21.801\times 238.9) + 9.61\times 6]\times 100}{81.91} + 5.85\times 54 = 6744.8\ \text{ccal/kg}$				
		Gross CV*dafb* (MJ/kg) = 6744.8 ccal/kg × 0.004186 = **28.234 MJ/kg**				

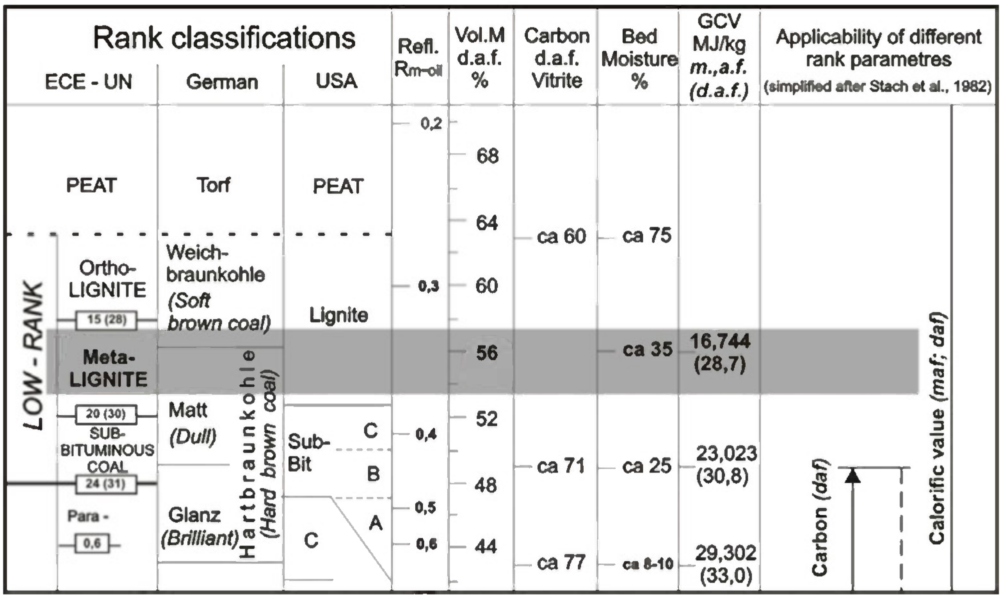

Fig. 4. ECE-CSE-UN 1998 (Economic Commission for Europe – Committee on Sustainable Energy – United Nations), German and the USA classification of low-rank coals. The grey field indicates coalification rank of the coal matter from the TER-1/03 borehole.

Sl. 4. ECE-CSE – UN 1998 (Economic Commission for Europe – Committee on Sustainable Energy – United Nations), nemška in ameriška klasifikacija premogov nizke stopnje karbonizacije. Sivo polje označuje stopnjo karbonizacije drobcev premoga iz vrtine TER-1/03.

Net CV*arb* = Gross CV*arb* – 0.212H – 0.024M,
where H = hydrogen (%) and M = moisture (%), and
Gross CV*dafb* = (Gross CV*arb* / Combustible matter) × 100 (Eq. 1 in Tab. 1)

Therefore, Gross CV*dafb* of the investigated coal material is 28.14 MJ/kg.

According to the ECE-UN CLASSIFICATION (1998), the Gross CV*dafb* of 28.14 MJ/kg classifies the investigated coal material into the "metalignite" coalification rank (Fig. 4). Even a little higher Gross CV*dafb*, 28.23 MJ/kg, is reported for the same sampled material by MARKIČ et al. (2007) using somewhat different Net-to-Gross CV recalculation (Eq. 2 in Tab. 1).

A second coalification rank parameter is the "in vitrain" carbon content at the dry ash-free basis (C*dafb*) (Fig. 4) as analysed by the ultimate analysis. "In vitrain" means that the C*dafb* value refers to the low ash (< 10 %) vitrinitic (or huminitic) coaly matter, or in other words, to the C content of the organic matter (C_{org}). C*dafb* of the investigated sample by ultimate analysis is 67.65 % (Tab. 1), and is almost entirely organic carbon as analysed by Leco in the Acme Lab (Tab. 2).This C*dafb* value confirms the metalignite rank as well (Fig. 4). Carbon content in Table 2 slightly differs from that in Table 1 because of somewhat different analytical techniques (different laboratories) and because the material analysed was not exactly the same in both cases regarding its moisture content. C_{tot} in Table 2 is very close to the mid value between C*arb* and C*db* in Table 1.

Table 2. Contents of minor element oxides, trace elements (Ba, Ni, Sc), total sulphur (Stot), total and organic carbon (Ctot and Corg), and of loss on ignition (LOI) in the "whole" coal matter from TER-1/03. Inorganic matter is considered as the sum (in %) from SiO_2 to Sc.

Tabela 2. Vsebnosti oksidov podrejenih prvin, slednih prvin (Ba, Ni, Sc), skupnega žvepla (Stot), skupnega in organskega ogljika (Ctot in Corg) ter žaroizguba (LOI) v vzorcu drobcev premoga iz vrtine TER-1/03. Anorganski delež je vsota (v %) od SiO_2 do Sc.

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
%	%	%	%	%	%	%	%
1.86	0.84	1.29	0.36	1.48	0.03	0.09	0.11
P_2O_5	MnO	Cr_2O_3	LOI	TOT/C	TOT/S	ORG/C	SUM
%	%	%	%	%	%	%	%
0.04	0.01	0.00	92.30	58.44	1.82	58.31	98.42

Geochemical (minor and trace elements) characterisation of the TER-1/03 coal

Minor element composition

Minor element composition (in oxide form), together with the loss on ignition (LOI), total carbon and sulphur contents (C_{tot}, S_{tot}) and organic carbon (C_{org}) content of the sampled coal material is presented in Table 2. Because the ash content is low, the contents of minor elements, which form inorganic matter, are also very low. Therefore, a better insight into the inorganic matter composition is gained by recalculation to a 100 % ash basis as quoted in Table 3. Coal ash is not identical to its mineral matter, but is a relatively good approximation to it. Table 3 shows that ash of the investigated sample is mainly composed of the following five oxides:

Table 3. Contents of minor element oxides recalculated to 100 % inorganic matter.

Tabela 3. Vsebnosti oksidov podrejenih prvin, preračunane na 100 % anorganske snovi.

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3
%	%	%	%	%	%	%	%	%	%	%
30.41	13.73	21.09	5.89	24.20	0.49	1.47	1.80	0.65	0.16	0.02

Table 4. Contents of trace elements in the "whole coal" matter from TER-1/03 borehole in comparison to the KETRIS & YUDOVICH's (2009) world coal ashes and world coals.

Tabela 4. Vsebnosti slednih prvin v vzorcu drobcev premoga iz vrtine TER-1/03 ter primerjava s pepeli premogov sveta in premogi sveta, kot sta jih objavila KETRIS & YUDOVICH (2009).

Element	All world coal ashes -Clarkes (K. & Y., 2009) in µg/g	All world coals -Clarkes (K. & Y., 2009) in µg/g	Coal from TER-1/03 (this study) in µg/g	Coal from TER-1/03 versus Clarkes for all world coals (very low and very high indices; rounded)
Co	32	5.1	4.7	
Cs	6.6	1.0	0.6	
Ga	33	5.8	4.7	
Hf	8.3	1.2	0.5	
Nb	20	3.7	7.7	
Rb	79	14	5.1	
Sn	6.4	1.1	<1.0	
Sr	740	110	26.1	0.2
Ta	1.7	0.28	<0.1	
Th	21	3.3	2.1	
U	16	2.4	14.6	**6**
V	155	25	272.0	**11**
W	6.9	1.1	4.9	**4**
Zr	210	36	50.0	
Y	51	8.4	13.2	
La	69	11	6.2	
Ce	130	23	12.4	
Pr	20	3.5	1.47	
Nd	67	12	6.6	
Sm	13	2.0	1.5	
Eu	2.5	0.47	0.55	
Gd	16	2.7	2.04	
Tb	2.1	0.32	0.34	
Dy	14	2.1	2.06	
Ho	4.0	0.54	0.42	
Er	5.5	0.93	1.47	
Tm	2.0	0.31	0.17	
Yb	6.2	1.0	1.50	
Lu	1.2	0.20	0.21	
Mo	14	2.2	18.5	**8**
Cu	92	16	18.5	
Pb	47	7.8	4.3	
Zn	140	23	52.0	
Ni	76	13	15.8	
As	**47**	**8.3**	**116.1**	**14**
Cd	1.2	0.22	0.1	
Sb	6.3	0.92	11.2	**12**
Bi	5.9	0.97	0.6	
Ag	0.61	0.095	0.3	**3**
Au (ppb)	22	3.7	1.1	0.3
Hg	0.75	0.10	0.33	**3**
Tl	4.9	0.63	0.2	0.3
Se	8.8	1.3	1.2	
Ti	4650	800	659	
Cr	100	16	0	

SiO_2 (30.4 %), CaO (24.2 %), Fe_2O_3 (21.1 %), Al_2O_3 (13.7 %), and MgO (5.89 %), representing together 95 % of the ash matter. The five oxides are in the molar ratio 0.53 : 0.45 : 0.14 : 0.14 : 0.15. X-ray diffraction was not made; therefore, the true mineral composition of ash (or mineral matter) can only be speculated. Since C_{tot} of the whole coal is almost entirely C_{org} it means that CaO does not derive from Ca-carbonates but is probably at least partially bound organically in the form of chelate complexes. Predominant content of SiO_2 is attributed to silica minerals (quartz), and partly, with Al_2O_3, to clay minerals. Negligible content of K_2O excludes occurrence of illite. Fe_2O_3, together with sulphur, can be attributed to pyrite.

Trace element geochemistry

Trace element composition of coal from the discussed TER-1/03 borehole is presented in Table 4. It is compared to the averages (the Clarke values according to Ketris & Yudovich, 2009) of coal ashes and "whole" coals, respectively. Comparisons of trace element contents in Slovenian coals and/or coal ashes with world averages as cited by some older sources are given in Pirc & Žuža (1989), Uhan (1993), Kočevar (2000), and Markič (2006).

In the right-most column of Table 4, the most remarkable depletions (values < 0.33) and the most remarkable enrichments (values > 3) of individual elements in the TER-1/03 coal in comparison to the Clarke values for coals after Ketris & Yudovich (2009) are given. It is clearly evident that As is the most enriched element in our TER-1/03 case, for nearly 14-times (×) in comparison to the world coals. Followed are very significant enrichments of Sb (12 ×), and V (11 ×). A little less outstanding enrichments stand for Mo (8 ×), U (6 ×), W (4 ×), Ag (3 ×), and Hg (3 ×). Taking into account the low accuracy of As content as found by analysing the CRM 180 standard material (see Chapter Accuracy and precision of trace element analytics) the As enrichment can be lower, maybe only a half of the content as measured in the Acme Laboratory, but still significant.

In Slovenia, some of the above mentioned enriched elements quite often occur in ore deposits (e.g. Sb in Trojane, Mo with Pb and Zn in Mežica, U in Žirovski vrh, Ag with Pb, Zn, Hg, in Litija, Hg in Idrija (Drovenik et al., 1980, and the references there-in)). Economic As ore occurrences are not known from geological formations of Slovenia, neither are known economic ore occurrences of V and W. However, significant V enrichments are known from some terra rossa (beauxite) districts of the Dinaric Karst areas along the Adriatic Sea (Croatia, Montenegro).

As, together with U and Mo enrichment occurs in the lignites of Dacota (USA) (Yudovich & Ketris, 2005). These coals are defined as the "Dacota" type of in-coal As occurrence. There, the enrichments are interpreted as a consequence of low-temperature water percolation through tuffaceous sands that epigenetically affected lignite in the underlying coal-bearing strata. Rocks of a somewhat similar type (Smrekovec andesite and its tuff, Grad basaltic tuff) exist also in NE Slovenia, but according to data by Kralj (1996, 2000, 2003), these rocks are "normal" in As contents (not exceeding 5–10 µg/g). Similar is true for most magmatic and metamorphic rocks of NE Slovenia and their soils, respectively (Zupančič, 1994; Trajanova, 2013; Trajanova, Zupančič, pers. comm., 2014). In the Pohorje Mountains (W hinterland of the Mura-Zala Basin), As contents of soils in the O horizon (uppermost organic rich part of the A horizon) of the granodiorite and eclogite basement rock vary between 2 and 6 µg/g, whereas in A and B soil horizons above serpentinite As contents vary between 30 and 60 µg/g (Zupančič, pers. comm., 2014). In the rocks of Pohorje, only As content in granodiorite is reported to be up to 21 µg/g (Zupančič and Plaskan, pers. comm. 2014).

Conclusion

Coal material from the TER-1/03 borehole corresponds to the Lendava petrographic type of coal i.e. humic coal. Due to lower ash content, the TER-1/03 coal is slightly higher in grade than the Lendava coal. In both cases, the coalification rank is similar, a little above Gross CV*dafb* 28 MJ/kg. The C*dafb* content of 67.65 % can be compared to the C*dafb* values between 67 and 68 % as typical for coals of the Pannonian and Pontian age. As it was determined by the paleontological studies of ostracods performed in the 1980s the Lendava coals are of the Pontian age. Coal and the coal bearing sediments from the TER-1/03 are most probably of the Pontian (Upper Miocene) age as well.

In the TER-1/03 coal material (coal cuttings) the arsenic (As) content is surprisingly high – more than 14-times above the average (Clarke) value for the world coals. U and Mo are also highly enriched. Arsenic content in the TER1/03 coal resembles the "Dacota type coal" significant for high As content where As was sorbed epigenetically by lignite from low-temperature groundwaters.

It is also interesting that the lignite from Globoko (Krško Basin, E Slovenia), which is of a similar paleo-geoenvironmental type as the Lendava coal and the coal from the TER-1/03 well, shows similarly elevated As contents.

Therefore, more stratigraphically regional geologically oriented investigations of As contents, modes of occurrence, processes of formation and geological sources would be interesting in the continuation of the geochemical research of coals and organic-rich sediments in our country as well as in broader region. Similar is true for the other geochemically enriched elements (Sb, V, Mo, U) mentioned in this paper, and the CAI (coal afinity index) elements.

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