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Distribution and Mobility Potential of Trace Elements in the Main Seam of the Most Coal Basin



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ABSTRACT

The Most Basin represents a coal basin with a long mining history in the Czech Republic. The majority of palaeoenvironmental and geochemical studies have been focused on the upper part of the coal-bearing Most Formation where the coal is generally enriched in As, Cr, Ni, Cu and Zn. This study evaluated the distribution of V, Cr, Ni, Cu, Zn, Pb, Se, As, and Mn from the lower part. Regarding to the transport of inorganic elements into environment, the evaluation of mobility potential was also conducted.

The total of 51 samples were collected from the Lower Bench in the Holešice Member. The chemical analyses were performed together with optical microscopy. The X-ray spectroscopy and ICP-MS were used to detect trace element contents in the study set of samples. 4 samples were subjected to the Sequential Extraction Procedure. The prepared leachates were analysed using the ICP-MS method.

In total, 13 elements were screened in samples within the study profile. The mode of occurrence is the key factor for identifying a potential source of the trace elements. All evaluated trace elements (V, Cr, Ni, Cu, Zn, Pb, Se, As and Mn) leached most in the oxidisable fraction. On the other hand, As, Mn, Ni, Zn and Cd leached in more mobile fractions, e.g. reducible and acid.

1. Introduction

The study of trace elements in coal provides not only useful data related to the sedimentological environment, but also reveals information required to minimise the environmental impact during the use of coal. Inorganic components in the coal can originate from several sources: 1) original organic matter, 2) formation during the stages of coalification, 3) carrying away by water or wind, 5) products of alteration of primary minerals. Trace elements, as a part of the inorganic components of coals, have deserved much attention and many studies have been done on trace element content and their distribution on subbituminous and bituminous coals (Adedosu et al., 2007; Finkelman, 1995; Lewinska-Preis et al., 2009; Ren et al., 1999; Suárez-Ruíz et al., 2006; Swaine, 1990; Zhuang et al., 2012, among many others). On the contrary, such conventional studies are scarce for low-rank coals (Gentzis et al., 1996). The modes of occurrence of trace elements vary greatly among coals. In low-rank coals, elements are usually organically bound, but with the progress of coalification, the elements are removed by expulsion of moisture and by changes in the chemical structure of

the organic matter (Ward, 2002; Li et al., 2007; Finkelman et al., 2018). Elements bound with discrete minerals remain unchanged (Ward, 2002). The fate of trace elements during coal conversion processes has become a matter of concern due to the large amount of coal that is often used for energy production. The behaviour of trace elements during coal combustion depends on their concentration, mode of occurrence, and combustion parameters. The organically associated trace elements tend to be vaporised, either escaping into the atmosphere or adsorbed on the fine fly ash particles upon combustion in the furnace. The inorganically associated elements are generally non-volatile and tend to retain in the bottom ash and/or the fly ash particles upon combustion. On the other hand, the presence of trace elements in coal may help in understanding phenomena such as the geological history of coalbearing sequences in sedimentary basins, the conditions ongoing due to coal seam formation, the depositional environment, and the influence of tectonics (Dai et al., 2012).

The mobility potential has been successfully evaluated in coal by the modified Sequential Extraction Procedure (SEP) (Cabon et al., 2007). The general principle of the method is to gradually leach the elements

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Fig. 1. Location of the Most Basin with a marked position of the active Bílina (Bi), Libouš (Li) and ČSA open cast mines (modified from Mach et al., 2013).

with a decreasing pH agent. The mobility potential of any trace element increases in the following order: oxidisable, reducible and acid and allows to predict its behaviour in environment under given conditions.

The Most Basin (Late Eocene-Early Miocene) represents an economically significant coal basin for the Czech Republic with only surface mining (Rajchl et al., 2009). The basin belongs to the group of Podkrušnohorská basins (Fig. 1), being a subject of detailed palaeoenvironmental and geochemical studies for its unique sedimentary sequence (Havelcová et al., 2012, 2013, 2015; Mach et al., 2013; Matys Grygar and Mach, 2013; Rajchl et al., 2008; Teodoridis et al., 2011; Teodoridis and Sakala, 2008). The basin formation started during the late Eocene and Oligocene by the intensive volcanic activity. The sedimentation followed by the clastic and organic deposits from the end of the Oligocene to the early Miocene (Mach et al., 2014). During the late Eocene-Oligocene, an intense alkaline volcanism mainly of basaltic character brought the pyroclastic materials and lava thick-bodies into the sedimentary basin, establishing the volcanic Střezov Formation. The following Most Formation is a unique coal-bearing strata (Fig. 2) subdivided to the Duchcov, Holešice, Libkovice and Lom members. The lowermost Duchcov Member contains alluvial sediments, followed by the Holešice Member. The last-mentioned member represents the Main Seam gradually passing to the Libkovice Member. The fine-grained lacustrine clays and lacustrine clay sediments form the uppermost Lom Member (Pešek and Sivek, 2016).

According to the geochemistry and mineralogy, two main complexes were distinguished in the Most Basin. The Lower Bench, including Duchcov Member and lower part of the Holešice Member, contained a higher content of Al, Ti, Nb, Zr, Cr. While the high content of Si, Mg, K, Rb and Cs was typical for the Upper Bench, forming the upper part of the Holešice Member (Elznic et al., 1998). This division was further supported by Mach et al. (2014) with using the significant correlation proxies, e.g. Al, K, Ti.

Taking into account these previous findings, the present work evaluates the mobility potential and the final distribution of V, Cr, Ni, Cu, Zn, Pb, Se, As, Mn in the Lower Bench (Holešice Member) of the Main Seam in the Most Coal Basin.

2. Material and methods

2.1. Samples and methods

Fifty-one samples were collected from the Bílina Mine in the Most Basin. The evaluated set represents a continuous vertical profile of the Holešice Member in the Lower Bench (Fig. 2). The proximate (moisture content W^a , volatile matter content V^d and ash yield content A^d) and ultimate analyses (CHNS), together with the calorific value Q_s^d , were conducted in all samples according to ISO 17246, 17247 and ISO 1928. The element migration potential in environment was evaluated based on the Sequential Extraction Procedure (SEP). In order to postulate conclusion for the Holešice Member, two samples from the Lower Bench (Bil 26 and Bil 0) and two from the Upper Bench (ČSA 48 and Lib 21) were chosen according to variation in the ash yield A^d and the sulphur content S^d . The sample set was evaluated with the principal component analysis (PCA) using the Statistica software. Variables in the



Fig. 2. Stratigraphic column of the Most Basin with stressing the Lower Bench – a white rectangular object (adapted from Mach et al., 2013).

PCA analysis were clustered into groups according to loadings higher than 0.5 which are considered to describe factors only.

2.2. Optical microscopy

An Olympus BX51 microscope with a Zeiss Photomultiplier MK3 system was used to measure the random reflectance (R_r) with oil immersion and lens with 40 × magnification. The evaluation was carried out in accordance with the ISO 7404 standard. The random reflectance values were determined from particulate polished sections by the SpectraVision software, calibrated by spinel (R = 0.422%), sapphire (R = 0.596%) and yttrium aluminium garnet (R = 0.894%) standards. With the same apparatus with fluorescence system, macerals groups of huminite, liptinite, and inertinite were identified according to ISO 7404 and in accordance with the principles brought forward by Taylor et al. (1998); ICCP (2001); Sýkorová et al. (2005); Pickel et al. (2017). The determination of liptinite macerals was performed using the UMSP 30 Petro microscope with a fluorescence system.

2.3. Chemical analyses

Prior to the chemical analyses, all the samples were sieved (mesh size $< 63 \,\mu$ m) and homogenised. All samples were dried, homogenised and pulverised prior the analyses. The CHNS contents were determined using with the Flash FA 1112 Thermo Finningan CHNS/O microanalyser.

The screening of 10 trace elements (V, Cr, Mn, Ni, Cu, Zn, As, Se, Cd and Pb) in samples involved the X-ray spectroscopy (XRF) using the Innov-X Systems portable XRF analyser. An amount of 1 g was introduced into a plastic pellet for the XRF analysis. The tool was set to a power of first X-ray 1–40 kV with exposure time 40 s and the power of second X-ray was 2–10 kV with exposure time 40 s. In order to verify the accuracy of measurements, reference materials of a known composition, e.g. Metranal 19, 32, 34, NIST 2702, 2781, were used.

To verify the absolute concentration of study elements, the total content of major elements (Al, K, Ti) and trace elements (V, Cr, Mn, Ni, Cu, Zn, As, Se Cd and Pb) was determined in 16 samples with the Inductively-Coupled Plasma Mass Spetrometry Agilent 7700x ICP-MS, Japan. An amount of 60 mg of each sample was burnt under 500 °C for 2 h in order to decompose carbonaceous substances as described in ISO 23380. The coal ash of 16 samples was treated by aqua regia and diluted by Milli-Q water for the ICP-MS analysis. The results from the coal ash analysis were converted to a whole coal basis.

Additionally, the 4-four samples were assigned to chemical fractionation. The leachates were analysed in the same manner as the original coal samples. 50 mg of a sample was gradually treated with chemical reagents introduced in Cabon et al. (2007). The sequence of chemical reagents was adopted so that carbonates would be first removed by the acetic acid. Then, coal ash leachates and leachates from the procedure were extracted with the microwave digestion (MARS 6, CEM Corporation, USA). Total trace element contents obtained in the leachates were used to derive percentages of each element leached by each of the 4 chemical reagents. The standard reference material SARM 19 for low rank coals were used to validate recoveries for individual elements. Methodology was validated by analysis of spiked samples and median recoveries were for individual metals within the range of 96–107%.

3. Results

3.1. Ultimate and proximate analyses

The ultimate and proximate analyses illustrated the variability of a vertical profile (Table 1, Fig. 3). The ash yield (A^d) significantly fluctuated with depth, ranging from 17.4 to 87.7 wt% throughout and reflected the varying amount of the detritus at the time of the deposition. The samples with the ash yield content higher than 50% were according to the ISO 11760 (2005) classified as coaly claystones. The study set of coaly claystones showed the variable V^d content, varying from 11.6 to 32.3 wt% and also the calorific values ($Q_s^{d} = 0.8-12.1 \text{ MJ} \cdot \text{kg}^{-1}$).

The nitrogen (N^d) content fluctuated evenly within a narrow interval throughout the profile in coal samples from 0.3 to 0.9 wt% and 0.01 to 0.5 wt% in coaly claystone samples, respectively. The hydrogen content (H^d) ranged in the same narrow interval, in coal samples from 2.4 to 4.5 wt% and 1.3–3.2 wt% in coal claystone samples. The sulphur content (S^d) varied in coal from 0.03–2.7 wt% and greatly fluctuated in coaly claystone samples from 0.2 to 6.4 wt%.

3.2. Organic petrography

The random reflectance values (R_r) of coals showed values from 0.31 to 0.39% (mean value of ~0.35%) confirming that the coal rank (UN-ECE, 1998) for the Lower Bench of the Holešice Member corresponded to lignites. For the coaly claystones huminite reflectance was slightly lower, ranging from 0.24 to 0.38% (Fig. 3). No clear depth

Table 1

Bulk chemical parameters (wt%) in samples from the Holešice Member.

	Depth (m)		Proximate analysis			Ultimate anal	ysis			
Sample	From	То	%W ^a	%A ^d	%V ^d	%C ^d	%H ^d	%N ^d	%S ^d	$Q_s^{\ d}$
Bil 1	0.00	0.13	7.1	19.5	43.7	52.9	4.5	0.9	0.9	22.7
Bil 2	0.13	0.19	5.2	44.4	37.3	36.9	3.6	0.6	0.6	14.3
Bil 3	0.19	0.94	1.9	83.5	16.2	2.8	1.7	0.0	2.7	0.8
Bil 4	0.94	1.04	3.4	60.6	24.8	19.4	2.8	0.3	0.6	8.7
Bil 5	1.04	1.17	2.4	74.2	25.3	10.4	2.3	0.1	0.2	4.4
Bil 6	1.17	1.35	2.8	68.7	22.2	14.2	2.6	0.2	0.6	6.5
Bil 7	1.35	1.83	2.1	81.7	16.4	6.4	1.9	0.1	0.1	1.5
Bil 8	1.83	1.98	6.8	36.0	37.3	38.1	3.7	0.6	3.0	16.0
Bil 9	1.98	2.28	3.2	54.3	24.4	20.8	2.7	0.3	0.6	11.4
Bil 10	2.28	2.58	6.8	26.6	42.0	48.4	3.9	0.7	1.4	20.1
Bil 11	2.58	2.64	2.4	66.2	32.3	17.9	1.7	0.2	0.1	2.9
Bil 12	2.64	2.77	6.0	30.2	40.0	45.4	4.1	0.7	2.3	19.1
Bil 13	2.77	2.93	1.8	83.2	15.3	4.9	1.7	0.1	0.1	0.8
Bil 14	2.93	3.18	2.5	71.8	21.5	15.2	2.3	0.2	0.6	4.8
Bil 15	3.18	3.61	2.3	74.4	17.7	8.7	2.0	0.1	0.2	3.8
Bil 16	3.61	3.71	4.4	38.8	35.1	36.8	3.9	0.5	1.5	17.1
Bil 17	3.71	3.83	6.8	23.7	39.6	45.2	4.0	0.8	6.4	21.5
Bil 18	3.83	4.10	2.1	80.1	16.0	5.9	1.9	0.1	0.5	1.5
Bil 19	4.10	4.22	5.9	24.8	37.2	41.5	3.8	0.7	3.9	20.8
Bil 20	4.22	5.32	1.4	87.3	11.6	1.9	1.3	0.0	0.1	0.8
Bil 21	5.32	5.50	2.1	64.5	27.2	17.6	2.9	0.2	0.6	8.4
Bil 22	5.50	5.70	2.6	62.4	24.9	18.2	2.8	0.2	1.2	8.7
Bil 23	5.70	5.90	2.3	69.9	24.0	15.7	2.7	0.2	0.1	5.8
Bil 24	5.90	6.08	4.8	51.9	30.0	26.5	3.2	0.4	2.1	12.1
Bil 25	6.08	6.23	2.4	73.0	20.5	10.9	2.4	0.1	0.3	4.8
Bil 26	6.23	6.25	4.0	55.3	29.5	28.8	3.1	0.5	1.2	11.0
Bil 27	6.25	6.28	7.8	36.9	31.1	36.5	3.5	0.7	2.0	17.4
Bil 28	6.28	6.58	1.4	86.6	12.3	2.5	1.4	0.0	2.2	0.8
Bil 29	6.58	6.70	1.4	83.1	12.9	4.5	1.4	0.1	0.2	0.8
Bil 30	6.70	7.35	1.2	83.4	12.8	1.4	1.3	0.0	0.1	0.8
Bil 31	7.35	7.65	1.9	79.3	17.0	7.3	1.9	0.1	0.5	2.0
Bil 32	7.65	7.94	5.5	31.7	36.7	44.4	3.9	0.6	1.7	18.8
Bil 33	7.94	8.22	2.7	76.0	18.9	10.6	2.1	0.1	0.3	3.5
Bil 34	8.22	8.56	6.5	43.7	45.4	46.9	4.0	0.6	1.4	15.1
Bil 35	8.56	9.31	1.5	87.7	12.2	1.4	1.4	0.0	0.0	0.8
Bil 38	9.89	9.91	4.7	22.7	34.3	57.2	3.9	0.6	0.2	23.6
Bil 39	9.91	10.01	3.4	39.4	36.9	38.3	4.2	0.4	1.3	17.8
Bil 40	10.01	10.14	6.3	17.4	42.6	54.7	4.5	0.8	1.5	23.9
Bil 41	10.14	10.29	2.2	77.9	19.1	10.5	2.2	0.1	0.2	2.9
Bil 42	10.29	10.42	5.3	25.8	36.1	40.7	3.6	0.5	1.5	20.9
Bil 44	11.02	11.37	6.3	21.9	39.9	52.2	4.2	0.6	1.5	22.1
Bil 45	11.37	11.59	2.0	80.5	16.5	6.4	1.8	0.0	0.1	1.6
Bil 46	11.59	11.69	3.5	61.6	27.0	24.6	3.0	0.3	0.7	9.0
Bil 47	11.69	11.99	2.3	79.8	18.4	9.7	2.1	0.1	0.1	2.4
Bil 48	11.99	12.29	2.9	62.9	25.2	21.4	2.7	0.2	0.6	8.5
Bil 50	12.69	12.74	2.4	64.7	26.1	19.3	2.9	0.2	0.4	8.4
Bil 51	12.74	12.96	4.6	31.4	38.8	39.2	3.4	0.5	1.2	18.7
Bil 54	13.74	13.77	3.4	52.9	29.6	22.6	2.4	0.3	0.8	9.9
Bil 55	13.77	13.78	3.1	44.4	33.6	34.0	2.4	0.3	1.7	13.7
B11 57	13.85	14.25	5.2	24.0	42.0	50.5	4.1	0.6	1.2	21.5
B11 0	-	-	5.5	31.3	39.8	43.3	4.1	0.6	3.1	17.6
L1D 21	-	-	3.9	49.6	33.5	30.4	3.3	0.8	2.5	12.4
CSA 48	-	-	8.9	26.7	40.5	38.5	3.4	0.4	7.1	15.1

Note: Grey lines highlight the coaly claystone samples. ${}^{\sigma}$ Standard deviation. d Dry basis. a Analytical sample. ${}^{*}Q_{s}{}^{d}$ – calorific value in dry basis (MJ·kg⁻¹), ${}^{n.d.}$ Not determined.

trend for huminite reflectance (Fig. 3) has been observed within the interval examined.

The huminite maceral group was the predominant organic component followed by the liptinite maceral group and the scarce inertinite with the exception of two coal samples (Bil 55 and Bil 38) in which the inertinite content varied from 40.40 to 48.30 vol%. The mineral matter as identified in optical microscopy made up clays as the main inorganic component, variable content of carbonates and pyrite, quartz being very scarce.

3.3. Trace element distribution

The Pearson Correlation Coefficients were calculated in the data set,

analysing the content of trace elements with the XRF and ICP-MS method (Table 2). We state that all trace elements evaluated with exception of Se, Cd and Cu can be reliably analysed by the non-destructive technique. The trace element values obtained from ICP-MS and XRF analysis are shown separately in Table 3 and Supplement.

Elements (namely As, Ni, Pb, V, Cr.) occurring in increased amounts in the lower part of the Holešice Member have been evaluated. The assessment of concentration of the above-mentioned elements in the Lower Bench proved a higher fluctuation of the values within the interval 4.10 and 6.23 m compared to the lower part of the profile (Fig. 4 and Supplement Table).

Results have shown that the maximum of V ($1186 \text{ mg} \text{kg}^{-1}$); Cr ($244 \text{ mg} \text{kg}^{-1}$); As ($53 \text{ mg} \text{kg}^{-1}$) and Pb ($33 \text{ mg} \text{kg}^{-1}$) content clearly



Fig. 3. Changes of ash yield content (A^d), nitrogen (N^d), sulphur (S^d) and random vitrinite reflectance (R_r) with depth in the Lower Bench of the Holešice Member.

 Table 2

 Comparison data of XRF with ICP-MS method using the Pearson correlation coefficient.

Element	V	Cr	Mn	Ni	Cu	Zn	As	Se	Cd	Pb
v	0.71									
Cr	0.71	0.85								
Mn	-0.38	-0.20	0.88							
Ni	0.09	0.30	0.44	0.69						
Cu	0.51	0.67	0.34	0.47	0.46					
Zn	-0.14	0.03	0.80	0.26	0.48	0.68				
As	-0.05	0.12	0.11	-0.01	-0.30	-0.37	0.78			
Se	-0.18	-0.16	0.55	0.18	0.03	0.34	0.00	0.00		
Cd	-0.28	-0.12	0.55	0.22	0.21	0.24	0.31	0.12	0.12	
Pb	0.59	0.75	-0.02	0.45	0.00	-0.44	0.45	0.76	0.32	0.84

Bold: Data from ICP-MS analysis.

Italics: Data from XRF analysis.

Significance: $p \leq .05$.

corresponded with the highest sulphur content S^d (3.9 wt%) in the depth 4.10 m, while a sulphur-rich position at the depth 3.71 m (6.4 wt %) is only related to the elevated content of As (56 mg·kg⁻¹) and Ni (306 mg·kg⁻¹). The relatively high amount of pyrite (3.8 and 4.1 vol%) based on petrographic composition (Supplement Table) reflected on As and Ni enrichment at both depths 3.71 and 4.10 m, respectively.

No significant trend has occurred in Cu, Zn, Mn and Cd (Supplement Table). All these elements behaved quite uniformly throughout the profile, having less than two maxima peaks. The manganese Mn (1698 mg·kg⁻¹) and Zn (1606 mg·kg⁻¹) maxima occurred in the upper part of the profile (2.58 m depth). The position was characterised by a high amount of carbonates (25.0 vol%) according to petrographic composition (Supplement Table). Additionally, Cu content showed only one maximum in the depth 10.29 m. The cadmium (Cd) content varied uniformly throughout the profile without any maximum.

The detailed distribution has proved the high variability in the element content with isolated extreme values. Thus, using the average

as a statistic parameter, characterising the whole profile, would distort the values especially for, V, Cr and Ni.

4. Discussion

4.1. Mode of occurrence of trace elements

The results of the PCA revealed that 62.85% of the dispersed variable could be assigned to two factors (Fig. 5). The high positive loadings for Ti (0.84), C^d (0.80), V (0.91), Cr (0.90), Ni (0.85), Cu (0.71) and Pb (0.88) displayed a high positive Factor 1. The elements were probably organically associated and/or originated from Ti-bearing minerals.

In contrast, a high positive loading for As (0.79) and S^d (0.52) have been found in the Factor 2. Therefore, the origin of As from sulphide minerals is greatly expected. The high negative loadings for A^d in the Factor 1; and for K and Al in the Factor 2 correlated with none of the evaluated elements. They have been clustered in the opposite side in

Table 3

The concentration of 10 trace elements and 3 major elements	nents in selected samples (ICP-MS method).
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Sample	Ala	K ^a	Ti ^a	V	Cr	Mn	Ni	Cu	Zn	As	Se	Cd	Pb
Bil 3	30.4	0.9	0.2	38.3	25.2	7.0	15.0	14.0	32.1	1.4	11.6	0.01	4.2
Bil 8	23.2	0.6	0.8	166.1	67.1	69.6	75.4	45.0	22.7	15.8	19.6	0.22	11.3
Bil 9	28.0	0.8	0.3	51.6	25.6	19.0	25.1	19.5	18.7	1.7	11.6	0.02	2.9
Bil 11	12.9	0.4	0.3	19.0	11.9	445.7	104.2	5.1	437.7	1.1	12.3	1.31	1.6
Bil 17	20.6	0.6	0.8	180.5	62.1	70.3	157.2	24.4	31.8	27.0	22.4	0.15	15.3
Bil 18	29.4	0.8	0.3	27.0	20.0	4.4	16.6	11.9	8.6	1.5	8.4	0.02	2.1
Bil 19	24.8	0.7	0.7	416.9	141.5	8.7	175.7	84.0	45.5	20.9	7.8	0.25	16.9
Bil 25	31.3	0.7	0.2	39.6	20.8	3.0	17.6	16.6	14.1	1.4	9.7	0.02	2.1
Bil 26	27.8	0.9	0.4	147.3	54.2	4.6	57.7	18.8	10.9	12.4	11.6	0.06	14.4
Bil 35	24.8	0.7	0.2	41.9	24.3	14.0	11.6	9.4	9.4	1.5	10.5	0.01	2.9
Bil 39	25.2	0.7	0.3	30.0	20.9	10.4	18.1	11.7	22.2	2.1	17.3	0.38	2.4
Bil 42	24.3	0.6	0.4	201.3	77.2	101.1	102.6	112.6	78.3	6.1	10.7	0.35	6.5
Bil 51	17.9	0.5	0.5	98.9	48.2	196.5	34.2	18.8	45.8	2.6	10.0	0.12	4.8
Bil 0	25.4	0.7	0.6	170.9	81.6	49.4	63.3	35.5	24.9	14.6	10.5	0.66	12.8
Lib 21	15.5	0.4	0.5	26.7	20.4	738.0	26.0	20.0	58.3	37.2	16.1	0.28	2.7
CSA 48	1.2	0.1	0.1	4.3	4.5	34.7	23.6	2.1	13.1	217.2	1.4	0.22	2.9

Bold: content in original sample $(mg \cdot kg^{-1})$.

^a Content in original sample (g·kg⁻¹).

Fig. 6. We assume that inorganic part, composing of clay minerals, having less importance for binding trace elements in the study set of samples.

As mentioned Bouška and Pešek (1999) and Rieder et al. (2007), the weathered iron disulphides from the Ore Mountain Range were expected to be the main source of material entering the Bílina delta during the Miocene. Trace elements, e.g. Cu, Zn and Pb elements generally originate from sulphide minerals, for instance chalcopyrite (CuFeS₂), sphalerite (ZnS) and galena (PbS). Although, we have not found the significant correlation between Cu, Zn, Pb and total sulphur. Finkelman et al. (2018) acknowledged that Cu might be associated either with clays or organically associated. They also added that Zn could be present in a small proportion in silicates or organically associated in the

matrix (Sia and Abdullah, 2011; Equeenuddin and Tripathy, 2016; Liu et al., 2016; Finkelman et al., 2018).

The V, Cr and Ni contents tended to increase simultaneously with ash yield content A^d. Despite difficulties in finding an appropriate source of the mentioned elements, we have used the geochemical proxies to have been successfully introduced in various studies. For instance, illite content variation can be explained by the K/Ti ratio (Hofmann et al., 2001), the Ti/Al ratio indicate the sediment provenance (Matys Grygar et al., 2016) and K/Al is convenient as the proxy for chemical weathering intensity (Clift et al., 2014; Matys Grygar et al., 2014). Higher contents of trace elements (e.g. V, Ni, Cr) were detected at the upper part of the profile. Simultaneously, the minima of K/Ti ratio and maxima of Ti/Al were reached at the upper part (Fig. 6). A



Fig. 4. Vertical variation of As, Cr, As and Pb in the Holešice Member (Lower Bench).



Fig. 5. Results of principal component analysis (PCA) of samples from the Holešice Member.



Fig. 6. The distribution of the geochemical proxy Ti/Al in the profile from the Lower Bench.

significant dependence of trace element content on the ash yield content has not been found. On the contrary, it was found that the sample position in the profile was more significant. This distribution can be explained by the contribution of the volcanic material with the higher content of the trace elements to the basin (Mach et al., 2014). Thus, the precise age of the sequence is the key factor allowing to predict the potential elements content.

4.2. Trace element mobility

The broad spectra of trace elements (Cr, Mn, V, Ni, Cu, Zn, As, Se, Cd and Pb) were evaluated in order to monitor the potential mobility in the Main Seam of the Holešice Member (Supplement Table). As non-homogenous strata, the selection was done to cover natural variability

of the Main Seam.

The sample Bil 26 characterised high values of ash yield content A^d (55.3 wt%), low carbon content C^d (28.8 wt%) and sulphur content S^d (1.2 wt%). The sample Bil 0 contained a high content of C^d (43.3 wt%) and S^d (3.1 wt%), with low A^d (31.3 wt%).

The content of all rated trace elements, except Mn, was dominantly associated with an oxidisable fraction (> 65% leached, Fig. 7). They can be also interpreted as elements easily bound to sulphides and/or organic matter (Tessier et al., 1979). Thus, the all trace element evaluated are thought to be easily mobilised under oxidising conditions. On the other hand, the manganese (Mn) partial immobility owing to the high association in the residual fraction (79% leached) in the Lower Bench could be doubted for its negligible low content (4.6 mg·kg⁻¹, Table 3). All trace elements evaluated were rarely found to be bound to reducible and/or acid fractions in the Lower Bench (< 31% leached). The most dissolved element in all mobile fraction is vanadium.

For the overall mobility evaluation of the Holešice Member, the samples from the Upper Bench – Lib 21 and ČSA 48 were assigned to be discussed. These samples differed on ash yield and the sulphur content ($A^d = 49.6 \text{ wt\%}$, $S^d = 2.5 \text{ wt\%}$, $A^d = 26.7 \text{ wt\%}$ and $S^d = 7.1 \text{ wt\%}$, respectively). The oxidisable and reducible fractions were dominant in the ash rich sample Lib 21. The mobilisation of Zn, V, Cu, Cr and Mn varied from 50 to 88% leached in the oxidisable fraction. The arsenic (As) and nickel (Ni) content was highly bound on the reducible fraction, varying from 50 to 81%. It follows that the elements were easily associated with the Fe–Mn oxides. Thus, reducible conditions could easily mobilise these elements in the environment (Tessier et al., 1979). The acid and residual fractions were negligible for all trace elements, except for Cd and Pb, with less than < 24% and < 4% leached, respectively.

Concerning the sulphur-rich sample ČSA 48, manganese (Mn), Cd, Zn and Ni were most associated with the acid fraction (> 48% leached). The fraction is very liable, covering elements bound on carbonates. A decrease of pH to mildly acid could cause the mobilisation of trace elements in environment (Tessier et al., 1979) Moreover, Cr, Cu and Pb contents were dominantly associated with the oxidisable fraction (> 55% leached). Arsenic (As), Ni and V were also mostly bound to the mobile fractions, particularly 80% of Ni content distributed between the reducible and oxidisable fraction. Simultaneously, the 83% of As content redistributed between the acid and reducible fraction.

5. Conclusions

Our results have provided a detailed distribution of trace elements within the Lower Bench of the Holešice Member (Most Formation). The dominant maceral group is huminite with mean random reflectance $R_r = 0.32\%$. The mean of huminite reflectance does not show a significant trend throughout the profile of the Lower Bench. The study samples are classified as lignites and coaly claystones.

Ash yield (A^d), a general parameter of coal, cannot be used to estimate trace element content in the study profile. Our results did not prove A^d to correspond with the increased amount of trace elements throughout the whole Lower Bench section. The high variation of Ti/Al in the study profile set has shown that the volcanic material is expected to carry itself the increased amount of trace elements, especially, V, Cr, Ni, As and Pb. In addition, pyrite has been confirmed to be a good carrier of As in the matrix examined.

The mobility potential of trace elements evaluated, using the Sequential Extraction Procedure, has demonstrated readily solubility under oxidising conditions in the Lower Bench of the Holešice Member. Compared to that, different environmental conditions for trace elements have been found in the Upper Bench. Reducing and acidic conditions greatly dominated for As, Mn, Ni, Zn and Cd with respect to their solubility. The results document the coal bearing sediments in the Holešice Member to be an important natural source of V, Cr, Ni, As and Pb entering the environment in increased amounts.



Fig. 7. The results of the Sequential Extraction Procedure for samples from the Lower (Bil 26, Bil 0) and Upper Bench (Lib 21, ČSA 48) of the Holešice Member. The trace element order from left-to-right corresponds to its decreasing total content in the original sample.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coal.2018.07.005.

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