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Multielemental composition of some Slovenian coals determined with k_0-INAA method and comparison with ICP-MS method

Multielementna sestava nekaterih slovenskih premogov določena s k_0-INAA metodo in primerjava z ICP-MS metodo

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Ključne besede: k_0-instrumentalna nevtronska aktivacijska anliza (k_0-INAA), multielementna sestava, premog, PCA analiza, Slovenija

Abstract

In this multi-elemental study, 34 elements (Ag, As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hg, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, Yb, Zn and Zr) were analysed in Slovenian coals from operative (Velenje) and non-operative (Kanižarica and Senovo) coal mines and an imported Indonesia coal using k_0-Instrumental Neutron Activation Analysis (k_0-INAA) and compared to inductively coupled plasma-mass spectroscopy (ICP-MS). Weaker regressions between both methods ICP-MS and k_0-INAA are obtained for following elements: Cs, Co, Eu, Se, Sm and Tb with low concentration (below 1 mg/kg). The k_0-INAA data are comparable to the ICP-MS data for the majority of elements. The levels of major elements measured with k_0-INAA are as follows: Ca>Fe>K>Na>Sr>Ba. Minor and trace elements, as well as rare earth elements (REEs), are comparable with coal values worldwide. Data of trace elements in coal are important since they are related to air emissions. According to our data obtained with both methods (ICP-MS and k_0-INAA) we can conclude that concentrations of trace elements, which impact to human health and are combusted (Indonesian and Velenje coal) in Slovenia are comparable to world averages coal.

Izvleček

V tej raziskavi smo izmerili s k_0-INAA (instrumentalno nevtronsko aktivacijsko analizo) metodo nekaj izbranih slovenskih premogov iz velenjskega premogovnika in ne operativnih premogovnikov: Kanižarica in Senovo. Prav tako smo s to metodo analizirali vzorec iz Indonezije (uvožen premog) in ga primerjali z že objavljenimi rezultati pridobljenimi z ICP – MS (masna spektrometrija z induktivno sklopljeno plazmo) metodo. S k_0-INAA metodo smo določili naslednje elemente: Ag, As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hg, Hf, K, La, Mo, Na, Nd, Rb, Sb , Sc, Se, Sm, Sr, Ta, Tb, Th, U, Yb, Zn in Zr. Rezultati meritev pridobljeni s k_0-INAA metodo so za večino elementov, obravnavanih v tej raziskavi, primerljivi z rezultati meritev pridobljenih z ICP-MS metodo. Slabše regresije med metodami ICP-MS in k_0-INAA dobimo le pri nekaterih elementih (Cs, Co, Eu, Se, Sm and Tb) za katere so značilne nizke koncentracije (pod 1 mg/kg). Koncentracije glavnih elementov merjenih s k_0-INAA metodo v premogu se znižujejo kot sledi: Ca> Fe> K> Na> Sr> Ba. Elementi z nizkimi koncentracijami in elementi redkih zemelj (REE) so primerljivi z vrednostmi premoga po vsem svetu. Podatki slednih elementov v premogu so pomembni, ker so povezani z emisijami v zraku. Glede na naše podatke pridobljene z obema metodama (ICP-MS, k_0-INAA) lahko zaključimo, da so koncentracije slednih elementov, ki vplivajo na človekovo zdravje in jih sežigamo (premog iz Velenja in Indonezije) v Sloveniji primerljivi s povprečnimi vrednostmi svetovnih premogov.

Introduction

The chemical analysis of coal includes, as well as, proximate (Khandelwal and Singh, 2010, Yi et al., 2017) (moisture, volatile compounds, ash content, fixed carbon) and ultimate analyses (carbon, hydrogen, sulphur, oxygen, and nitrogen), the analysis of major, minor and trace elements. Usually, these elements are measured using inductively coupled plasma-mass spectrometry (ICP-MS) (Finkelman et al., 2018) and instrumental neutron activation analysis (k_0-INAA) (Wagner and Matiane, 2018, Lin et al., 2018) methods. Other methods for determining-trace elements include inductively coupled plasma optical emission spectrometry (ICP-OES) (Finkelman et al., 2018), hydride generation atomic absorption spectrometry (HAAS) (Chen et al., 2011) and X-Ray Fluorescence spectrometry (XRF) (Chen et al., 2011). It is widely known that these trace elements can occur in a wide variety of chemical forms or modes of occurrence, which determines the environmental, economic, technological impact, which in some cases can be significant (Finkelman, 1995, 2018). Twenty-five potential harmful trace elements (PHTEs) are typically present in coal in inorganic and organic forms (Radenovič, 2006). Among them As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Se, Sb and U are all potential air pollutants (Gürdal, 2008). Ketris and Yudovich (2009) include rare earth elements, yttrium, and scandium (REY + Sc) in the table of coal Clarke values, which has been a highly useful tool for making geochemical comparisons of coals globally.

Indonesian coals are generally low in ash and sulphur, but have high content of volatile matter. They are classified as low rank coals with low caloric value. The sulphur content varies from 0.1 to 1 % (Internet 1). Elemental composition (wt %, dry basis) of TOT S varied for Velenje samples from this study from 1.4 to 3.9 %, Kanižarica from 1.6 to 2.2 % and Senovo 1.9 % (Burnik Šturm et al., 2009).

The geological composition of the Velenje basin is described in detail in Brezigar et al. (1987). The origin of the Velenje basin is related to the transtention between Šoštanj and Smrekovec faults. In the pre-Pliocene basement of the basin, Triassic carbonates and dolomites prevail on the northeastern side of the Velenje fault, while Oligocene to Miocene clastic strata, consisting predominantly of marls, sandstones and volcanoclastics are dominant on the south-western side of the fault. The alkaline, calcium-rich environment during formation of Velenje basin also caused a relatively high degree of gelification, which is significantly higher than the degree of gelification observed in other lignites (Markič & Sachsehofer, 1997; Šlejkovec & Kanduč, 2005; Markič & Sachsehofer, 2010) as well as coals investigated in our study. A well known relation between alkalinity and gelification was clearly ascertained in the case of the Velenje lignite. Lignite samples with the highest calcium contents were also the samples with the strongest gelification (Markič & Sachsenhofer, 1997). The macroscopic description of the lignite samples, in term of lithotypes, was determined following the lithotype classification criteria for brown coals (lignites) provided by the International Committee for Coal Petrology (ICCP, 1993) and are described by Burnik Šturm et al. (2009). All of the samples from the Velenje excavation field -50/C in this study are classified as gelified detrital lignite (Kanduč et al., 2018). The lithological columns for Senovo, Kanižarica and Trbovlje are also presented in Burnik Šturm et al. (2009) and references therein (Brezigar, 1987; Kuščer, 1967; Markič et al., 1991). The macroscopic description of the lignite samples in terms of previous petrological (Markič & Sachsenhofer, 1997), geochemical and isotopic studies of light elements C, H, O, N, S (Bechtel et al., 2003; Kanduč et al, 2005; Burnik Šturm et al., 2009; Kanduč & Šlejkovec, 2005; Kanduč et al., 2012; Kanduč et al., 2018; 2019, Liu et al., 2019) were performed in the frame of various research projects. For example, three different lithotypes (xylitic, gelified and matrix) of Pliocene lignite for the Velenje basin, Slovenia, were investigated to establish the variations of biomarker compositions in solvent extracts and stable isotope composition of carbon and nitrogen in bulk material (Liu et al., 2019). All of these studies were focused on the Velenje basin since it is currently the only actively mined basin in Slovenia and is one of the biggest underground coal mines in Europe. All three of the Velenje lithotypes reflect the composition of the original plant material in the paleomire (Markič & Sachsenhofer, 1997). Arsenic speciation studies and the different forms of calcite present in the coal suggest that bacterial activity was a significant factor during sedimentation of the basin (Kanduč & Šlejkovec, 2005; Kanduč et al., 2018; Kanduč et al., 2019a). The analysis of other geological matrixes such as coalbed gas (Kanduč & Pezdič, 2005; Kanduč et al., 2012, Sedlar et al., 2014) and groundwater (Kanduč et al., 2014; Kanduč et al., 2019b) reveal more evidence of bacterial activity during sedimentation of the basin.

In the study of Kanduč et al. (2019a) organic and inorganic coal samples from -50/C excavation field of Velenje basin were measured using ICP-MS and revealed that the concentrations of the majority of the analysed elements were either equal to or below the global average for coal. Exceptions were Mo (7.76 ± 4.76 μg/g, 3.5 times higher) and U (5.24 ± 3.23 μg/g, 1.8 times higher) in organic-rich samples. It was found that higher than normal are concentrations of U (5-15 ppm – in comparison to 0.5-10 ppm concentrations in world coals), and of Mo (5-20 ppm – in comparison to 0.1-10 ppm in in world coals). Both elements are presumed to be organically bound (Markič & Sachsenhofer, 2010).

This study aims to present results of major, minor and trace elements measured using k_0-INAA method in coal samples collected from operative (Velenje) and non-operative (Kanižarica and Senovo) Slovenia coal mines. The study also analysed an Indonesia coal supplied by the thermal power plant Moste. Additionally, one of the objectives was to compare k_0-INAA and ICP-MS methods used to analyse the same coal samples (Kanduč et al., 2019a, Supplementary material) from Velenje coal mine and perform a statistical analysis (PCA-Principal Component Analysis) of all data (Velenje, Senovo, Kanižarica, Indonesia coals) measured with k_0-INAA method.

Methods

Sampling locations were taken from a local borehole database in the local coordinate system from the Velenje coal mine. Coordinates were then transformed to Gauss-Krüger D48 Slovenian national coordinate system and indicated on a hill-shaded relief map generated using the ESRI ArcGIS mapping software (Fig. 1). Figure 1A was produced using data from the Shuttle Radar Topography Mission SRTM data at 90 m spatial resolution. A more detailed map (Fig. 1B), was created using the digital elevation model at a 1 × 1 m spatial resolution, using LiDAR data form the national scanning campaign of the Slovenian territory (ARSO, 2014). Figure 1C includes the position of excavation field (-50/C) and cross-section of Velenje basin with main geological and tectonic units.

Samples of coal were collected from the following mining areas in Slovenia (Fig. 1): Senovo (3 samples), Kanižarica (4 samples), Velenje basin (7 delivery roadway samples, and 18 samples from excavation field -50/C), Indonesia (1 sample) in years 2004, 2005 and 2013. The Moste thermal power plant provided the sample of Indonesian coal.

For k_0-INAA analysis, samples (240-290 mg) were sealed in a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). For the determination of long-lived radionuclides, samples and standards (Al-0.1 %Au IRMM-530R disc of 7 mm in diameter and 0.1 mm thick) were stacked together and fixed in a polyethylene ampoule in sandwich form and irradiated for 12 hours in the carousel facility (CF) of a 250 kW TRIGA Mark II reactor (Jožef Stefan Institute, JSI) at a thermal neutron flux of 1.1×E+12 $cm^{-2}\ s^{-1}$.

Each sample was measured three times after 2, 8-13 and 25-30 days cooling time on three absolutely calibrated HPGe detectors with 40 % and 45 % relative efficiency. Measurements were carried out at a distance such that the dead time remained below 10 % with negligible random coincidences. The detectors with 40 % relative efficiency were connected to a MULTIPORT II (Canberra) computerized multichannel analyser (MCA) in LT mode operating with Genie™ 2000 spectroscopy software, while the detector with 45 % relative efficiency was connected to a DSPEC PLUS (Ortec) multichannel analyser in ZDT mode operating with Maestro®-32 spectroscopy software.

The HyperLab (2002) program was used for peak area evaluation, whereas for the determination of f (thermal to epithermal flux ratio) and α (a parameter which represents the epithermal flux deviation from the ideal 1/E distribution) the "Cd-ratio" method for multi-monitor was applied (Jaćimović et al., 2003). The values obtained for f = 28.63 and α = -0.0011 were used to calculate the element concentrations. The elemental concentrations and effective solid angle calculations were performed using the KayWin® (Kayzero for Windows, 2011) software package.

Ranges of uncertainties with coverage factor k = 1 (%) for measured elements with k_0-INAA method is as follows: i) uncertainty for elements: As, Br, Ca, Ce, Cs, Fe, Na, Sc, U, and Zn ranges from 3.5 to 7.3 % and ii) uncertainty for elements: Au, Ba, Co, Cr, Eu, Ga, Hf, Hg, K, La, Mo, Nd, Rb Sb, Se, Sm, Sr, Ta, Tb, Th, Yb, ranges from 3.5 to 28 %. Measured elements with higher concentration have lower uncertainties, while elements with lower concentration have higher uncertainties.

Chemical analysis of Velenje coal samples (13-2123, 13-2125, 13-2130, 13-2134, 13-2138, 13-2141, 13-2145, 13-2157, 13-2162) were performed with ICP – MS method in ACME lab Canada (http://acmelab.com/services/). For the analysis of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, MnO, TiO_2,

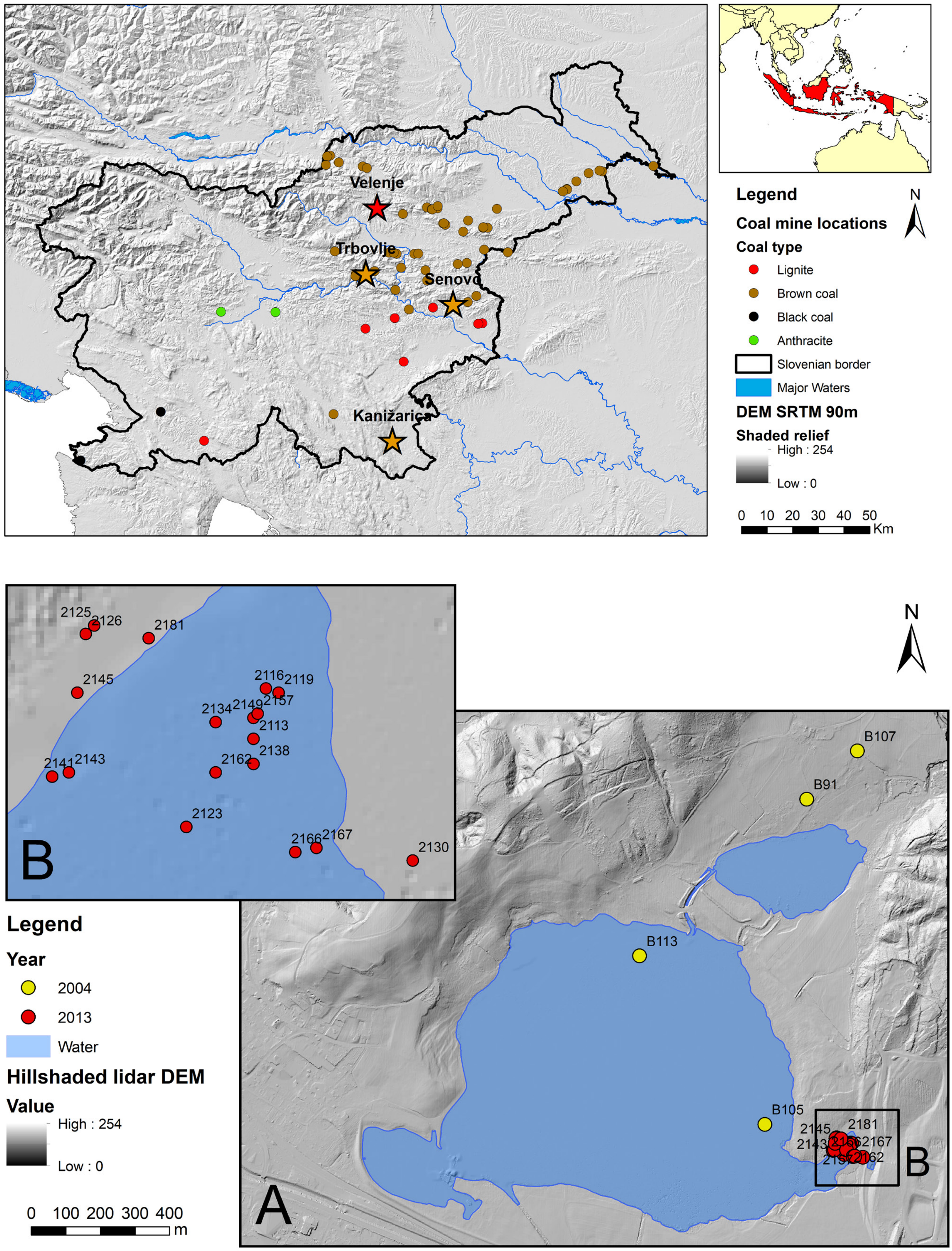

Fig. 1. General map of coals located in Slovenia showing the study area of sampled coals from Slovenia mines: Velenje Coal Basin (active coal mine, n = 25), Kanižarica (closed, n = 4), Senovo (closed, n = 3), and Indonesia (coal imported in Slovenia, n = 1). Velenje sampling locations from years 2004, n = 4 (B91, B105, B107, B113) and 2013, n = 18 (2113, 2116, 2119, 2123, 2125, 2126, 2130, 2134, 2138, 2141, 2143, 2145, 2149, 2157, 2162, 2166, 2167, 2181). B. Detailed map of Velenje sampling locations from years 2004 and 2013 are presented. C. Position of excavation field -50/C from where samples were taken and cross-section of the central part of the Velenje basin (modified from Brezigar, 1987) with main geological and tectonic units.

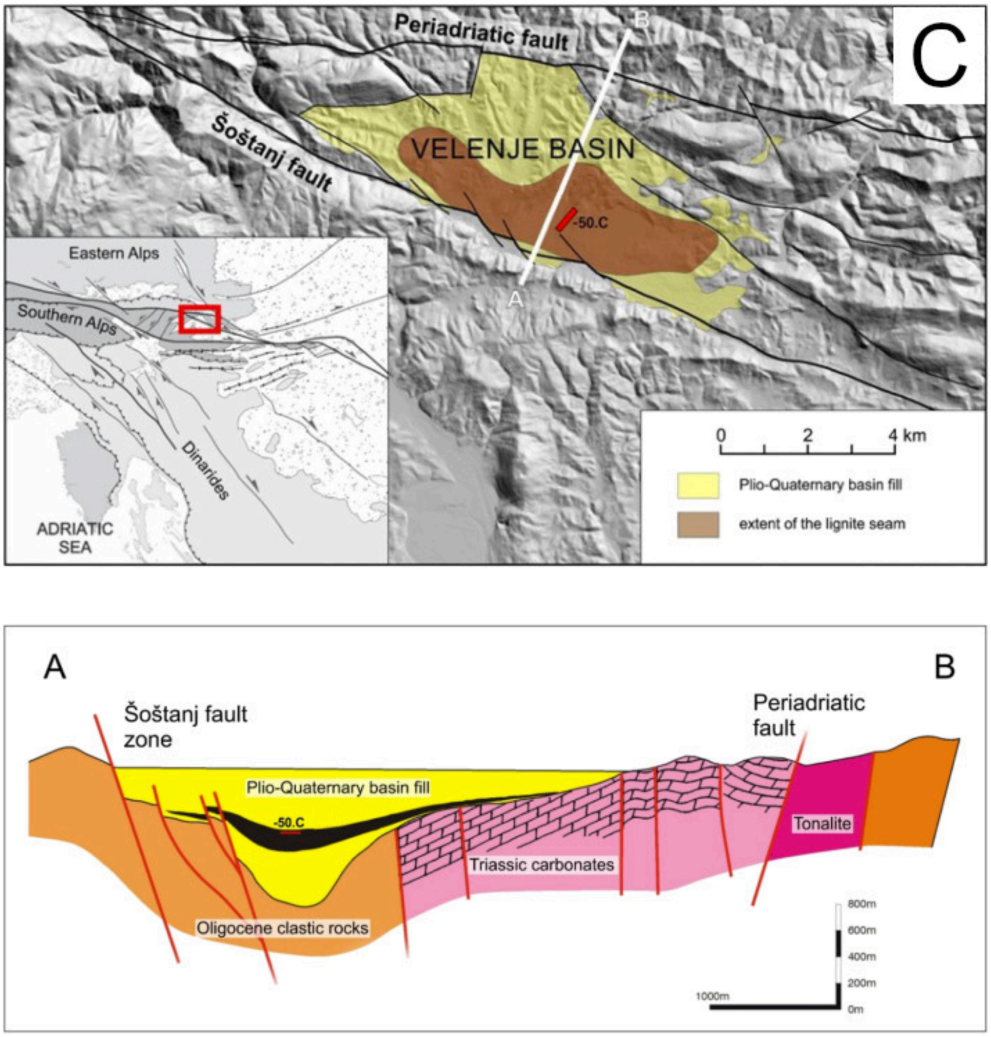

Fig. 1.

P_2O_5, Cr_2O_3, Ce, Co, Cu, and Zn samples were mixed with a $LiBO_2/Li_2B_4O_7$ flux. Crucibles were fused in a furnace. The cooled beads were dissolved in ACS grade nitric acid and analyzed by ICP and or ICP-MS.

Other elements (Ce, Co, Cs, Dy, Er, Eu, Gd, La, Ni, Nb, Nd, Pr, Rb, Sm, Sr, Tb, U, Th, V, Zr, Y) were measured with ICP-MS method. Total carbon (TOT C) and total sulphur (TOT S) were measured using LECO Carbon –Sulphur analyzer. The mean limits of detection for both elements were 0.02 %. Loss on ignition (LOI) was determined by igniting a sample split and then measuring the weight loss.

For Ag, As, Au, Bi, Cd, Hg, Mo, Ni, Pb, Sb, Se, Tl, and Zn analysis, prepared samples were digested with modified Aqua Regia solution of equal parts of concentrated HCl, HNO_3 and MiliQ H_2O for 1 h in a heating block or in a hot water bath at 95°C. Samples were made up to volume witgh diluted HCl. Sample splits of 0.5 g were analyzed optional 15 g or 30 g digestion available for AQ200. Samples were analyzed using inductively coupled-mass spectrometry (ICP-MS). The following standards were used for quality assurance: STD-SO-18, STD-GGC-02, STD-GS311-1 and STD OREAS45EA.

Statistical analysis was conducted using the R language (R Core Team, 2019), and the significance model was set at $p<0.05$. A Spearman's correlation analysis was used to identify the relationships between 27 elements (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Tb, Th, U, Yb and Zn) with complete data sets. The crossed-out values indicate where p-values exceeded 0.05.

Principal component analysis (PCA) was used to differentiate (same as for Spearman correlation analyses) between the coal from the different mines. Due to the broad range of elemental concentrations, the dataset was central log-ratio transformed. Studied mines were grouped as "Open" and "Closed". The principle component plots were made using ggplot2 in R (Wickham, 2016).

Results and discussion

Tables 1 and 2 give the results of the k_0-INAA of 34 elements (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Tb, Th, U, Yb, Zn) for Velenje, Senovo, and Kanižarica mines and for an imported Indonesian coal. In a previous study by Kanduč et al. (2019a), ten oxides (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, Cr_2O_3), LOI (Loss on ignition), TOT C (Total carbon), TOT S (Total sulphur) (Kanduč et al., 2019a), along the following toxicologically and environmentally relevant elements: As, Ba, Ce, Co, Cs, Cu, Dy, Er, Eu, Gd, Hf, La, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Se, Sm, Sr, Tb, Th, U, V, Y, Zn, Zr were measured in the organic-rich component of the Velenje samples. In this study, nine samples from the Velenje coal mine (13-2123, 13-2125, 13-2130, 13-2134, 13-2138, 13-2141, 13-2145, 13-2157, 13-2162), were measured using ICP-MS and k_0-INAA, while all other samples in this study were measured using only k_0-INAA. For studying elemental composition of coal with k_0-INAA method we choose only Velenje samples (from year 2013) that were organic rich, besides Kanižarica, Senovo and Indonesia coal samples that were sampled in years 2004 and 2005.

Results of ICP – MS of major elements, LOI, TOT C, TOT S in coal samples (13-2123, 13-2125, 13-2130, 13-2134, 13-2138, 13-2141, 13-2145, 13-2157, 13-2162) collected from excavation field -50/C of Velenje basin are presented in Table 3a. Results of ICP – MS of trace elements in coal samples (13-2123, 13-2125, 13-2130, 13-2134, 13-2138, 13-2141, 13-2145, 13-2157, 13-2162) collected from excavation field -50/C of Velenje basin are presented in Table 3b. Data (REEs) for coals from other locations (two power plants: Jungar (China), Tutuka (SA), Matla (SA), and the Witbank Coalfield (SA) are included for comparison purposes (Table 4).

For quality assurance and quality control (QA/QC), in the study we used the certified reference material BCR-180 Gas Coal (Fig. 2). The results obtained by k_0-INAA are in good agreement with the certified data for As, Hg, Se and Zn. It should be mentioned that expanded uncertainty (k=2) of mass fraction of Hg obtained via Hg-203 at 279.2 keV is relatively high in comparison with certified value due to correction from the mass fraction of Se via Se-75 at 279.5 keV, which was about 70 % (Fig. 2).

Among the major elements, Ca prevails. Major oxides (CaO, Na_2O, K_2O, TiO_2) and ultimate analysis (LOI, TOT C, TOT S) of the coal samples (13-2123, 13-2125, 13-2130, 13-2134, 13-2138, 13-2141, 13-2145, 13-2157, 13-2162) range as follows (Table 3 a): CaO from 1.91-5.21 %, Na_2O ranges from 0.04 to 0.13 %, K_2O ranges from 0.007-0.08 %, TiO_2 ranges from 0.07 to 0.08 %, TOT C ranges from 50.6 to 57.1 %, TOT S ranges from 1.17 to 2.46 %, and LOI (Loss on ignition) ranges from 86.7 to 97.1 % (Kanduč et al., 2019a). Figure 3 represents the major oxides (MgO+CaO, Na_2O+K_2O, SiO_2+Al_2O_3+Fe_2O_3) present in samples of lignite. The data were obtained from the study by Kanduč et al. (2019a) and are presented in Table 3a. The major oxides in the Velenje coal samples are CaO and MgO, suggesting that lignite was formed in a Ca-alkaline rich environment (Markič and Sachsenhofer, 1997). The most prevalent oxide is CaO (from 1.91 to 5.21 %). The concentration of oxides from the Velenje samples decrease in the following order: $CaO>Fe_2O_3>Al_2O_3>SiO_2>MgO>Na_2O>K_2O>TiO_2$. Only two Velenje coal samples (13-2134, 13-2145) have CaO + MgO concentrations less than 70 % (Fig. 3).

Figure 4 A-C shows plots of the major (Ba, Ca, Fe, K, Sr), minor (As, Br, Ce, Co, Cr, La, Mo, Nd, Rb, Sc, U, Zn) and trace element levels (Cs, Eu, Hg, Sb, Se, Sm, Ta, Tb, Th, Yb) for each of the coal mine samples (Senovo, Kanižarica, Indonesia, Velenje). From Figure 4A it can be observed that among major elements Ca prevailed for Velenje coal mine samples, while in one sample of Senovo (Senovo 3) and Kanižarica (Kanižarica 15) Fe prevails. Some samples from Velenje mine (13-2166, 13-2167, 13-2181), from excavation field -50/C have high concentrations of Ca in the range from 163700 to 307100 mg/kg (Fig. 4 A), which is in compliance with thesis of Ca-rich environment during sedimentation of Velenje basin. Among minor elements there are huge differences between coal samples between mines. The highest concentration of As, Br, Ce, Cr are observed in Kanižarica coal samples (Kanižarica 6, Kanižarica 15). Cr and Mo prevail in Velenje coal samples, while Br and Cr prevail in Senovo coal samples (Fig. 4 B). Kanižarica coal samples have also the highest concentration of rare elements (Cs, Eu, Hf, Ta, Th, Se, Sm) (Fig. 4 C). Sm and Th are enriched in three Velenje samples (B91, B105, 13-2149) (Fig. 4 C). Among all minor and trace elements Kanižarica coal samples have the highest concentrations (Figs. 4 B, C).

Figure 5 presents box-plots of the k_0-INAA data for all coal samples. From the box-plots it appears that the abundances of Ca>Fe>K>Na>Sr>Ba prevail among major elements and Mo>Zn>U>Cr>As>Br in the case of mi-

Table 1. Elements (Ag, As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hf, Hg, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, Yb, Zn, Zr) measured with k_0-INAA method in following coal samples: Senovo (Sen., n = 3), Indonesia (Indon., n = 1), Kanižarica (Kan., n = 4), Velenje (Vel., n = 7), sampled in years 2004 and 2005.

Code	**B91 Vel.**	**B105 Vel.**	**B106 Vel.**	**B106 Vel.**	**B113 Vel.**	**B113 Vel.**	**j.v. 3123 (1,8) Vel.**	**Sen.1**	**Sen.2**	**Sen.3**	**Indon.**	**Kan.6**	**Kan.9**	**Kan.19**	**Kan.15**
Element	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Ag	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
As	5.77	5.15	1.59	0.07	2.36	0.09	14.3	7.98	2.98	7.46	1.08	8.98	5.75	3.98	8.88
Au	<LD	<LD	0.0044	0.0002	0.0007	0.0001	<LD	0.0042	<LD	<LD	<LD	<LD	<LD	<LD	<LD
Ba	<LD	37.6	4.85	0.79	52.8	2.0	106	100	158	36.3	37.5	38.4	31.5	39.7	142
Br	8.71	5.92	1.77	0.07	5.76	0.21	4.02	1.08	1.43	0.12	1.95	1.90	2.05	7.56	2.02
Ca	16032	13401	3321	126	16854	592	10686	8812	9955	4436	1740	9576	15839	28496	8523
Cd	<LD	<LD	<LD	0.3	<LD	0.35	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
Ce	12.0	10.4	0.64	0.03	1.84	0.07	3.55	1.37	2.69	0.73	2.62	20.1	2.42	1.35	56.6
Co	1.28	2.05	0.24	0.01	0.21	0.01	0.71	7.82	0.54	0.22	1.88	10.7	3.02	0.54	16.1
Cr	12.3	16.3	6.81	0.39	2.54	0.19	2.75	22.6	26.3	7.26	10.1	86.0	24.5	44.9	222
Cs	1.37	2.89	0.42	0.02	0.237	0.010	0.55	0.34	0.27	<LD	0.24	3.78	0.76	0.55	13.7
Eu	0.34	0.23	<LD	0.004	0.059	0.010	0.13	0.102	0.199	0.111	0.056	0.67	0.096	0.072	1.21
Fe	9054	12501	896	32	3032	106	5199	5889	8321	119325	8631	16044	5173	6700	22968
Ga	2.70	5.64	<LD	0.07	<LD	0.05	<LD	2.05	2.25	<LD	0.78	7.33	1.67	1.79	18.3
Hf	0.24	0.44	0.038	0.003	0.075	0.005	0.099	0.102	0.196	<LD	0.133	1.28	0.178	0.154	3.08
Hg	0.39	0.17	0.27	0.02	0.064	0.009	0.104	0.22	0.08	0.11	0.03	<LD	<LD	<LD	<LD
K	1343	2874	225	23	270	27	331	244	466	65.0	216	2097	244	277	9099
La	5.58	5.94	0.31	0.02	0.89	0.05	1.41	0.75	1.66	0.43	1.27	11.8	2.46	1.60	31.2
Mo	9.53	11.1	0.53	0.05	9.11	0.33	23.7	6.78	4.05	0.19	0.06	39.0	34.2	17.1	28.8
Na	572	1625	354	12	742	26	706	282	90.6	47.0	55.9	207	104	275	533
Nd	5.59	5.27	<LD	0.20	0.73	0.18	1.83	1.77	3.46	1.17	1.60	9.79	1.46	<LD	25.5
Rb	8.98	22.5	1.64	0.15	1.57	0.14	3.11	2.00	3.37	<LD	2.10	29.6	3.76	3.51	105
Sb	0.75	1.18	0.085	0.006	0.34	0.01	1.58	0.64	0.32	0.83	0.042	1.70	0.70	0.36	1.55
Sc	1.43	3.09	0.202	0.007	0.64	0.02	0.93	1.37	2.53	0.82	0.56	8.34	1.01	0.67	15.4
Se	1.11	0.46	0.14	0.03	0.19	0.02	0.83	1.36	0.62	4.52	0.15	10.8	5.99	10.4	17.1
Sm	1.39	0.98	0.071	0.003	0.204	0.007	0.49	0.47	0.84	0.38	0.25	2.75	0.42	0.28	2.52
Sr	52.7	36.5	7.23	1.88	43.7	2.6	25.2	128	188	41.9	10.8	64.7	70.6	137	199
Ta	0.091	0.166	<LD	0.013	0.029	0.003	0.030	<LD	0.029	<LD	0.020	0.28	0.049	0.044	0.88
Tb	0.146	0.134	0.009	0.002	0.028	0.002	0.075	0.070	0.130	0.082	0.032	0.416	0.062	0.050	0.71
Th	4.46	2.40	0.15	0.01	0.356	0.014	0.49	0.85	1.17	<LD	0.35	3.79	0.58	0.51	9.79
U	63.4	7.87	0.67	0.03	2.38	0.08	8.23	4.38	4.23	0.25	0.15	65.9	43.7	50.7	36.4
Yb	0.28	0.47	0.031	0.003	0.096	0.004	0.213	0.201	0.405	0.274	0.099	1.48	0.206	0.137	2.56
Zn	72.4	18.7	5.75	0.33	3.64	0.24	21.1	26.8	7.58	4.27	13.8	46.4	11.2	5.99	126
Zr	<LD	<LD	<LD	7	<LD	27	<LD	4.41	8.59	<LD	<LD	41.0	<LD	<LD	134

<LD – values lower than detection limit

Table 2. Elements (Ag, As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hf, Hg, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, Yb, Zn, and Zr) measured with k_0-INAA method in following coal samples: Velenje (n = 18), excavation field -50/C, sampled in year 2013.

Code	**13-2113**	**13-2116**	**13-2119**	**13-2123***	**13-2125***	**13-2126**	**13-2130***	**13-2134***	**13-2138***	**13-2141***	**13-2143**	**13-2145***	**13-2149**	**13-2157***	**13-2162***	**13-166**	**13-2167**	**13-2181**
Element	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Ag	<LD	<LD	<LD	<LD	<LD	0.5	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
As	1.26	1.88	3.17	1.88	1.69	1.87	5.26	2.43	2.66	1.55	1.48	0.72	2.88	1.29	1.83	0.21	0.81	1.11
Au	<LD	<LD	<LD	<LD	<LD	0.00051	<LD	<LD	<LD	<LD	0.00029	0.00046	<LD	0.0005	0.0005	<LD	<LD	<LD
Ba	41.7	343.0	13.1	23.7	37.7	12.7	27.1	14.5	93.9	73	28.4	2.8	15.3	95.5	48.3	147	238	127
Br	6.58	6.07	6.69	6.60	7.57	8.75	5.65	8.73	5.81	7.02	6.92	2.41	1.95	6.03	6.8	0.59	2.02	2.93
Ca	16580	41280	20790	18460	20780	12950	30110	16370	28760	17170	13930	10920	129300	15220	31320	307100	246900	163700
Cd	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
Ce	1.11	1.50	0.92	0.61	1.88	1.16	1.62	2.43	1.28	1.14	2.39	0.74	5.64	0.32	1.88	3.87	1.28	1.06
Co	0.26	0.23	0.49	0.29	0.35	0.36	0.411	0.554	0.287	0.301	0.321	0.022	0.407	0.242	0.186	0.016	0.12	0.082
Cr	2.32	1.13	2.26	1.74	2.95	2.52	4.76	5.94	2.39	1.54	4.1	<LD	4.09	1.32	1.54	0.26	1.26	0.7
Cs	0.11	0.04	0.08	0.07	0.22	0.17	0.21	0.626	0.161	0.046	0.54	<LD	0.26	0.045	0.121	<LD	0.122	0.046
Eu	0.02	0.04	0.03	0.02	0.05	0.029	0.051	0.049	0.035	0.043	0.059	0.028	0.787	0.014	0.047	0.093	0.093	0.039
Fe	1590	2039	2390	1438	2165	2326	5868	5035	3565	908	1279	153	4827	2216	2826	198	1474	1289
Ga	<LD	<LD	<LD	<LD	<LD	<LD	<LD	1.42	<LD	<LD	0.96	<LD	1.1	<LD	<LD	<LD	<LD	<LD
Hf	0.07	0.03	0.05	0.04	0.07	0.051	0.081	0.125	0.054	0.032	0.079	<LD	0.066	0.037	0.052	<LD	0.028	0.017
Hg	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
K	197	95.20	147	146	237	304	342	687	238	119	565	18.4	232	93.9	141	15.9	124	<LD
La	0.65	0.88	0.58	0.36	1.10	0.671	0.99	1.41	0.756	0.637	1.18	0.262	1.14	<LD	0.94	1.93	0.8	0.579
Mo	6.9	11.10	8.9	5.4	11.1	13.8	7.84	25.8	21.7	8.88	9.51	2.06	4.19	11.6	15.9	<LD	5.2	3.87
Na	762	675.00	1058	874	611	739	1073	798	813	688	923	364	787	712	847	232	606	398
Nd	0.52	1.09	0.34	0.36	0.62	0.49	0.8	0.94	0.52	0.59	1.45	0.45	8.07	0.31	0.88	1.96	0.58	0.59
Rb	1.28	0.41	1.11	0.85	1.80	1.85	2.31	7.15	1.86	0.9	4.52	<LD	1.96	0.59	1.03	<LD	0.95	<LD
Sb	0.19	0.22	0.21	0.23	0.31	0.365	0.394	0.614	0.37	0.221	0.253	0.01	0.87	0.228	0.259	0.009	0.096	0.083
Sc	0.34	0.21	0.28	0.26	0.39	0.341	0.522	0.97	0.31	0.313	0.682	0.029	3.98	0.28	0.279	0.036	0.205	0.418
Se	0.25	0.22	0.43	0.31	0.16	0.37	0.53	0.36	0.32	0.26	0.75	<LD	<LD	0.21	0.29	<LD	0.149	0.071
Sm	0.08	0.25	0.10	0.06	0.27	0.132	0.574	0.319	0.08	0.158	0.239	0.108	3.3	0.245	0.295	0.417	0.297	0.216
Sr	23.80	147.00	32.0	24.20	63.70	14.6	62	18.9	80.8	43.3	14.2	<LD	33.4	18.9	87.9	817	1010	540
Ta	0.01	<LD	0.02	0.02	0.02	0.016	0.031	0.036	0.017	<LD	0.033	<LD	0.04	<LD	<LD	<LD	<LD	<LD
Tb	0.02	0.02	0.01	0.01	0.02	0.017	0.026	0.036	0.018	0.026	0.03	0.013	0.509	0.012	0.021	0.038	0.042	0.02
Th	0.24	0.13	0.22	0.17	0.35	0.272	0.339	0.714	0.27	0.169	0.579	0.013	0.712	0.169	0.199	0.041	0.182	0.063
U	4.68	6.38	3.50	1.81	5.15	4.99	12.9	8.65	6.19	4.73	3.05	0.092	6.2	8.72	5.23	0.85	1.97	2.85
Yb	0.05	0.03	0.04	0.03	0.06	0.059	0.076	0.123	0.053	0.049	0.094	0.015	1.28	0.045	0.051	0.045	0.04	0.041
Zn	6.89	8.91	4.82	2.59	2.53	12.3	22.4	8.99	10.4	4.05	20.6	4.2	20.1	22	9.55	1.01	9.31	2.75
Zr	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD

*Samples measured with ICP – MS method
<LD – values lower than detection limit

Table 3a. Results of ICP – MS of major elements, LOI, TOT C, TOT S in coal samples (Kanduč et al., 2019a, Supplementary material) for samples (13-2123, 13-2125, 13-2130, 13-2134, 13-2138, 13-2141, 13-2145, 13-2157, 13-2162) collected from excavation field -50/C from Velenje basin.

Sample ID	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	MnO (%)	LOI (%)	TOT C (%)	TOT S (%)
13-2123	0.48	0.29	0.23	0.34	2.99	0.11	0.01	0.007	0.01	0.02	93.1	55.7	1.89
13-2125	0.52	0.43	0.29	0.46	3.19	0.08	0.01	0.01	0.01	0.01	92.7	53	1.59
13-2130	1.3	0.9	1.41	0.33	5.14	0.13	0.07	0.03	0.02	0.02	86.7	50.8	2.46
13-2134	1.22	0.99	0.83	0.45	2.32	0.1	0.08	0.08	0.02	0.02	91.6	53.1	2.28
13-2138	0.38	0.32	0.52	0.33	4.98	0.1	0.02	0.007	0.01	0.05	88.8	52.9	2.1
13-2141	0.22	0.21	0.08	0.3	3.05	0.09	0.007	0.007	0.01	0.01	93.6	57.1	1.81
13-2145	0.02	0.01	0.028	0.07	1.91	0.04	0.007	0.007	0.007	0.007	97.1	50.6	1.17
13-2157	0.23	0.2	0.34	0.37	2.36	0.09	0.007	0.007	0.02	0.02	93.5	55.2	1.86
13-2162	0.25	0.21	0.36	0.35	5.21	0.1	0.07	0.07	0.04	0.04	87.6	51.6	2.16

Table 3b. Results of ICP – MS of trace elements in coal samples (Kanduč et al., 2019a, Supplementary material) for samples (13-2123, 13-2125, 13-2130, 13-2134, 13-2138, 13-2141, 13-2145, 13-2157, 13-2162) collected from excavation field -50/C from Velenje basin.

Sample ID	As	Hg	Mo	U	Th	Zn	Ba	Co	Se	Ce	Cs	Eu	La	Nd	Rb	Sm	Sr	Tb
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
13-2123	1.3	0.01	3.9	2	0.2	4	23	0.14	0.35	0.7	0.2	0.014	0.7	0.21	0.7	0.035	29	0.007
13-2125	1	0.03	6.7	5.7	0.3	3	43	0.5	0.35	2.1	0.2	0.03	1.4	0.8	1.3	0.2	71.8	0.02
13-2130	4.9	0.04	6.1	13.9	0.6	19	35	0.9	0.8	4.5	0.3	0.09	2.7	1.6	4.7	0.25	87.1	0.04
13-2134	2	0.06	22.6	8.1	0.6	14	19	0.4	0.7	3	0.6	0.05	1.7	1.5	6.7	0.18	20	0.04
13-2138	1.5	0.03	12.7	6.7	0.4	11	121	0.5	0.35	1.3	0.1	0.03	1.2	0.5	1.5	0.035	108.5	0.02
13-2141	1.3	0.02	6.1	4.5	0.14	13	97	0.4	0.7	1.8	0.07	0.04	1.1	0.6	0.4	0.035	60.2	0.03
13-2145	0.5	0.007	1.8	0.07	0.14	2	7	0.14	0.35	0.8	0.07	0.014	0.07	0.41	0.007	0.08	4.4	0.02
13-2157	0.8	0.04	9.2	7.8	0.3	20	99	0.14	0.35	1.1	0.07	0.014	0.7	0.021	0.4	0.035	20.4	0.02
13-2162	1.6	0.03	10.6	4.4	0.3	10	58	0.2	0.35	2.8	0.1	0.02	1.4	1.1	0.5	0.035	108.6	0.02

Table 4. Concentration of REEs (Rare Earth Elements) with Coal Clarke values and coals combusted in a thermal power plant ((Jungar power plant, Tutuka power plant (coal, ash), Matla power station)) and Witbank coalfield. Also ranges and averages of Velenje, Kanižarica, Senovo and Indonesia coal samples are presented for comparison.

	REE (mg/kg)													
	Coal Clarke valuesb		Jungar Power Plant, Chinac			Tutuka Power Station SAd		Matla Power Station SAe	Witbank Coalfield, SAf	Velenje (range and average, n = 18) g, measured with ICP-MS method	Vel. k_0-I-NAA (n = 25, ave.)	Kan., k_0-INAA (n = 4)	Sen., k_0-INAA method (n = 3)	Indo., k_0-INAA method (n = 1)
	Hard coal	Hard coal ash	Coal	Fly ash (Economizer)	Fly ash (Wet)	Coal	Ash	Fly ash	Coal (No. 2 Seam)					
La	11±1	76±3	41.2	85.4	104.3	39.9	91.4	81.55	9.72–34.16	<0.1–4.1 (1.60±0.90)	1.20	11.78	0.95	1.27
Ce	23±1	140±10	71.8	141	178	91.6	182.4	189.78		0.7–9.5 (2.73±1.99)	2.33	20.11	1.6	2.62
Pr	3.4±2	26±3	8.1	17.3	21.5	9.5	19.7	18.35		0.05–1.29 (0.30±0.29)				
Nd	12±1	75±4	27.6	58.5	72.5	30.8	81.8	63.5		<0.3–6.1 (2.21±1.34)	1.41	12.26	2.13	1.6
Sm	2.2±0.1	14±1	5.2	10.6	13.5	5.3	14.4	11.93	1.94–5.27	<0.05–1.42 (0.20±0.31)	0.41	0.56	1.49	0.25
Eu	0.43±0.02	2.6±0.1	0.9	1.8	2.4	0.9	2.7	2.35	0.26–0.77	<0.02–0.31 (0.05±0.06)	0.09	0.51	0.14	0.06
Gd	2.7±0.2	16±1	4.7	9.1	11.7	4.2	12.6	10.4		0.06–1.00 (0.22±0.20)				
Tb	0.31±0.02	2.1±0.1	0.7	1.4	1.8	0.6	1.9	1.6	0.25–0.66	<0.01–0.13 (0.03–0.03)	0.05	0.31	0.09	0.03
Dy	2.1±0.1	15±1	4.2	8.6	10.8	3.3	11.9	9.5		0.05–0.54 (0.18±0.11)				
Ho	0.57±0.04	4.8±0.2	0.8	1.7	2.1	0.7	2.4	1.97		<0.02–0.58 (<0.02)				
Er	1±0.07	6.4±0.3	2.4	4.9	6.2	1.9	6.7	5.38		<0.03–0.19 (0.08±0.05)				
Tm	0.3±0.02	2.2±0.1	0.3	0.7	0.9	0.3	1	0.77		<0.01–0.23 (<0.01)				
Yb	1.0±0.06	6.9±0.3	2.3	4.8	6	1.8	6.5	5.27		<0.05–1.60 (<0.05)	0.13	1.09	0.29	0.1
Lu	0.2±0.01	1.3±0.1	0.3	0.7	0.9	0.3	0.9	0.72		<0.01–0.23 (<0.01)				
Y	8.2±0.5	57±12	20.4	42.1	54.2	17.5	64.9	52.3		0.3–2.4 (0.91±0.51)				
Sc	3.7±0.2	24±11	-	-	-	9.7	26.5	24.94	2.72–6.79	<1-13 (<1)	0.63	6.36	1.57	0.56

[a]Taylor and McLennan (1985), [b]Ketris and Yudovich (2009), [c]Dai et al. (2010),[d]Akinyemi et al. (2012),[e]Eze et al. (2013),[f]Hart et al. (1982),[g]Kanduč et al. (2019a)

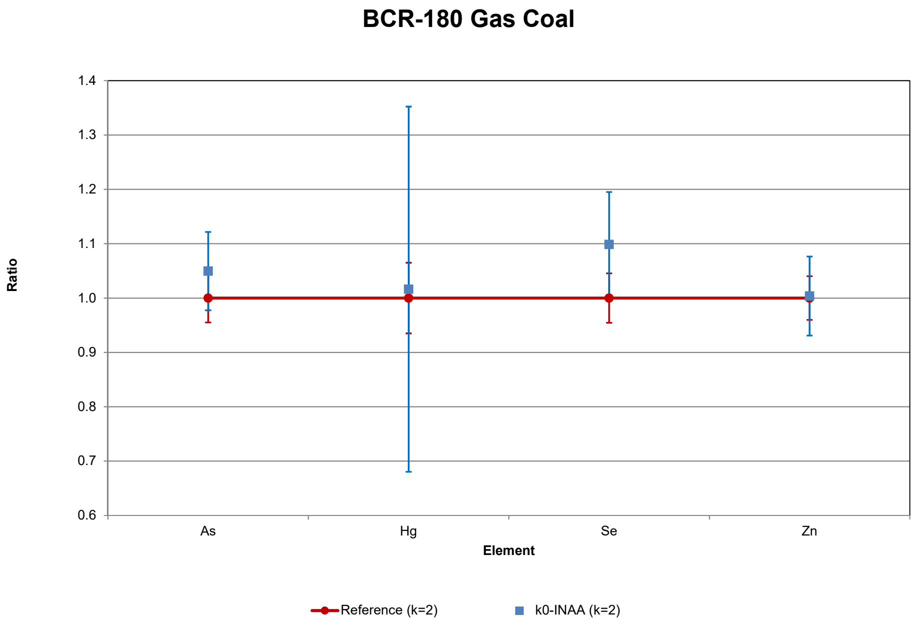

Fig. 2. QA/QC chart of measured parameters (As, Hg, Se, Zn) by k_0 – INAA, comparison with BCR-180 Coal Gas.

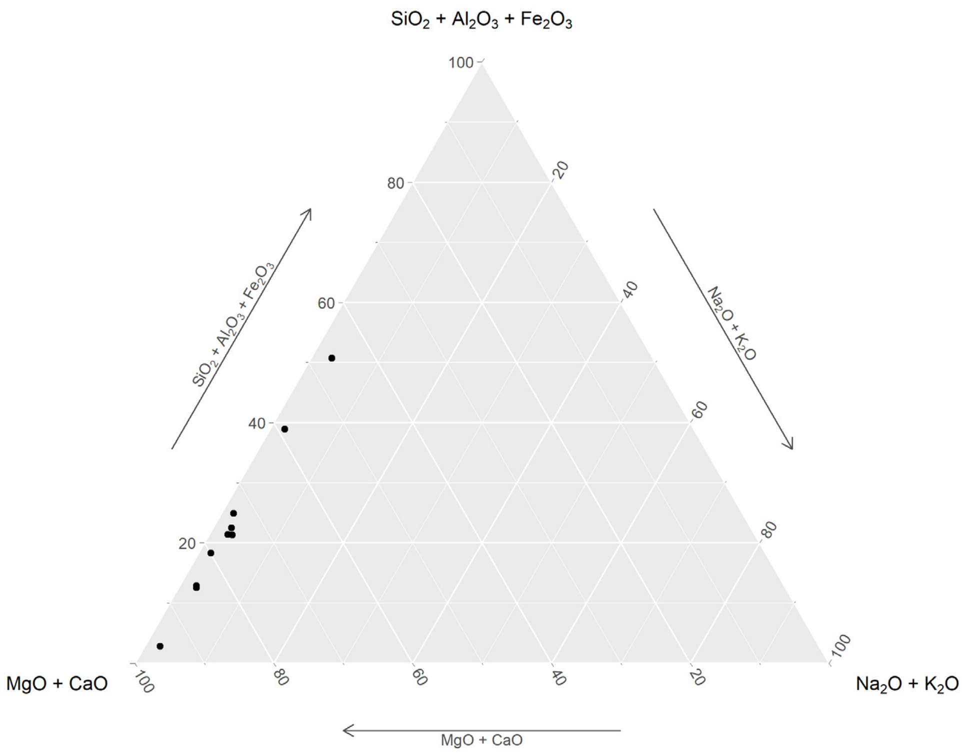

Fig. 3. Ternary plot of components: MgO+CaO/Na_2O+K_2O/SiO_2+Al_2O_3+Fe_2O_3 in gelified lignite samples (13-2123, 13-2125, 13-2130, 13-2134, 13-1238, 13-2141, 13-2145, 13-2157, 13-2162) determined with ICP-MS method (Kanduč et al., 2019a).

nor and trace elements. The elements: Ag, Au, Cd, Ga, Zr were excluded from plots since they were not measured in all of the coal samples, but are presented in Tables 1 and 2.

Among the 16 REEs (Table 4) recorded in coals from other locations (Taylor and McLennan, 1985, Ketris and Yudovich, 2009, Dai et al., 2010, Akineyeni et al., 2012, Eze et al., 2013, Hart et al., 1982, Kanduč et al., 2019a) only eight elements (Ce, Eu, La, Nd, Sc, Sm, Tb and Yb were determined using k_0-INAA and compared with published REEs values (mg/kg) in coal Clarke values, Jungar Power Plant (China), Tutuka Power Station (SA), Matla Power Station (SA) Witbank Coalfield (SA) (Wagner and Matiane, 2018) and the Velenje basin coal samples measured by ICP-MS. From a comparison of the data, all eight elements from this study (Velenje, Senovo, Kanižarica and Indonesia) and the data for the coal from other locations fall in the same range.

A comparison of the data for As, Ba, Ce, Co, Cs, Eu, La, Mo, Nd, Rb, Se, Sm, Sr, Tb, Th, U and Zn obtained using k_0-INAA and ICP-MS (Tables 3a and 3b) in samples 2123, 2125, 2130, 2134, 2138,

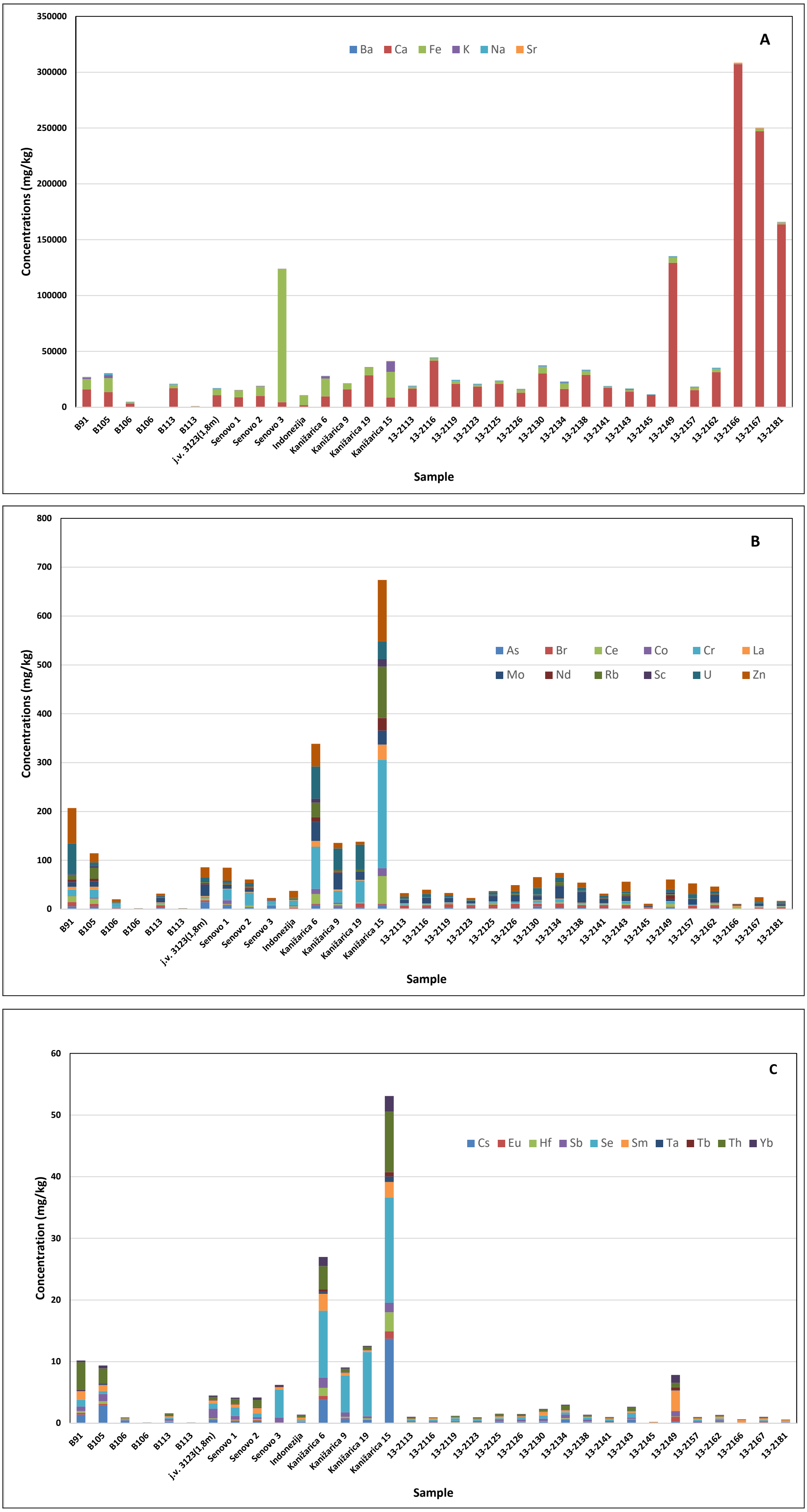

Fig. 4. Elemental composition of coals (major: Ca, Fe, K, Sr, Ba , minor: As, Br, Ce, Co, Cr, La, Mo, Nd, Rb, Sc, U, Zn and trace elements: Cs, Eu, Hg, Sb, Se, Sm, Ta, Tb, Th, Yb) from different locations (Velenje, Senovo, Kanižarica, and Indonesia) measured with k_0-INAA method.

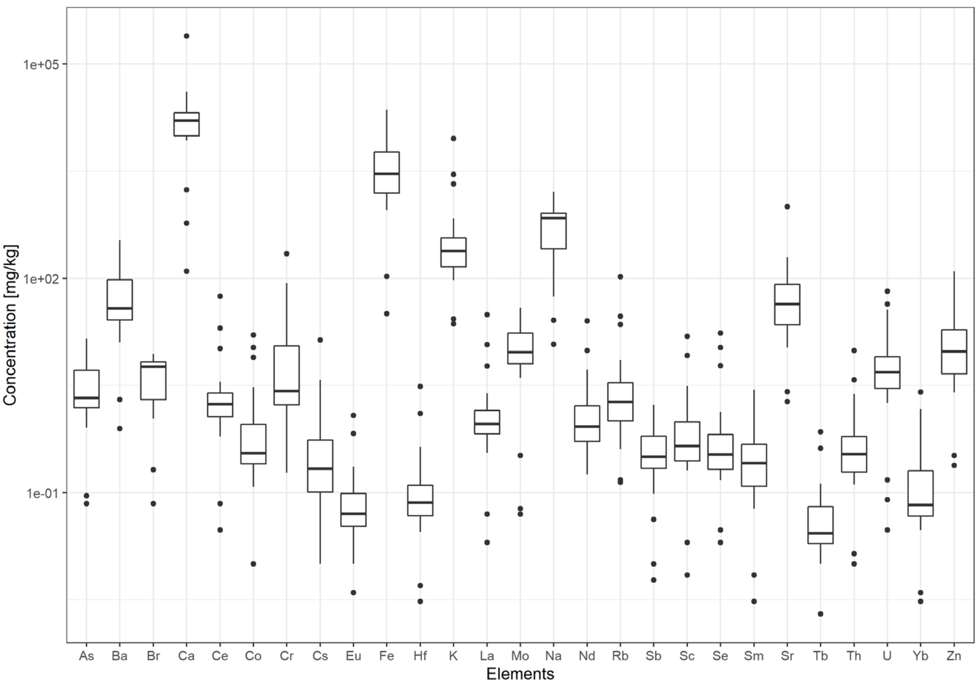

Fig. 5. Box – plot diagrams of major, minor and trace elements on "log scale" for coals from four mines (Kanižarica, Senovo, Indonesia, Velenje).

2141, 2145, 2157 and 2162 revel a strong positive correlation (R^2>0.8) in the case of As, Ba, Cs, Mo, Nd, Sr and U, (Fig. 6 A-D) and a good positive correlation (R^2 from 0.6 to 0.8) was observed for Zn and Rb (Figs 6 B-C). Though less strong, correlations (R^2 < 0.6) were found for Co, Eu, La, Se, Sm, Tb and Th (Figs. 6 C-D), which occur in low concentrations (< 1 mg/kg).

Figure 7 shows the Spearman correlations (R^2>90 %) for parameters (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Tb, Th, U, Yb, Zn) measured with k_0-INAA method from four different mining locations (Kanižarica, Senovo, Indonesia, Velenje). Spearman's correlation analysis revealed strong positive correlations (R^2>0.95) between the following elements: Ce-La, Cs-Rb, Cs-Sc, Hf-Sc, Eu-Tb, Cs-Tb, Sc-Tb, Cs-Yb, Hf-Yb, Sc-Yb, and Th-Yb.

Principle component analysis (Fig. 8) reveals a strong gradient along the first PCA axis (49.5 %) and has the highest positive correlation with trace elements (e.g., Ce, Co, and Cs) and highest negative correlation with main elements (e.g. Ca, Na, B). These elements have the most discriminant power separating coals from open (Velenje and Indonesia) and closed (Kanižarica and Senovo) coal mines. The second axis explains an additional 16.1 % of the variance and correlates positively with Ba, Sr and negatively with U, Sb according to PCA multi-elemental grouping (Fig. 8).

Conclusion

Coal samples from Slovenia (Kanižarica, Velenje, and Senovo) and Indonesia were sampled and analysed by k_0-INAA in 2003, 2004 and 2013, while the Velenje coal mine samples (2013) was measured using both k_0-INAA and ICP-MS to compare results obtained using both methods. Based on the comparison of both methods, it can be concluded that k_0-INAA method is very accurate compared to ICP-MS method with no possibility of losses of material and contamination. A good correlation between both methods was obtained for Ba, Sr, Mo, Zn, U, As, Rb, Nd, while a weak correlation was observed for Th, Se, Cs, Eu, Sm and Tb.

The major elements determined by k_0-INAA in the Velenje lignite samples (n = 25) are Ca>Fe>Na>K>Sr>Ba while for minor and trace elements Zn>Zr>Mo>U>Br>Cr. In the coal samples from the Kanižarica mine (n=4), the levels of the main elements are Fe>Ca>K>Na>Sr>Ba, while for minor and trace elements Cr>Zr>U>Zn>Rb>Mo. In samples from Senovo mine (n = 3) the main elements are Fe>Ca>K>Na>Sr>Ba, and for trace elements Cr>Zn>As>Zr>Mo, whereas in the Indonesia coal had the following composition of main elements: Fe>Ca>K>Na>Ba>Sr and trace elements: Zn>Cr>Ce>Co. In all cases, Fe and Ca are the most abundant elements, while among trace elements; Zn and Cr are the most abundant. The levels of trace elements of samples from all investigated mines were also in the same range reported in the literature for other mining

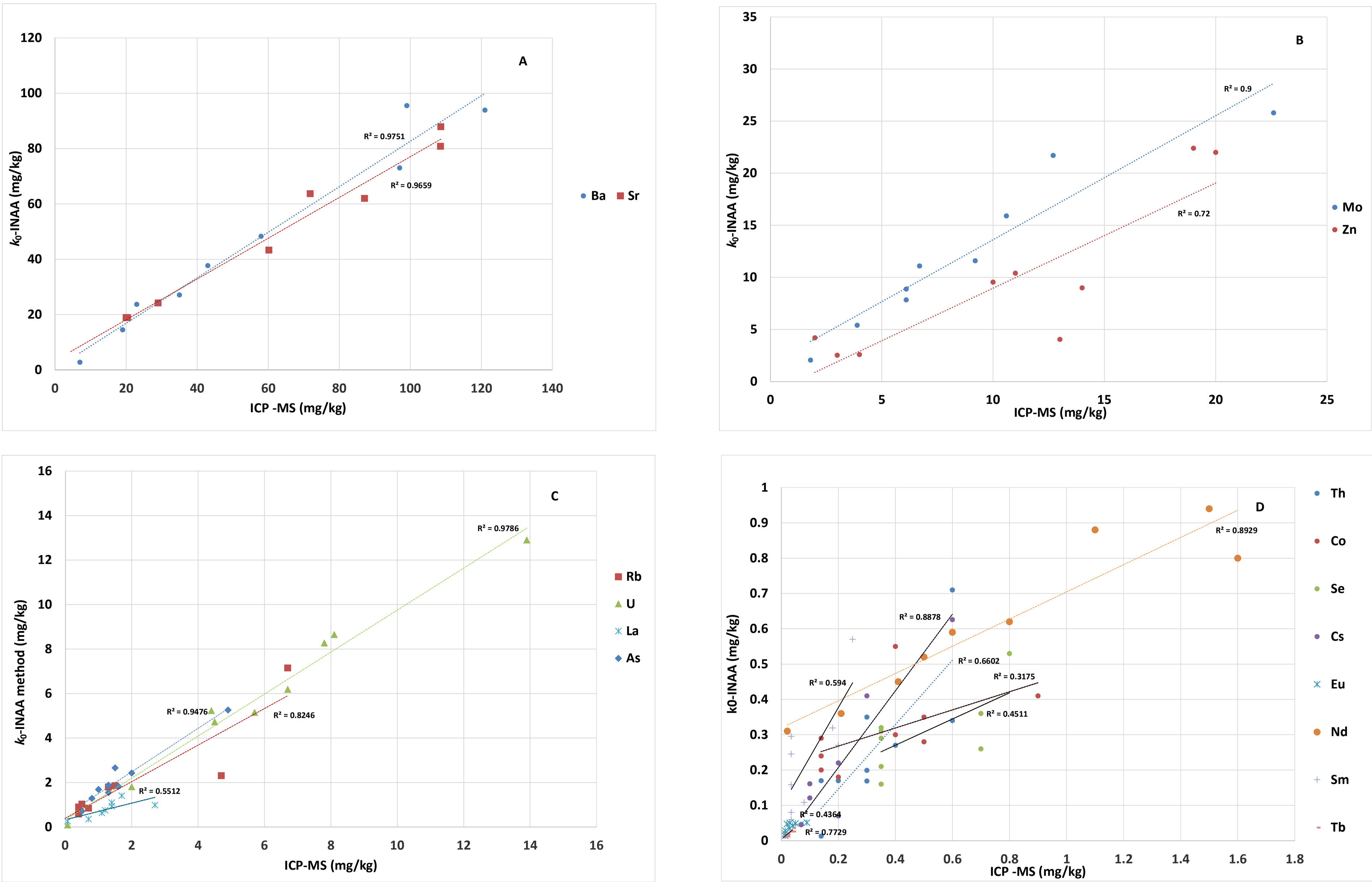

Fig. 6. Comparison between ICP – MS and k_0-INAA methods for 16 measured parameters in nine samples (Rb, U, La, As, Mo, Zn, Th, Co, Se, Cs, Eu, Nd, Sm, Tb, Ba, Sr) in coal. A. Correlation of Ba and Sr between ICP-MS and k_0-INAA. B Correlation of Mo and Zn between ICP-MS and k_0-INAA C. Correlation of Rb, U, La, As D. between ICP-MS and k_0-INAA. Comparison of Th, Co, Se, Cs, Eu, Nd, Sm, Tb between ICP-MS and k_0-INAA.

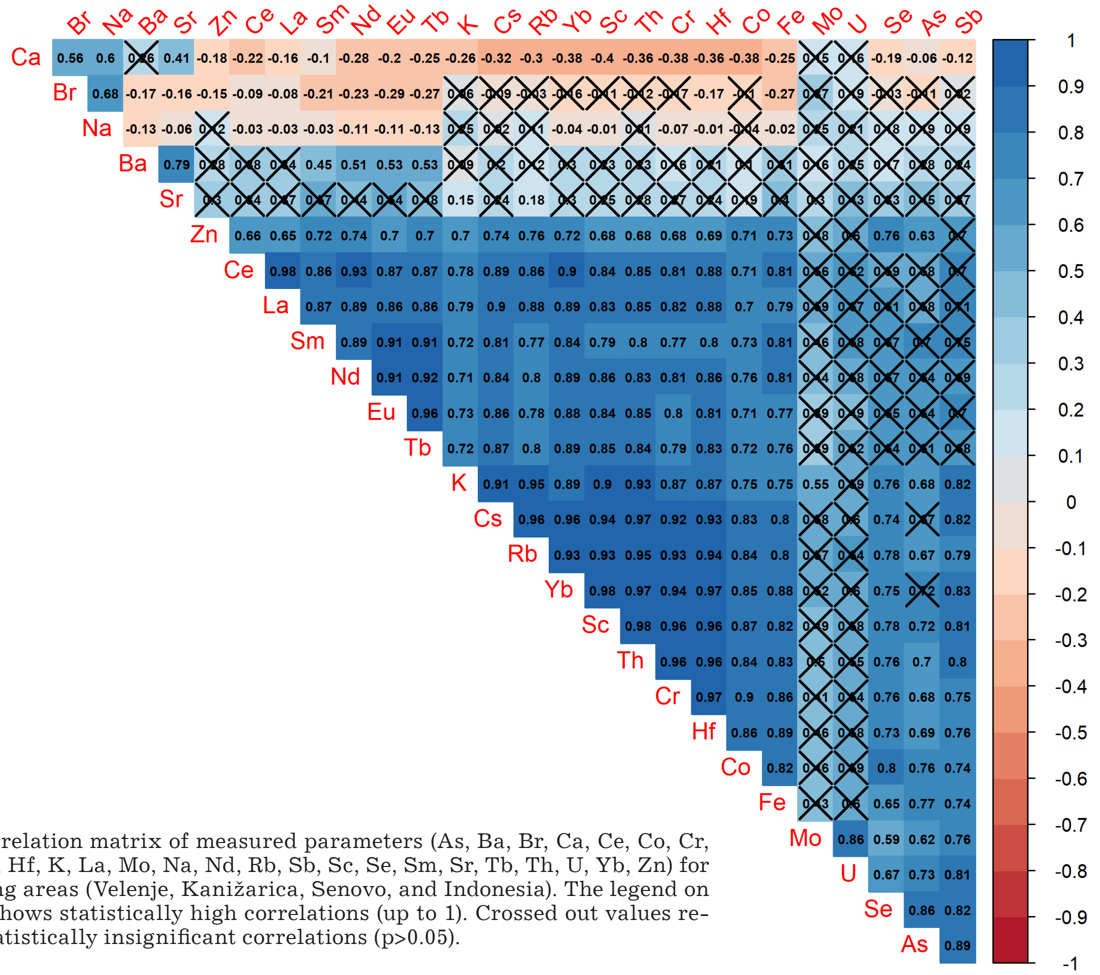

Fig. 7. Correlation matrix of measured parameters (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Tb, Th, U, Yb, Zn) for four mining areas (Velenje, Kanižarica, Senovo, and Indonesia). The legend on the right shows statistically high correlations (up to 1). Crossed out values represent statistically insignificant correlations (p>0.05).

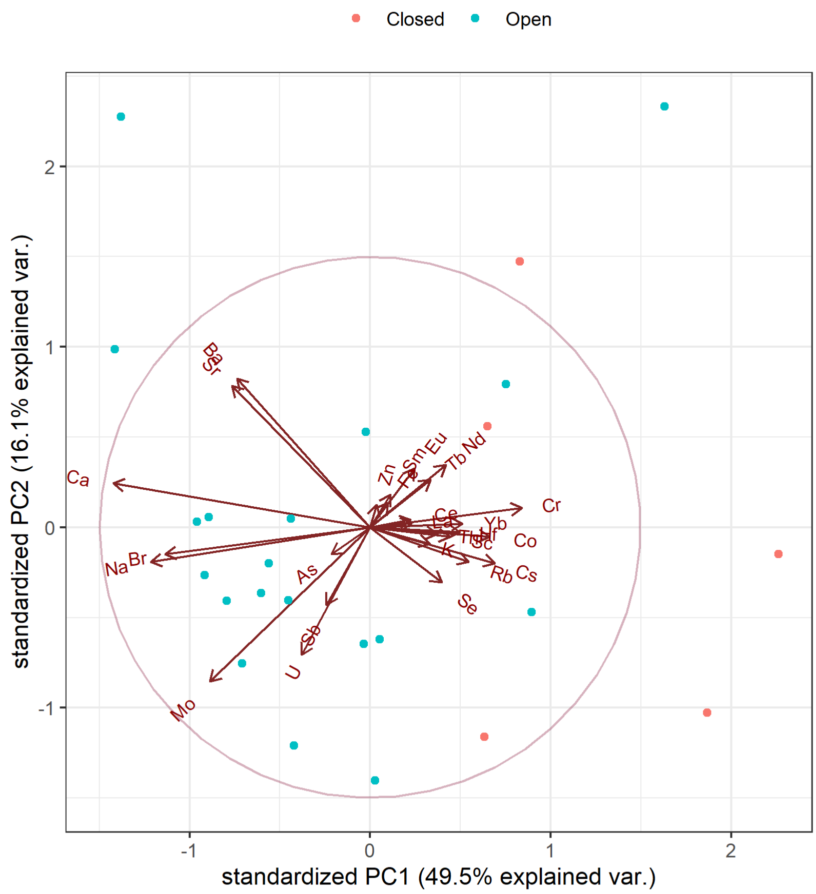

Fig. 8. PCA analysis of measured parameters (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Tb, Th, U, Yb, Zn) from different mining areas (Velenje-open, Kanižarica-closed, Senovo-closed, and Indonesia-open).

regions (SA and China). Principal component analysis based on 27 elements (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hg, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Tb, Th, U, Yb, Zn) revealed good discrimination between coal from the closed (Senovo, Kanižarica) and open mines (Velenje, Indonesia).

Further geochemical investigations of coal are required to investigate composition (proximate, ultimate analysis, major, minor and environmentally sensitive trace elements) of coal from active excavations in the Velenje coal mine in Slovenia, which is combusted in the Šoštanj thermal power plant and represents 30 % of energetic source in Slovenia. These analyses are essential to ensure the quality of combusted coal, which is related to atmospheric emissions.

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