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High arsenic (As) content in coals from Neogene deposits of the Pannonian Basin in Slovenia

Visoka vsebnost arzena (As) v premogih iz neogenskih plasti Panonskega bazena na območju Slovenije

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Dedicated to Professor Jože Pezdič on the occasion of his 70th birthday

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Ključne besede: premog, arzen (As), Panonski bazen, neogen, Slovenija

Abstract

High contents of arsenic (As) in coal samples from four localities within Neogene deposits of the Pannonian Basin in Slovenia are presented and discussed in this paper. Data from three localities represent interval samples of coal cuttings from wells TER-1 (Terbegovci), Sob-3g (Murska Sobota), and MD-1 (Mislinjska Dobrava). The fourth locality is Globoko, where the main lignite seam was analysed already in 1989. The oldest are coal samples from the MD-1 well which are supposed to be of the Lower Miocene age (except for the shallowest one, which is of the Plio-Quaternary age). Coal samples from the TER-1 and Sob-3g wells are of the Upper Miocene age (Mura Formation). The lignite sample from Globoko is of the Upper Miocene age too (Pontian; Globoko Formation). Most samples were prepared for the ICP-MS method analysis as "whole coal", dry, pulverized lab-samples, weighting ca. 10 g. The results show for all "whole coals" samples considerably increased contents of As: 22.7, 111.4, 222.1, and 131.4 µg/g for the Lower Miocene (?), and 84.5 µg/g for the Plio-Quaternary coals from MD-1 well, 392 µg/g for coals from the Sob-3g well, and 116 µg/g for a coal from the TER-1 well (both Upper Miocene – Mura Formation). In the case of Globoko, not "whole coal" but its high temperature ash was analysed and showed As content as high as 170 µg/g applying AAS method of analysis, and even 260 µg/g applying the ICP-MS. Origin of As could be pre-Neogene rocks of the hinterland and/or Neogene calc-alkaline volcanites. Mineral-gas exhalations from the under-continental upper mantle, containing As, could also be a source of this highly volatile element.

Izvleček

V članku predstavljamo in razlagamo rezultate o visoki vsebnosti arzena (As) v vzorcih premoga iz štirih lokalnosti znotraj neogenskih plasti na območju Panonskega bazena v Sloveniji. Podatki iz treh lokalnosti predstavljajo intervalne vzorce drobcev premoga iz vrtin TER-1 (Terbegovci), Sob-3g (Murska Sobota) in MD-1 (Mislinjska Dobrava). Četrta lokalnost je Globoko, kjer je bil glavni lignitni sloj analiziran že leta 1989. Najstarejši premog je iz vrtine MD-1 in je spodnjemiocenske starosti, razen najzgornejšega vzorca, ki je pliokvartarne starosti. Premogi iz vrtin TER-1 in Sob-3g so zgornjemiocenske starosti (Murska formacija). Lignit iz Globokega je tudi zgornjemiocenske starosti, določneje, pontijske (Globoška formacja). Večina vzorcev je bila pripravljena za analizno metodo ICP-MS kot vzorcev »celotnega premoga«. Laboratorijski vzorci so bili suhi, uprašeni in so tehtali okoli 10 g. Rezultati so pokazali za celotne premoge naslednje vsebnosti As: 22,7; 111,4; 222,1 in 131,4 µg/g za spodnjemiocenske premoge in 84,5 µg/g za plio-kvartarni premog iz vrtine MD-1 ter 392 µg/g za premoge iz vrtine Sob-3g in 116 µg/g za premog iz vrtine TER-1. Lignit iz Globokega je bil analiziran kot visokotemperaturni pepel z metodama AAS in ICP. Prva je pokazala vsebnost As 170 µg/g, druga pa 260 µg/g. Izvore As in njegove vezave na organsko/mineralno premoško snov je iskati v pred-neogenskih kamninah zaledja, v alkalnih neogenskih vulkanitih in morda tudi kot posledico plinsko-mineralnih razplinjevanj iz zgornjih delov plašča pod kontinentalno skorjo.

Introduction

This paper presents a continuation of the paper by Markič & Brenčič (2014), which described a finding of high arsenic (As) content in coal cuttings from the TER-1 well. In this well they found the As content in the Miocene coal matter as high as 116 µg/g. Contents of As in coal samples from three additional localities, i.e. from the Sob-3g and MD-1 wells, and from the mine workings at Globoko are presented in this paper. All four localities are situated in the Slovenian part of the Pannonian Basin System (PBS). They are shown in Fig. 1 and cited in Table 1 (upper part in grey). TER-1 was a water-supply well drilled in 2003 at Terbegovci ca. 12 km SW of Murska Sobota (NE Slovenia). Sob-3g was a geothermal well drilled in 2012 at Murska Sobota (NE Slovenia). MD-1 was a geothermal well drilled in 2005 on Mislinjska Dobrava S of Slovenj Gradec (N Slovenia). The fourth locality, Globoko, was a lignite exploration area in the northern part of the Krško Polje basin (E Slovenia), where dozens of boreholes were drilled and the lignite seams were explored with underground mine workings between 1981 and 1988 (Markič & Rokavec, 2002).

Occurrence of As in coals of Slovenia attracted a significant attention for the first time with the study of the Velenje lignite. Geochemical study of this intermontane (out of PBS) Pliocene lignite (Markič, 2006) revealed that it is a Ca-characteristic ortho-lignite depleted in almost all trace elements in comparison to the Clarke values. The only exceptions were uranium (U) and molybdenum (Mo) contents, which are about 3 (U) and 6 (Mo) times higher in the Velenje lignite than are the Clarke values for coals of the world as cited in Ketris & Yudovich (2009). Another anomaly was detected for arsenic (As) – not so much in the content but in bonding. Namely, Šlejkovec & Kanduč (2005) pointed out on the basis of special extraction procedures that As in the Velenje lignite is both organically and inorganically bound. “At least partial” organic bonding of As (together with even higher organic bonding affinity of U and Mo) was first mentioned in the author’s yearly report for the Velenje Lignite Mine for 2002/2003 (Markič et al, 2004) based on the fact that As was not considerably depleted in lignite versus inorganic sediments in the roof and the floor deposits. This indication – and a general statement that As is an environmentally hazardous element – focused us to investigate this element more in detail in other coals outside the Pannonian Basin as well. Besides Velenje, few data existed for brown coals of Trbovlje, Senovo, and Kanižarica, published by Pirc & Žuža (1989), and Šlejkovec & Kanduč (2005). These data are gathered in lower part of Table 1.

Methods

Coal samples from Neogene deposits of the Pannonian Basin interpreted in this study were collected from four localities shown in Fig. 1 and cited in Table 1 (upper part in grey). All samples, except for the Globoko one, were coal cuttings from not-cored wells. Coal cuttings of mm–cm dimensions were collected from several cm–dm thick coal interlayers not precisely defined by thickness and depth. Coal cuttings were therefore joined from several intervals (because not weigh enough separately) into composite coal cuttings samples. Coal cuttings from the TER-1 well were collected and analysed as one composite sample from a 14.5 m long interval in a depth of 141.0–155.5 m (Markič & Brenčič, 2014). Coal cuttings from the Sob-3g well were collected from a 35 m long interval in a depth of 460–495 m. Five coal cuttings samples were analysed from the MD-1 well, one from a depth of 25 m and other four from four 2–4 m thick intervals in a depth of 742–1030 m. In Globoko, the main lignite seam (2.2 m thick) from exploration mine workings was analysed on trace elements already in 1989, and results were published by Pirc & Žuža (1989).

Samples from the wells TER-1, Sob-3g, and MD-1 were prepared for the Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) method for the main and trace elements analysis as “whole coal”, dry, pulverized lab-samples, weighting ca. 10 g. In the case of Globoko (Pirc & Žuža, 1989), not “whole coal” but its high temperature (750–950 °C) ash was analysed using both Atomic Absorbtion Spetroscopy (AAS) and ICP-MS method. Therefore, results between Globoko and the three well localities are not directly comparable. Even recalculation to a unique basis would not be relevant because As is a highly volatile element.

Coal from the TER-1 well (Markič & Brenčič, 2014) was extensively analysed comprising proximate, ultimate and calorific value analysis, loss on ignition, and analyses of total sulphur, total organic carbon, and of minor and trace element contents. In the mentioned paper, also methods of preparation and laboratory analyses have been described in detail, together with comments on accuracy and precision of trace element analytics, which are also valid for this study. Coals from the Sob-3g and MD-1 wells were not analysed for their calorific value and ash content.

In presenting results of a coal analysis (proximate, ultimate, geochemical etc.), the basis of analysis must be cited to which the data are reported on. It should be precisely cited, whether the analysis is on the "whole coal basis" or on the "ash basis" etc. (e.g. Thomas, 1992; ISO Standards). In the case of expression of results from different bases to a unique basis, recalculations are needed (e.g. Thomas, 1992; ISO Standards). Concerning analyses of ash, which is obtained with ashing at high temperatures (750–950 °C), it is important to consider volatility of certain elements. Arsenic (As) is very sensible in this sense. Some other highly volatile elements are Hg, I, Se, B, Br, Ge, Mo (e.g. Huggins, 2002; Ketris & Yudovich, 2009). Therefore, these elements are better to be analysed on the "whole coal" basis. Previous analyses of coals in Slovenia, in last 25 years, also showed, that a great majority of elements in "whole coals" is above detection limits at ca. 10 g weigh samples.

Geological coal samples from Slovenia, collected by researchers of the Geological survey of Slovenia, are routinely analysed from the late 1980-ies onwards with the ICP method, mostly in the ACME Laboratory in Vancouver (Canada), after the 1st of January 2015 renamed to Bureau Veritas. Their own re-run testing, as well as our testing with duplicate samples and geo-standards exhibit a relevant reliability of the analysed values that we can use for further geological interpretations.

Results and Discussion

Ketris & Yudovich (2009) published average contents (the Clarke values or Clarkes) for trace elements for "whole coals" of the world, and for their ashes. Their Clarkes are medians. The Clarke value for As for all coals is 8.3 µg/g. The As Clarke value for brown coals is somewhat lower, 7.6 µg/g, and for hard coals somewhat higher, 9.0 µg/g. Coal ashes of brown coals have the As Clarke value of 48 µg/g and of hard coals of 46 µg/g.

In the book of Valković (1983) we find that the average content of As in coals of the world is 5 µg/g. Bowen (1979) and Swaine (1990) (both cited in Taylor et al., 1998, p.272) gave a range of As for "most" coals of the world to be 0.5–80 µg/g. In this paper, values by Ketris & Yudovich (2009) are taken into account.

Data for all coals in Slovenia analysed for As contents are presented in Table 1. It is evident that quite few data exist about As contents in coals of Slovenia, which are mainly Tertiary in age, humic by type and brown coals in rank, ranging from ortho- to meta-lignites and hard brown coals (Markič et al. 2007 and references there-in). In this paper, Clarkes after Ketris & Yudovich's (2009) are taken into account. For some coals, the age is not well defined, partly due to lack of age indicative fossils, partly due to lack of paleontological investigations. In these cases of Kanižarica and MD-1 well, geological descriptions from Basic Geologic Map of SFRJ 1:100.000 and analogies are considered. For some coals (MD-1 well, Sob-3 well) also rank is not precisely defined.

Coals cited in Table 1 are divided into Neogene paralic coals of the Pannonian Basin (MD-1, Globoko, TER-1 and Sob-3), coals within Mio-Pliocene and Pliocene deposits of intermontane basins (Velenje and Kanižarica), and Oligocene coals formed from biomass accumulation in gulfs of than existing periphery of the Paratethys (Senovo, Trbovlje). Only samples from MD-1 and Sob-3 wells were newly analysed for As contents for this study, while others have been already analysed in the past (Pirc & Žuža, 1989; Šlejkovec & Kanduč, 2005; Markič, 2006, and Markič & Brenčič, 2014).

According to the Basic Geological Map of Yugoslavia - Sheets Goričko (Pleničar, 1968), Slovenj Gradec (Mioč & Žnidarčič, 1977), Zagreb (Šikić et al., 1978), and Čakovec (Mioč & Marković, 1997), among coals of the Pannonian basin the oldest are coal cuttings samples from the MD-1 well, which are supposed to be of the Lower Miocene age (except for the shallowest one, which is of the Plio-Quaternary age) (Table 1). Coal cuttings samples from TER-1 and Sob-3g wells are of the Upper Miocene age (Mura Formation). The lignite sample from Globoko is of the Upper Miocene age too – lignite-bearing strata having been defined as the Pontian strata (Globoko Formation) (Markič & Rokavec, 2002 - after numerous reports of Ž. Škerlj in the 1980s on the Ostracoda fauna).

Table 1. Coals of Slovenia analysed for As content – for locations of the Neogene Pannonian Basin coals see Fig. 1. Coal rank is signed with oL – ortho-lignite; mL – meta-lignite, hbC – hard brown coal. All coals are humic. Number of samples is signed with "n". References are: (a): Pirc & Žuža, 1989; (b): Markič & Brenčič, 2014; (c): Šlejkovec & Kanduč, 2005; (d): Markič (2006). Types of basins and geological ages refer to coal/lignite-bearing sediments. As contents for Neogene coals from the Pannonian Basin are also written in Fig. 1. Reporting on different bases is signed with WC ("whole coal" analysis) and with HTA (high temperature ash analysis). Clarkes are medians for brown coals (for WC and HTA, respectively), ± values mean ±1σMe (σMe=(Q3-Q1)/2n1/2) Q1 and Q3 being quartiles, n= 66 (Ketris & Yudovich, 2009). Enrichment factor, rounded to a whole number, is ratio between As content in a coal of Slovenia versus the Clarke.

Coals of Slovenia analysed for As contents	Basin type	Age	Basis of analysis	As contents of coals in Slovenia (in µg/g)	Clarkes for As (in µg/g) for brown coals (for WC and HTA) (Ketris, & yudovich, 2009)	Enrichment factor (rounded)
MD-1 well: oL? cuttings (n=1) **THIS STUDY**	Pannonian Basin – Neogene – paralic coals	Plio-Quaternary	WC	**84.5**	7.6 ± 1.3	**11**
Globoko: oL seam (n=1) (a)		Pontian	HTA	**170^{AAS}, 260**	48 ± 7	**4-5**
TER-1 well: mL. cuttings (1 composite sample) (b)		Upper Miocene (Mura Fm.)	WC	**116.1**	7.6 ± 1.3	**15**
Sob-3 well: mL ? cuttings (1 comp. sample) **THIS STUDY**			WC	**392.1**	7.6 ± 1.3	**52**
MD-1 well: mL? cuttings (n=4) **THIS STUDY**		Lower Miocene?	WC	**131.4 222.1; 111.4; 22.7;**	7.6 ± 1.3	**17 29 15 3**
Velenje: oL seam (n=2) (a) Velenje: oL seam (n=5) (c) Velenje: oL seam (n=29) (d)	Intermontane basins	Pliocene	HTA WC WC	25^{AAS}, 30 1.59-14.3 2.5-23.9	48 ± 7 7.6 ± 1.3 7.6 ± 1.3	<1 <1-2 <1-3
Kanižarica: mL seam (n=4) (a)		Mio-Pliocene?	HTA	20-50	48 ± 7	<1
Senovo: hbC seam (n=1) (a)	Gulfs of Paratethys	Oligocene	HTA	50	48 ± 7	1
Trbovlje: hbC seam (n=5) (a) Trbovlje: hbC seam) (n=1) (c)			HTA WC	27-42^{AAS}, 40-50, 8.03	48 ± 7 7.6 ± 1.3	<1 1

ICP-MS analyses of "whole coal" samples for all coals from the Pannonian Basin showed considerably increased contents of As (Table 1) (Fig. 1): 22.7, 111.4, 222.1, and 131.4 µg/g for the Lower Miocene (?), and 84.5 µg/g for the Plio-Quaternary coals from the MD-1 well, 392 µg/g for coal from the Sob-3g well, and 116 µg/g for coal from the TER-1 well. In the case of Globoko, not "whole coal" but its (high temperature!) ash was analysed and showed as high as 170 µg/g (AAS analysis) and even 260 µg/g (ICP-MS analysis) As contents. In comparison to the Clarkes for brown coals (Table 1) the cited contents mean enrichment factors mostly above 10, extremely 29 (one coal in the MD-1 well), and even 52 in the coal from the Sob-3 well. Only two coals are not so much enriched in As – ortho-lignite from Globoko (analysed was ash) and the deepest coal sample from the MD-1 well (maybe even older than the Lower Miocene?). Their content of As is only 3–5 times greater than the Clarke.

Coals outside the Pannonian Basin (Tab. 1 – lower part) are characterized by "normal" As contents, with enrichment factors mostly below 1. Enrichment factor 3 was only detected for ash-rich lignite of the lower part of the Velenje lignite seam (Markič, 2006).

The question of As bonding of the high As containing coals of the Pannonian Basin, either organic or inorganic, rests unanswered in this paper. Sink and float analyses were not carried out. For some elements in the Trbovlje coal these were made only by Uhan (1993), but not for As. Arsenic compounds in low-rank coals (two from Slovenia – Velenje and Trbovlje – and one from the Sokolov Basin in the Czech Republic) were investigated by Šlejkovec & Kanduč (2005). They found a high As content in one coal from the Sokolov Basin – 142 µg/g in the Oligocene Josef coal seam - whereas other samples were low in As contents. They interpreted high As content in the Josef coal seam to be inorganically bound. Inorganic bonding was also ascertained

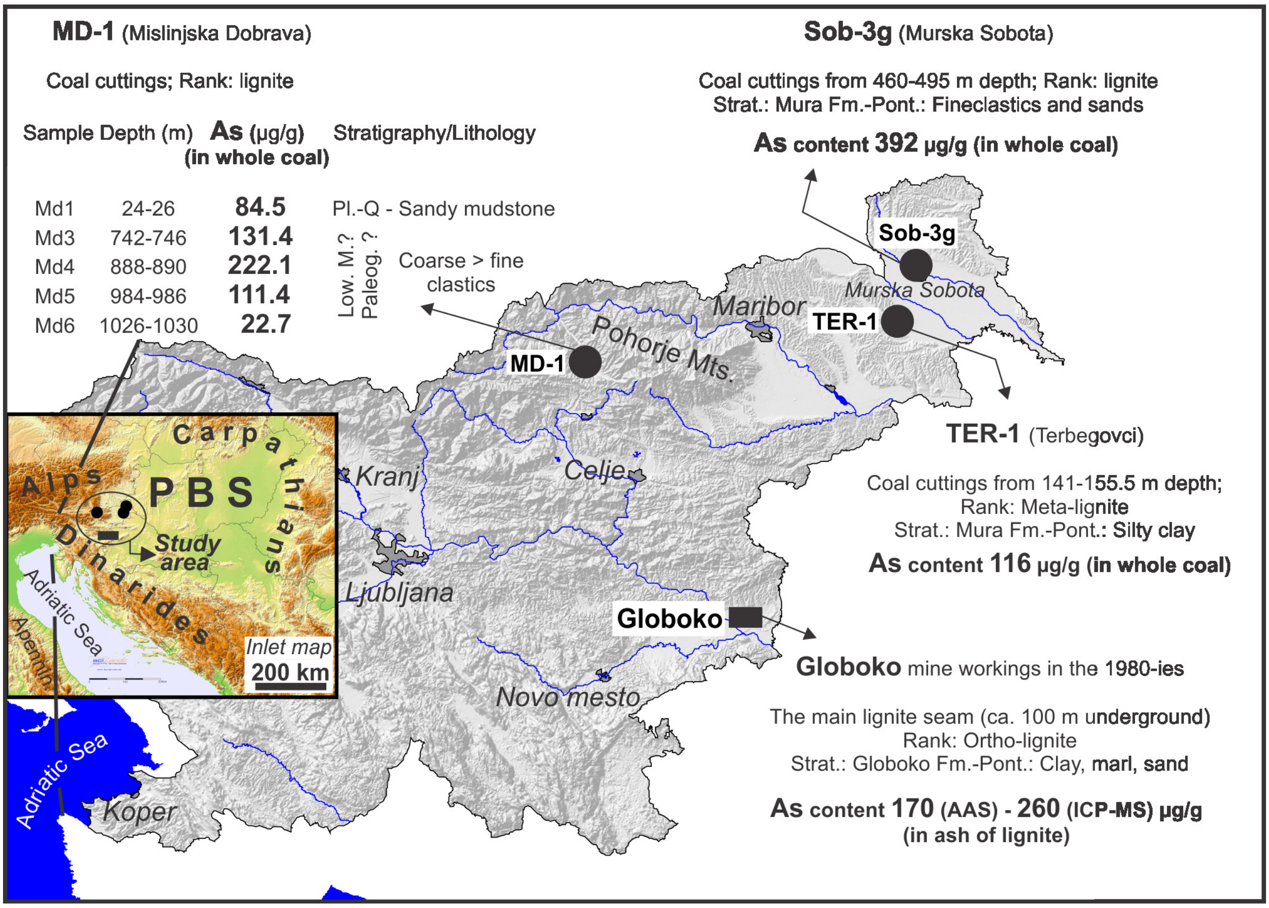

Fig. 1. Locations (TER-1, Sob-3g, MD-1 wells, and Globoko coal mining workings) with cited As contents in the Neogene coals of the Pannonian Basin (based on data from Table 1).

for the Trbovlje coal, with As content of only 8.03 µg/g. Low contents were determined by Šlejkovec & Kanduč (2005) in the Velenje lignite as well (between 1.59 and 14.3 µg/g), but a considerable organic bonding of As was interpreted for this lignite (Markič, 2004; Šlejkovec & Kanduč, 2005).

Ash content analyses for the Neogene coals have been only made for the Globoko lignite and for the TER-1 well. Both showed ash contents (HTA) <10 mass %. Coal from the Sob-3 and MD-1 wells was not analysed, but was macropetrographically clean with estimated <10 vol. % of mineral matter. If a low ash coal (of a low specific gravity) has a high As content this may indicate that As is organically bound, at least partly (Diessel, 1992, p.238, 239 - fig. 5.37 and table 5.10 after Warbrooke & Doolan, 1986).

Regardless of different bases of analyses and different constraints (lack of complete coal analyses), it is evident that the Pannonian Basin Neogene coals in Slovenia are considerably enriched in As contents. A question arises, what is the situation with coals in other parts/countries of the Pannonian Basin. High As content in the Neogene coals in Slovenia is not so much a question of these thin coals themselves, which do not have a high economic value (at present) - it is more a question of geochemical influence that As content could have on e.g. geothermal waters in water-bearing deposits with As-rich coals stratified within.

Concerning the origin of As in coals, main aspects have been presented in the paper of Markič & Brenčič (2014), taking into account published data by Zupančič (1994), Kralj (1996, 2000, 2003), and Trajanova (2013). To these authors, the Smrekovec andesite and its tuff, Grad basaltic tuff, magmatic and metamorphic rocks that form the hinterland of the Pannonian Basin and its basement do not contain more than 10 µg of As per gram of rock. The only known exceptions are A and B soil horizons above serpentinite in the Pohorje Mountains with As contents between 30 and 60 µg/g, and granodiorite with As contents up to 21 µg/g (Zupančič, pers. comm.; Zupančič & Plaskan, pers. comm.). Volcanism (calc-alkaline) during the Neogene could also contribute significantly to the geochemistry of the synchronous deposits including organic matter, which later developed to coals. For a wide discussion on As in world coals, the reader is referred to Yudovich & Ketris (2005).

As a contribution in the explanation of the As content - in fact As capture – in the organic matter in the Pannonian Basin may serve a very interesting work of Bräuer et al. (2016). Reading their explanation it becomes reasonable to suppose that As was maybe the result of degassing of the Earth's mantle and later "catching" to organic matter and/or its admixtured inorganic matter (see the concept of CAI – Coal Affinity Index, Ketris & Yudovich, 2009). Similar "mantle degassing" enrichments of economically highly interesting elements are known from the geological history: among the best known in Slovenia is Hg mineralization in Paleozoic and Triassic strata of Idrija caused by Middle Triassic volcanic activity initiated by degassing of the upper part of the Earth's mantle (Pirc & Herlec, 2009, p.533 - after cited authors there-in).

A similar story about "very deep gasses" was debated with respect to the origin of gasses in the Pliocene Velenje Lignite Mine (Kanduč & Pezdič, 2005) connected to very deep faults in the realm of the Periadriatic Fault System and the Šoštanj Fault, respectively (e.g. Vrabec & Fodor, 2006, and references there-in).

Conclusion

All available data for the Neogene coals of the Pannonian Basin in Slovenia show moderate to high enrichment in arsenic (As) content. However, results are based on samples from only four localities (Fig. 1). Number of samples is statistically low. Further investigations would be welcome but coal samples from wells are quite rarely available.

In the investigated "whole coal" samples from three localities (wells TER-1, Sob-3 and MD-1), As contents vary mostly in a range of 23–392 µg/g (slightly rounded), being the highest in the Sob-3 well from a depth interval of 460–495 m (Upper Miocene), and the lowest in the lowermost sample in the MD-1 well in a depth of 1026–1030 m (Lower Miocene) (Fig. 1, and Table 1). Other As contents are 116 µg/g in TER-1 well for a composite coal sample from a depth of 141.0–155.5 m (Upper Miocene), and 111, 131, and 222 µg/g in the MD-1 well in three depth intervals of 742–986 m (Lower Miocene).

In Globoko, the fourth locality (Fig. 1), the main lignite seam (2.2 m thick) was sampled. Its "high temperature ash" was analysed. Results showed as high as 170 µg/g (AAS analysis) and even 260 µg/g (ICP-MS analysis) As contents.

The Clarke value for As contents for brown coals is 7.6 µg/g, whereas for ashes of brown coals it is 48 µg/g. Ratio between As content in an individual coal in Table 1 and the Clarke value is termed as an enrichment factor. For the Pannonian Basin coals (Table 1 – upper part in grey), this factor is mostly above 10, extremely 29 (one coal in the MD-1 well), and even 52 in a coal from the Sob-3 well. Only two coals are not so much enriched in As – ortho-lignite from Globoko (analysed was ash) and the deepest coal sample from the MD-1 well. Their contents of As are only 3–5 times greater than the brown coal and ash Clarke values, respectively.

Coals outside the Pannonian Basin (Velenje, Kanižarica, Senovo, and Trbovlje) (Table 1 – lower part) do not exhibit any spectacular differences in As contents in comparison to the "world coals". Based on few available data, enrichment factors are mostly around or below 1. The only exception is the Velenje lignite. It was analysed for minor and trace elements with 29 samples. In the lower part of the lignite seam, which is ash--rich, As contents vary in a range of 10–25 µg/g, whereas in the upper part, which is ash poor, in a range of 3–10 µg/g.

We do not know As contents in coals of other areas of the Pannonian Basin. This fact may represent a challenge for international cooperation on As contents in coals of the Pannonian Basin, maybe as well as of As contents in Neogene deposits, including waters.

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