



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

Several very small collieries were in operation in the area of the Ormož-Selnica Antiform in the Mura-Zala sub-basin between the 1850s and 1970s. The only a little larger was the Mursko Središće colliery, with the highest production in 1965 and closed in 1972. Coal seams in the Mura Formation occur as numerous beds of brown coal which are relatively thin. Well ascertained are only those in a restricted area (ca. 60 km²) between Lendava (Slovenia) and Mursko Središće (Croatia), where they dip almost from the surface (under 10–20 m of Quaternary gravel) downwards to depths of not more than 400 m.

In general, they are poorly explored but were encountered by almost all deep oil, gas, and hydrogeological wells (Markič et al. 2011).

Anomaly

Arsenic (As) contents in Neogene deposits

Available data for the Neogene coals of the Pannonian Basin in Slovenia show moderate to high enrichment in arsenic (As) content (Markič, 2017). However, results are based on samples from only four localities (Tab. 1, Fig. 1) therefore number of samples is statistically low. Further investigations would be welcome but coal samples from wells are now quite rarely available as coal mines have been closed for several decades.

In the investigated “whole coal” samples from three localities (wells TER-1, Sob-3 and MD-1) in NE Slovenia, 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), “high temperature ash” from the main lignite seam (2.2 m thick) 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 content 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), 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.

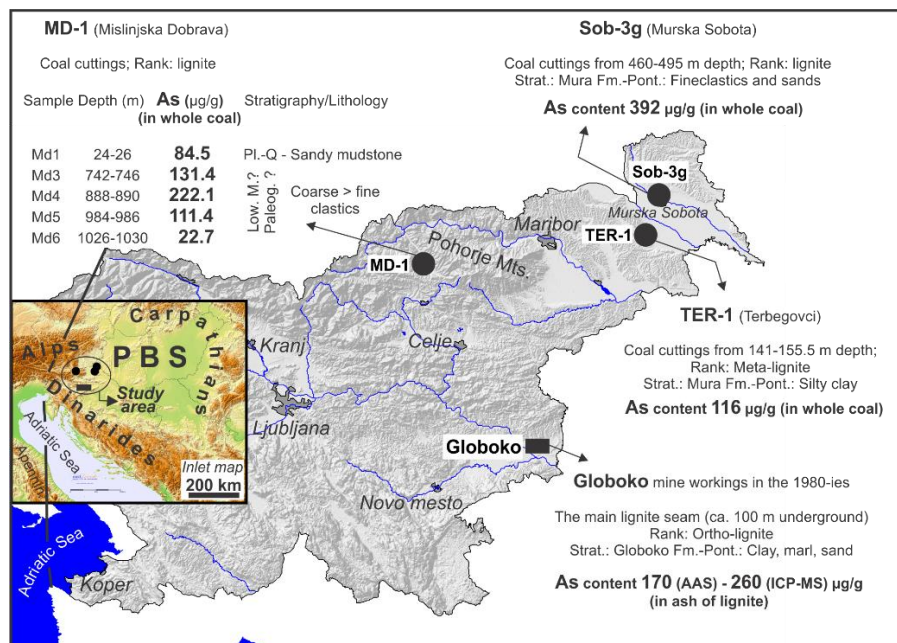


Fig. 1. Locations (TER-1, Sob-3g, MD-1 wells, and Globoko coal mining workings) with cited As contents in the Neogene coals of the Pannonian Basin (based on data from Table 1).

Coals outside the Pannonian Basin (Velenje, Kanižarica, Senovo, and Trbovlje) (Table 2) 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 are not informed on As contents in coals of other areas of the Pannonian Basin. This may be investigated in future.



Origin of As could be pre-Neogene rocks and/or Neogene calc-alkaline volcanites. Mineral-gas exhalations from the under-continental upper mantle, containing As, (Bräuer et al., 2016) could also be a source of this highly volatile element (Markič, 2017).

Arsenic (As) contents in groundwater

Neogene clastic aquifers represent important sources of fresh and thermal groundwater. Therefore, a question arises about As content in these waters, which are widely used as thermal, mineral, and potable waters.

We have performed a survey on fresh groundwaters in Slovenia (Lions et al. 2021), investigating natural background values (NBL's) of water samples from the national (ARSO) monitoring network taken in 2016. Among 179 sites, there were 39% springs, 33% shallow wells (below 30 m in depth), and 28% of boreholes with a maximum depth of 200 m. Regarding As, 63% of samples were below LOQ of $<1 \mu\text{g/L}$. The average was $0.57 \pm 1.61 \mu\text{g/L}$, median $0.5 \mu\text{g/L}$ – this value is also the same as assigned value for censored data ($\text{LOQ}/2_{\text{max}}$) and calculated 90th percentile, which we took as a threshold value for NBL. It is worth noticing that the highest reported As concentration was $16 \mu\text{g/L}$. The Slovenian threshold value for drinking water is $10 \mu\text{g/L}$. It is reported that higher geogenic concentrations are locally noticed in waters from Neogene sediments in Goričko (NE Slovenia), which are also enriched in iron and manganese.

If thermal waters are encountered, we can explain that few exceed the national drinking water standard. For thermo-mineral waters from Neogene sediments in NE Slovenia it is expected to have elevated concentrations, they can reach 30 to $35 \mu\text{g/L}$ of As in Mala Nedelja and Moravske Toplice. These might be also linked to coal occurrences as discussed above, however, the origin was never thoroughly investigated.

At the Slovenian coast, thermo-mineral water from Cretaceous limestone aquifer in Portorož, which is mixed with sea water, may reach about $20 \mu\text{g/L}$ of As. Surprisingly, elevated concentrations of about the same value were analyzed in thermal water in Bled, from Triassic carbonate rocks of the Julian Alps.

An interesting blog contribution for the GeoConnect3D project by Petrović-Pantić and Atanasković-Samolov (2021) informs us that Pliocene and Quaternary groundwaters in Vojvodina (Pannonian Basin, N Serbia) are considerably enriched in arsenic (As) contents.

Data



Table 1: Neogene coals of Slovenia with outstanding As content (see Fig. 1 for locations). 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): Markič, 2017) (b): Pirc & Žuža, 1989; (c): Markič & Brenčič, 2014; (d): Šlejkovec & Kanduč, 2005; (e): Markič (2006). Types of basins and geological ages refer to coal/lignite-bearing deposits. Reporting on different bases is signed with WC (“whole coal” analysis) and with HTA (“high temperature ash” analysis). Contents of As analysed with Atomic Absorbtion Analysis are marked with ^{AAS}. Arsenic Clarkes are medians for brown coals (for WC and HTA, respectively), $\pm$ values mean $\pm 1\sigma_{Me}$ (K & Y = Ketris & Yudovich, 2009). Enrichment factor, rounded to a whole number, is ratio between As content in the analysed coal versus the Clark.

Coals of Slovenia analysed for As contents	Basin type	Age	Basis of analys	As contents of coals in Slovenia (in $\mu\text{g/g}$)	Clarkes for As (in $\mu\text{g/g}$) for brown coals (for WC and HTA) (K & Y, 2009)	Enrich. Factor (rounded)
MD-1 well: oL? - composite of coal cuttings (n=1) (a)	Pannonian Basin – Neogene – paralic coals	Plio-Quaternary	WC	84.5	7.6 ± 1.3	11
Globoko: oL - whole coal seam sample (n=1) (b)		Pontian	HTA	170^{AAS}, 260	48 ± 7	4-5
TER-1 well: mL - composite of coal cuttings (n=1) (c)		Upper Miocene (Mura Fm.)	WC	116.1	7.6 ± 1.3	15
Sob-3 well: mL - composite of coal cuttings (n=1) (a)			WC	392.1	7.6 ± 1.3	52
MD-1 well: mL - composite of coal cuttings (n=4) (a)		Lower Miocene?	WC	131.4 222.1; 111.4; 22.7;	7.6 ± 1.3	17 29 15 3



Table 2: Coals in Slovenia with As contents within (or not considerably exceeding) the Clark values. Abbreviations, comments and references as in Tab 1.

Coals of Slovenia analysed for As contents	Basin type	Age	Basis of analysis	As contents of coals in Slovenia (in µg/g)	Clarks for As (in µg/g) for brown coals (for WC and HTA) (K & Y, 2009)	Enrich. Factor (rounded)
Velenje: oL seam (n=2) (b)	Intermontane basins	Pliocene	HTA	25 ^{AAS} , 30	48 ± 7	<1
Velenje: oL seam (n=5) (d)			WC	1.59-14.3	7.6 ± 1.3	<1-2
Velenje: oL seam (n=29) (e)			WC	2.5-23.9	7.6 ± 1.3	<1-3
Kanižarica: mL seam (n=4) (a)	Gulfs of Paratethys	Mio-Pliocene?	HTA	20-50	48 ± 7	<1
Senovo: hbC seam (n=1) (b)		Oligocene	HTA	50	48 ± 7	1
Trbovlje: hbC seam (n=5) (b)			HTA	27-42 ^{AAS} , 40-50,	48 ± 7	<1
Trbovlje: hbC seam (n=1) (d)			WC	8.03	7.6 ± 1.3	1

References

Bräuer, K., Geissler, W.H., Kämpf, K., Niedermann, S. & Rman, N. 2016: Helium and carbon isotope signatures of gas exhalations in the westernmost part of the Pannonian Basin (SE Austria/NE Slovenia): Evidence for active lithospheric mantle degassing. *Chemical Geology*, 422: 60-70, doi:10.1016/j.chemgeo.2015.12.016.

Ketris, M.P. & Yudovich, Ya.E. 2009: Estimations of Clarks for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *International Journal of Coal Geology*, 78/2, 135–148.

Lions, J., Devau, N., Elster, D. et al. 2021: A common methodology for calculating groundwater natural background levels of dissolved elements based on a lithological approach and anthropogenic influences. *Water* (article submitted in march 2021 for revision).



Markič, M., Turk, V., Kruk, B., ŠOLAR, S.V. 2011: Coal in the Mura Formation (Pontian) between Lendava (Slovenia) and Mursko Središče (Croatia), and in the wider area of NE Slovenia. *Geologija* 54/1, 97–120, doi:10.5474/geologija.2011.008.

Markič, M. 2006: Anorgansko-geokemična opredelitev velenjskega lignita v reprezentativnem profilu vrtine P-9k/92 (= Inorganic geochemical characterisation of the Velenje lignite in the representative P-9k/92 borehole profile – in Slovenian). *Geologija*, 49/2: 311–338, [doi:10.5474/geologija.2006.023](https://doi.org/10.5474/geologija.2006.023).

Markič, M. 2017: High arsenic (As) content in coals from Neogene deposits of the Pannonian Basin in Slovenia. *Geologija*, 60/2, 173-180, doi: 10.5474/geologija.2017.012

Markič, M. & Brenčič, M. 2014: High arsenic (As) content in the Upper Miocene coal matter from TER-1/03 borehole (Terbegovci – Sveti Jurij ob Ščavnici). *Geologija*, 57/1, 015-026, doi:10.5474/geologija.2014.002

Petrović-Pantić, T., Atanasković-Samolov, K. 2021: Arsenic in the groundwater of Vojvodina. [GeoConnect3d blog](#).

Pirc, S. & Žuža, T. 1989: Sledne prvine v premogih v SR Sloveniji (=Trace elements in coals in Socialist republic Slovenia (Yugoslavia) – in Slovenian). *Rudarsko-metalurški zbornik*, 36/2, 161–172.

Šlejkovec, Z. & Kanduč, T. 2005: Unexpected arsenic compounds in low-rank coals. *Environmental Science & Technology*, 39, 3450–3454.

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