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Assessment of geogenic input into Bilina stream sediments (Czech Republic)

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Abstract Over the past 100 years, the area along the River Bílina has been influenced by open-cast brown-coal mining, coal processing, petroleum refineries, and chemical plants. As a result, the extensive industrial activity has changed the overall character as well as the morphology of the landscape. A survey was underway to investigate the occurrence and distribution of various elements in the sediments of the River Bílina—a tributary of the River Elbe, a watercourse running through the Czech Republic and Germany—in order to discern the natural background from anthropogenic pollution. The study evaluated the content of selected elements (As, Zn, Pb, Cr, Ni, V, and Cu) in stream sediments of the River Bílina. Samples were taken at 20 sampling sites throughout the 82-km-long watercourse. For all the samples, the content of the elements was determined using ICP-MS after each of the sample was digested using HF and HNO_3. The results of analyses of elemental composition of stream sediments were compared with those found through such analyses made within the surrounding geological units—more specifically, Proterozoic crystalline, Tertiary volcanic, Quaternary loess, Neogene sediments, and Neogene coal. All the samples of the stream sediments examined revealed increased amounts of As, V, Ni, Cr, and Pb. Using the enrichment factor established on the basis of the regional geological background values proved that elevated levels of elements in stream sediments are not always the result of industrial contamination.

Keywords Origin of geogenic elements · Enrichment factor · Stream sediments · River Bílina · Czech Republic

Introduction

The content of main rock-forming and trace elements in recent fluvial sediments is an important indicator of the intensity of weathered underlying rocks and transporting conditions. Evaluating a potential risk and a degree of environmental pollution is incomplete without taking natural geological conditions and associated processes into account (Grba et al. 2015; Sindern et al. 2016; Singh et al. 2003). Recent reports that studied distribution of trace elements in stream sediments have revealed that

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distinguishing the origin of these phases is crucial for assessing the proportion of natural and anthropogenic sources (Bábek et al. 2015; Famera et al. 2013; Nováková et al. 2015; Sakan et al. 2014).

Elements enter fluvial systems through natural processes, such as physical and chemical weathering, as well as through human activities that include waste and sewage treatment, road runoff, or, atmospheric deposition coming from burning, mine tailings (Langedal 1997), traffic, and open-cast mining. These inputs present a significant portion of elements in the global geochemical cycle; as a result, detailed surveys at the regional level provide important information about element cycling (Doležalová Weismannová et al. 2015; Nováková et al. 2015; Rieuwerts and Farago 1996). Elements tend to adsorb onto organic matter, clays, hydrated oxides of iron and manganese, and, in particular, fine-grained particles; then, they enter the river system as complexes or hydrated ions (Vuković et al. 2014). Desorption of elements in stream sediments pose a significant threat to aquatic life due to potential bioaccumulation in tissues (Schäfer et al. 2015).

The River Bílina belongs to the most polluted tributaries of the River Elbe. Covering a total of 1071 km^2 approximately, the River Bílina catchment area is divided into a zone of mountain streams draining the Krušné Hory Mts., a flatland located in the Most Basin, and a territory lining the river stretch passing through the České Středohoří Mts. In this catchment area, the hydrological regime is influenced by anthropogenic activity; it is assumed that the area upstream of the place where the river enters the Jirkov Reservoir is the only portion with a natural hydrological regime (Kaiglová et al. 2015a, b).

The region has been known from the Middle Ages for metallic ore and brown-coal mining. The subsequent development of various industries was closely linked with brown coal mines which saw their biggest expansion in the 1960s to 1980s. Surface mining caused changes to deep circulation of groundwater with pressurized water entering from the underground into the area of open-cast mines directly. For these reasons, a system was developed to drain the catchment area; it replaced the small watercourses and altered, in terms of quantity and quality, the materials entering the River Bílina. Numerous studies have documented the degree of contamination of River Bílina sediments, water, and biota (Blahová et al. 2012; Jurajda et al. 2010; Kohušová et al. 2011; Kružíková and Svobodová 2012; Orendt et al. 2012; Pribylova et al. 2006). High levels of heavy metals, such as Hg, Cd, Cr, Cu, and Zn, were also found in River Elbe sediments downstream of the river's confluence with the River Bílina (Brügman 1995).

While the area has been the subject of numerous studies from the aspect of presence of toxic contaminants, the importance of geological background for the overall environmental burden of the river systems has still not been assessed. As a result, any data on the content of elements in geological units are only available in archives and databases. There are detailed studies that cover distribution of trace elements in the coal extracted in the Most Basin (Bouška and Pešek 1999; Pešek and Sivek 2016; Voroš et al. 2018; Fojtík et al. 2018). These results show that for brown coal and any other coal, Clarke values (Ketris and Yudowich 2009) regarding As, Cu, Cr, Ni, Pb, V, and Zn are significantly lower compared to the median of content of elements given for the upper and lower benches of the main coal seam in the Most Basin. In addition, an increased amount of all the trace elements mentioned above was found in the coal claystone (Fojtík et al. 2018). According to the published studies, enrichment factor (EF) can be used to assess any anthropogenic input into the environmental system and presents a good tool for evaluating heavy metal additions; hence, EF was calculated for selected elements in order to eliminate provenance effects in downstream trends. The main aim of this study was to define background levels of As, Zn, Pb, Cr, Ni, V, and Cu in sediments using known elemental composition of the surrounding geological units, as well as describe enrichment of the sediments from the River Bílina by calculating enrichment factors.

Material and methods

Description of samples

Twenty samples (Fig. 1) were collected in the River Bílina within its catchment area. Each sample was collected at 20 cm of the bottom layer. The total content was determined for each of the identified elements, i.e., As, Cu, Cr, Ni, Zn, Pb, and V. A total of 116 samples of rocks were used to characterize the potential entry of natural elements into the river system; they represent the main geological units—Proterozoic crystalline, Neogene volcanics, sediments and coal mass, and Quaternary loess. This information was compared with the present content of trace elements identified in stream sediments of the River Bílina (Table 1).

In upper reaches of the River Bílina, the geological basement is made up of the Krušné Hory Mts. crystalline complex (samples R001 and R002). This part of the catchment area lacks any broad floodplains, thus is characterized by a limited space for overbank sediment deposition. It is located in a remote area with low density of settlement and no direct industrial factors. Downstream of this territory, the greater surroundings of the town of Jirkov present a strongly anthropogenically transformed area. At sampling site R003, the stream was channelled; at sampling site R004, the riverbed is lined with concrete. Some extent of this reach was also enclosed in pipes. This section is known for an active open-cast mine located in the surroundings. Downstream of the piped reach, the channel cuts deep into the ground and its surroundings present a strongly anthropogenically affected area (sampling site R005). The river passes by a refinery (sampling sites R006–R008) to flow through the Most Corridor where it was turned into a medium- to deep-cut, stabilized, straight channel (sampling sites R009–R013). The area of the river passing through the České Středohoří Mts. (English: Central Bohemian Uplands) is characterized by the lowest amount of anthropogenic interventions except that the river channel was straightened and adjusted (R014–R018). Just upstream of the confluence with the River Elbe, there is a highly urbanized area with heavy anthropogenic modifications. From this part onwards, the channel of the River Bílina was completely straightened, made considerably deep-cut, and modified through engineering measures (R019–R020).

Sample preparation; trace element analysis

All samples were air-dried and, subsequently, sieved to achieve a grain size below 0.063 mm. The content of As, Cu, Cr, Ni, Zn, Pb, V, Al, and Ti was analyzed in the laboratory of Czech Geological Survey, Prague, Czech Republic (see http://geology.cz for details). The laboratory was accredited by the Czech Accreditation Institute under ISO 17025. The method of determining elements was as follows: 5 g was taken from each sample, placed in a high-pressure digestion vessel made of polytetrafluoroethylene and digested using 1 ml HF (40%) and 3 ml HNO_3 (65%). For Al and Ti, the determination was carried out using a flame atomic absorption spectroscope (Perkin-Elmer Analyst 200). For As, Cr, Ni, Zn, Cu, Pb, and V, the content was determined using ICP-MS Thermo Scientific X, Series 2. Arsenic was determined using hydride generation atomic absorption spectroscopy. The analytical procedure used solely analytical-grade reagents. Deionized water was used throughout the study. Analytical blanks were run in the same way as the samples.

The methodology was validated by analysis of the following certified reference materials: NIST SRM 2702 marine sediment; NIST SRM 2781 domestic sludge (either of them National Institute of Standards and Technology, USA) and METRANAL 32 sandy soil (Analytika Czech Republic). Limits of detection were established as follows:

$$\mathrm{Al} = 0.01\%; \mathrm{As} = 0.1\ \mu\mathrm{g\ g}^{-1}; \mathrm{Cr} = 2\ \mu\mathrm{g\ g}^{-1};$$
$$\mathrm{Cu} = 1\ \mu\mathrm{g\ g}^{-1}; \mathrm{Ni} = 5\ \mu\mathrm{g\ g}^{-1}; \mathrm{Pb} = 1\ \mu\mathrm{g\ g}^{-1};$$
$$\mathrm{Ti} = 7\ \mu\mathrm{g\ g}^{-1}; \mathrm{V} = 2\ \mu\mathrm{g\ g}^{-1}; \text{and } \mathrm{Zn} = 1\ \mu\mathrm{g\ g}^{-1}.$$

Normalization of the data was applied to the assessment of anomalous metal contribution using Al and Ti as proxies. The following formula was used for enrichment factor calculation:

$$EF = (A/An)/(B/Bn)$$

A	The content of the element in the river sample
An	The content of the normalized element in the river sample
B	The content of the element in the background samples
Bn	The content of the normalized element in the background samples

Local background values were calculated for each element as a median content for the dominant rocks within the catchment area. The background values from the Proterozoic rocks and the Neogene sediments were used as background levels to calculate EF for samples R001–R003 and R004–R020.

Results and discussion

Lithogenic origin

The River Bílina flows down from the Krušné Hory Mts. to territories known as the Most Basin and the

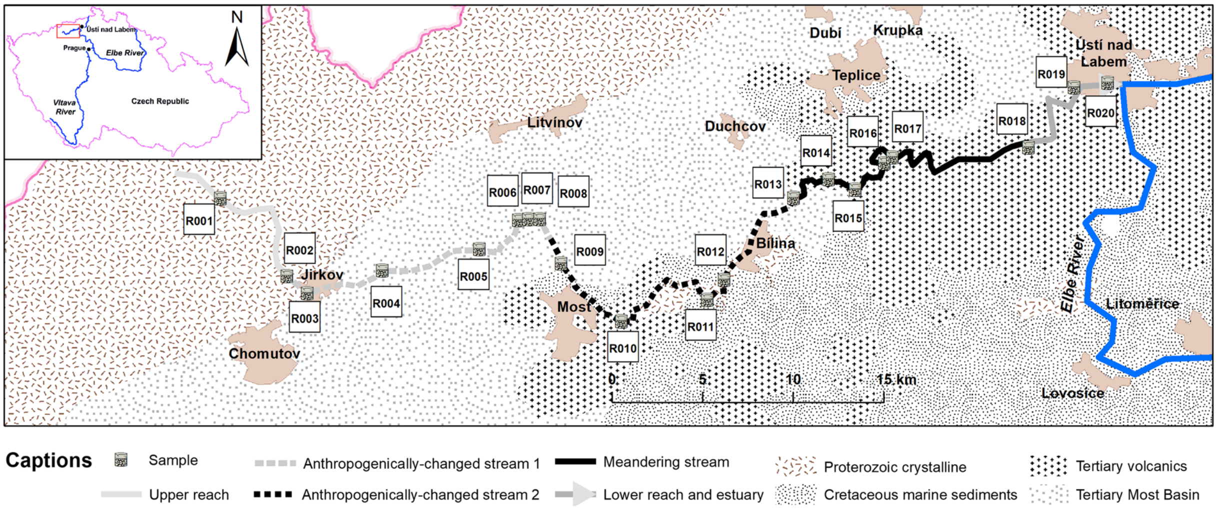

Fig. 1 The course of the River Bílina with indicated sampling sites and main geological units in the adjacent area. The watercourse is segmented based on the nature of its channel; the stretches are indicated in the distribution charts for each element

České Středohoří Mts. The geological background (Fig. 1) consists of the Proterozoic Krušné Hory Crystalline Complex (Vilímek and Raška 2016), Variscan volcanic rocks and granitoids (Cajz et al. 1999), Cretaceous marine sediments (Caracciolo et al. 2011), Neogene sediments (Pešek and Sivek 2016), and Quaternary loess and loess loams.

The reciprocal ratio of Al_2O_3, SiO_2, and TiO_2 allows distinguishing the mutual relations between the various rocks in the area (Fig. 2a, b). The Proterozoic crystalline and Neogene volcanic rocks present a primary source of material for Neogene and Quaternary sequences. Thus, association of studied elements should be comparable with them and a genetic relationship is expected (Bouška and Pešek 1999; Rieder et al. 2007). This is visible for values related to Proterozoic crystalline, Quaternary loess, and some Neogene clays (Fig. 2a).

Arsenic

The arsenic (As) content ranged from 21 to 969 μg g^{-1} in stream sediments (Fig. 3, Table 1). We found a lower As content in fluvial samples R001–R003 originating from the upper reach. Proterozoic crystalline is outcropping in the upper reach of the River Bílina catchment area. The amount of As significantly increased after the river entered into the area of open-cast coal mining, i.e., from sample R004 onwards. A continuous rapid decrease in As levels was observed down the stream (sample R004 to sample R019, Fig. 3). Significant drops of As

Table 1 The median content of the evaluated elements (μg g^{-1}) in the geological units. n.d. = under the limit of determination

Element	Proterozoic metamorphites $n = 14$	Tertiary volcanics $n = 43$	Tertiary coal $n = 10$	Tertiary sediments $n = 54$	Quaternary loess $n = 12$
As	2.5	3.5	40.4	2.5	33.0
V	61.0	n.d.	311.6	53.5	120.0
Cr	106.0	29.5	132.4	94.5	81.5
Ni	76.0	5.0	156.6	44.0	43.5
Cu	5.0	68.0	113.8	25.5	21.0
Zn	191.5	1006.0	63.2	199.0	265.0
Pb	17.5	3.5	34.6	14.0	24.5
Ti	3806.7	2577.8	4636.6	6414.5	5185.5
Al	72,982.3	110,029.1	n.d.	98,332.9	74,305.4

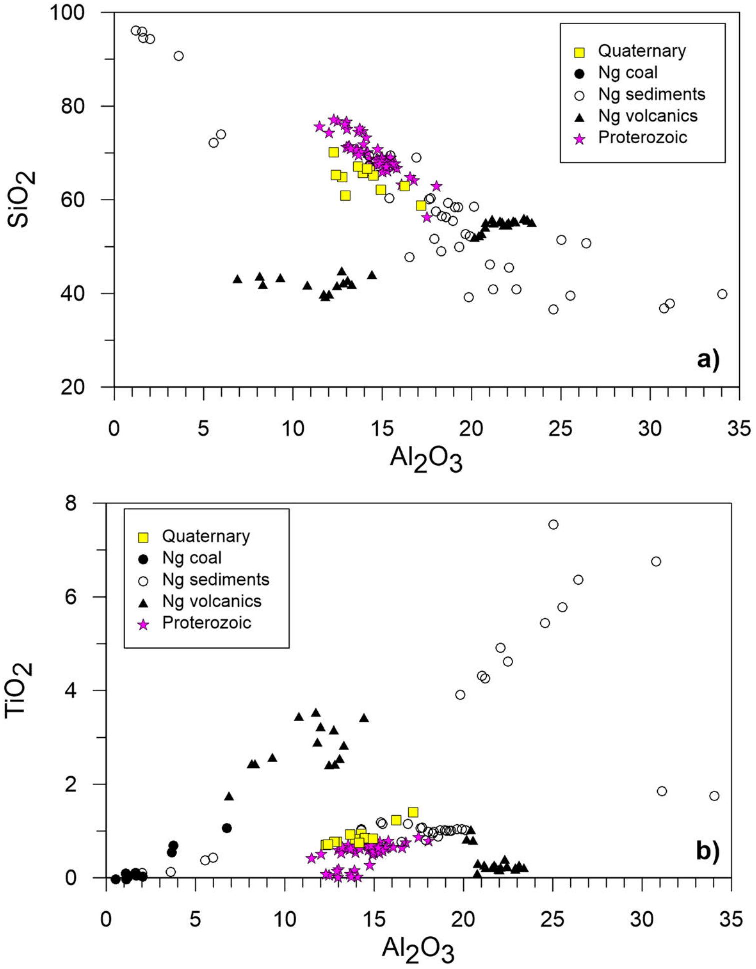

Fig. 2 **a** SiO_2-Al_2O_3 ratio (wt.%) in different types of rocky outcrops in the region. **b** Al_2O_3-TiO_2 ratio (wt.%) in main types of rocky outcrops in the region

values—displayed for samples R006, R011, and R014 in Fig. 3, could be interpreted by the arsenic content becoming diluted due to the tributaries (Fig. 1) that flow from areas not influenced by mining. Samples R018 and R019 were collected in the lowermost reach of the catchment area—one built up by Neogene volcanics, which explains the lowest As content for these samples.

Basic volcanic rocks and Neogene sediments contain low arsenic amounts while a highly variable content of the element was repeatedly documented for coal and

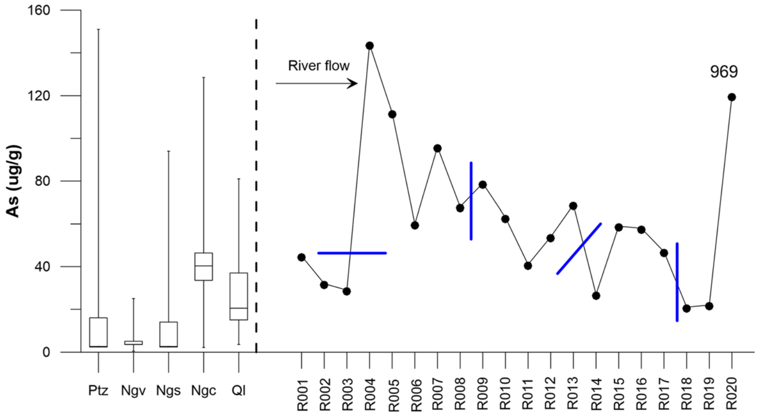

Fig. 3 The content of arsenic (μg g^{-1}) in the geological matrices related to the geological background and samples from River Bílina sediments (R001–R020). The individual river stretches indicated in Fig. 1 are indicated by the line. Captions: Ptz, Proterozoic; Ngv, Neogene volcanics; Ngs, Neogene sediments; Ngc, Neogene coal; Ql, Quaternary loess

Table 2 The content of study elements (μg g^{-1}) in stream sediments of the Bílina River

Sample	As	V	Cr	Ni	Cu	Zn	Pb	Ti	Al
R001	45.2	61.0	451.6	257.5	18.2	154.0	42.5	2757.6	59,010.3
R002	31.8	98.0	650.0	358.4	64.6	190.0	43.1	2517.8	55,570.3
R003	28.9	88.0	451.6	245.7	42.8	245.0	45.6	3776.8	64,144.0
R004	143.8	182.0	342.1	242.9	31.6	195.0	53.5	3776.8	69,277.6
R005	112.3	147.0	212.1	112.1	40.3	296.0	55.9	4735.9	81,132.6
R006	60.2	129.0	116.3	57.4	61.9	308.0	67.8	5035.7	74,464.1
R007	96.3	126.0	116.3	139.3	68.5	395.0	63.6	4855.8	72,876.4
R008	67.7	346.0	143.7	101.4	90.1	367.0	64.2	5455.3	75,469.7
R009	78.8	982.0	348.9	190.9	180.7	375.0	103.2	4436.2	69,118.8
R010	62.6	740.0	123.2	109.1	201.2	501.0	64.7	5335.4	60,651.0
R011	41.4	422.0	458.4	194.1	113.6	330.0	40.9	5155.6	61,656.5
R012	53.7	453.0	191.6	72.0	99.2	290.0	49.7	6534.4	63,614.7
R013	69.1	724.0	177.9	100.9	202.8	493.0	67.2	6774.2	66,631.4
R014	26.8	176.0	547.4	275.8	73.3	266.0	32.5	3417.1	48,743.1
R015	58.9	411.0	150.5	76.0	108.6	443.0	58.4	6474.4	64,144.0
R016	58.0	454.0	177.9	77.7	125.7	487.0	60.8	6954.0	66,472.6
R017	46.5	426.0	301.0	134.1	142.1	616.0	430.0	5335.4	56,681.7
R018	20.7	121.0	622.6	353.9	40.6	205.0	27.4	3477.0	50,912.9
R019	22.3	81.0	602.1	242.7	85.3	433.0	92.7	4256.3	52,871.1
R020	968.6	301.0	369.5	157.5	165.2	694.0	367.6	6354.5	55,464.4

Proterozoic rocks (Bouška and Pešek 1999; Pešek et al. 2005). This suggests that increased arsenic amounts probably originate from Neogene coal. It was found that no parent rock contains so much arsenic as the most polluted River Bílina sediments (Fig. 3). This can be caused by the high mobility of the element and its presence on surfaces exposed to rain. Considerable amounts of sorption can be assumed to be underway on hydrated Fe and Al oxides.

Copper

A low copper content was detected in Quaternary loess (median 14 μg g^{-1}) and Proterozoic rocks (Table 2). A higher copper content was detected in samples from Neogene volcanics and coal (Fig. 4). Contrary to the above, a lower Cu content was found in samples R001–R008 that represent the area of the upper and the middle reach of the watercourse. The Cu values started

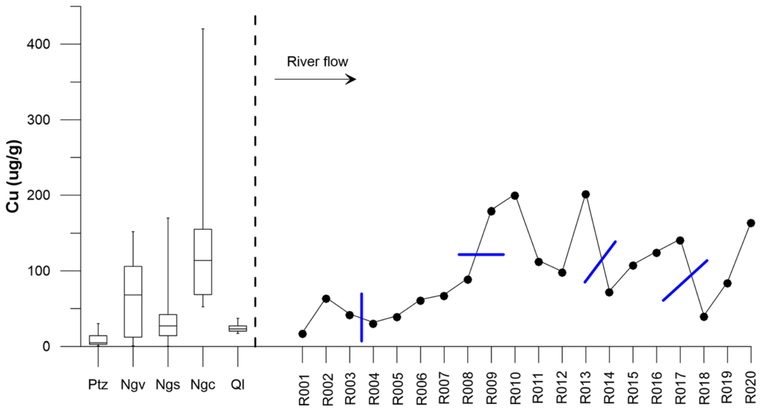

Fig. 4 The content of copper (μg g^{-1}) in the geological matrices related to the geological background and samples from River Bílina sediments (R001–R020). The individual river stretches indicated in Fig. 1 are indicated by the line. Captions: Ptz, Proterozoic; Ngv, Neogene volcanics; Ngs, Neogene sediments; Ngc, Neogene coal; Ql, Quaternary loess

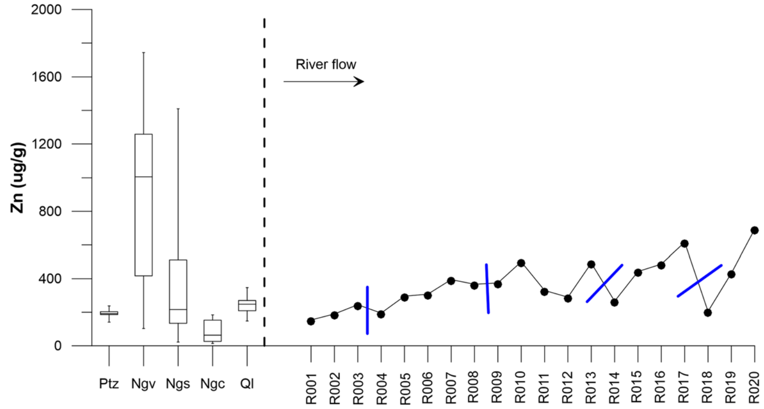

Fig 5 The zinc content (μg g^{-1}) in the geological matrices related to the geological background and samples from River Bílina sediments (R001–R020). The individual river stretches indicated in Fig. 1 are indicated by the line. Captions: Ptz, Proterozoic; Ngv, Neogene volcanics; Ngs, Neogene sediments; Ngc, Neogene coal; Ql, Quaternary loess

increasing from sample R009 to fluctuate downstream. The highest values were detected in samples R009, R010, and R013 that were collected from the wider surroundings of the towns of Most and Bílina. This part of the region is surrounded by open-cast mines and defunct tailings (Fig. 4).

The copper content ranged from 18 to 203 μg g^{-1} in the studied stream sediments and exceeded median values in parent rocks. The remarkable decrease in the Cu content as measured for samples R011, R012, R014, and R018 was influenced by the geological background consisting of Cretaceous sediments and Neogene volcanics. In contrast to the natural content of Cu (1–30 μg g^{-1}) in the rocks located in the Krušné Hory Mts., we assume that the element accompanies fine-grained Neogene deposits and coal in increased amounts (Fig. 4).

Table 3 Enrichment factor (EF) values for the content of As, V, Cr, Ni, Cu, Zn, and Pb in River Bílina stream sediments relative to Al and Ti as standardization elements

	As		V		Cr		Ni		Cu		Zn		Pb	
	EFAl	EFTi	EFAl	EFTi	EFAl	EFTi	EFAl	EFTi	EFAl	EFTi	EFAl	EFTi	EFAl	EFTi
R001	22.4	25.0	1.2	1.4	5.3	5.9	4.2	4.7	4.5	5.0	1.0	1.1	3.0	3.4
R002	16.7	19.2	2.1	2.4	8.1	9.3	6.2	7.1	17.0	19.5	1.3	1.5	3.2	3.7
R003	13.2	11.7	1.6	1.5	4.8	4.3	3.7	3.3	9.7	8.6	1.5	1.3	3.0	2.6
R004	81.6	97.7	4.8	5.8	5.1	6.1	7.8	9.4	1.8	2.1	1.4	1.7	5.4	6.5
R005	54.4	60.8	3.3	3.7	2.7	3.0	3.1	3.5	1.9	2.1	1.8	2.0	4.8	5.4
R006	31.8	30.7	3.2	3.1	1.6	1.6	1.7	1.7	3.2	3.1	2.0	2.0	6.4	6.2
R007	52.0	50.9	3.2	3.1	1.7	1.6	4.3	4.2	3.6	3.5	2.7	2.6	6.1	6.0
R008	35.3	31.8	8.4	7.6	2.0	1.8	3.0	2.7	4.6	4.2	2.4	2.2	6.0	5.4
R009	44.8	45.6	26.1	26.5	5.3	5.3	6.2	6.3	10.1	10.2	2.7	2.7	10.5	10.7
R010	40.6	30.1	22.4	16.6	2.1	1.6	4.0	3.0	12.8	9.5	4.1	3.0	7.5	5.6
R011	26.4	20.6	12.6	9.8	7.7	6.0	7.0	5.5	7.1	5.5	2.6	2.1	4.7	3.6
R012	33.2	21.1	13.1	8.3	3.1	2.0	2.5	1.6	6.0	3.8	2.3	1.4	5.5	3.5
R013	40.8	26.2	20.0	12.8	2.8	1.8	3.4	2.2	11.7	7.5	3.7	2.3	7.1	4.5
R014	21.6	20.1	6.6	6.2	11.7	10.9	12.6	11.8	5.8	5.4	2.7	2.5	4.7	4.4
R015	36.1	23.3	11.8	7.6	2.4	1.6	2.6	1.7	6.5	4.2	3.4	2.2	6.4	4.1
R016	34.3	21.4	12.6	7.8	2.8	1.7	2.6	1.6	7.3	4.5	3.6	2.3	6.4	4.0
R017	32.3	22.4	13.8	9.6	5.5	3.8	5.3	3.7	9.7	6.7	5.4	3.7	53.3	36.9
R018	16.0	15.3	4.4	4.2	12.7	12.2	15.5	14.8	3.1	2.9	2.0	1.9	3.8	3.6
R019	16.6	13.4	2.8	2.3	11.8	9.6	10.3	8.3	6.2	5.0	4.0	3.3	12.3	10.0
R020	686.9	391.1	10.0	5.7	6.9	3.9	6.3	3.6	11.5	6.5	6.2	3.5	46.6	26.5

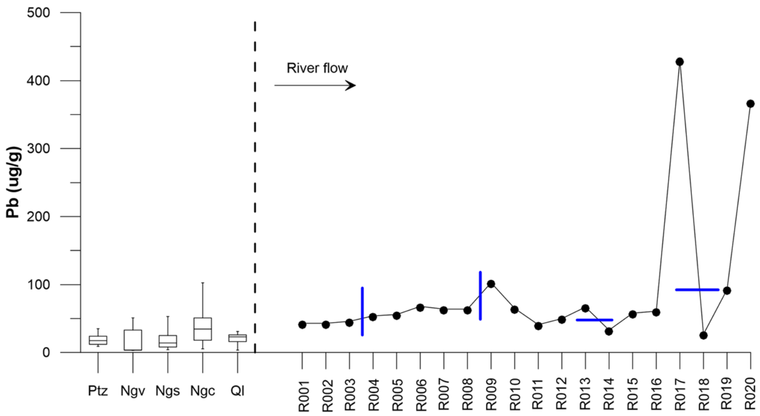

Fig 6 The lead content (μg g^{-1}) in the geological matrices related to the geological background and samples from River Bílina sediments(R001–R020). The individual river stretches indicated in Fig. 1 are indicated by the line. Captions: Ptz, Proterozoic; Ngv, Neogene volcanics; Ngs, Neogene sediments; Ngc, Neogene coal; Ql, Quaternary loess

Zinc

The results show that the Zn content in coal is lower than in stream sediments neighboring open-cast mines (Fig. 5). The median of the zinc content was 265 μg g^{-1}, 63 μg g^{-1}, and 1006 μg g^{-1} for Quaternary loess, Neogene coal, and Neogene volcanic rocks, respectively. In the investigated fluvial material, a highly variable content of Zn was observed (Fig. 5). The lowest values were found in the samples from upper reaches (R001–R004). The zinc content significantly varied in the samples from the middle and lower reaches. The highest values were noticed in sediments in the wider surrounding of the towns of Bílina and Teplice.

To conclude, we assume weathering of volcanic rocks and Neogene sandstones to be the main process affecting the zinc content in the sediments (Fig. 5). Since the EF Zn/Al Zn/Ti (Table 3) is rising from point R007, the input of zinc into the river system can be expected to be one of anthropogenic origin. Here, dissolved zinc is usually the issue; it comes from frequently used objects such as railings, barriers, and parts of bridges that undergo treatment using galvanizing or zinc-coating technology.

Lead

Lead (Pb) fluctuated in stream sediments throughout the flow of the River Bílina with concentrations (27–103 μg g^{-1}) being consistent with those found in the natural background of surrounding units (Fig. 6), i.e., Quaternary loess, Neogene volcanics and sediments and coal mass. The rare instances of extreme values in samples R017 (430 μg g^{-1}) and R020 (368 μg g^{-1}) revealed an unknown anthropogenic input. The EF Pb/Al and Pb/Ti (Table 3) identified in R004 increases downstream. It is possible to deduce that the extensive industrial activity in the region is responsible for the systematic anthropogenic input of lead into the river system; emission from industrial activity—except coal mining and processing—is typically considered an anthropogenic source.

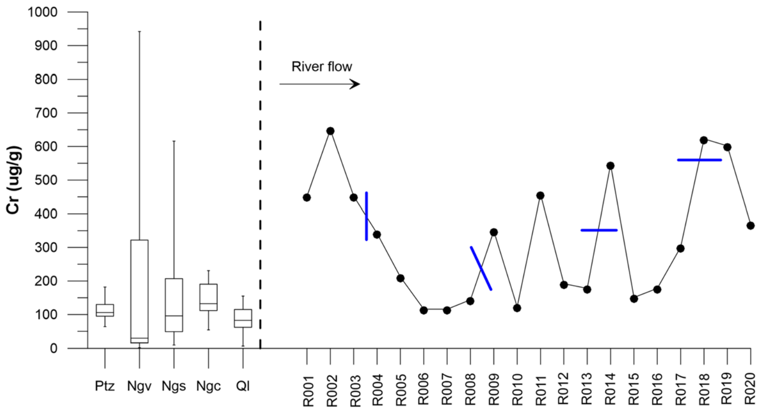

Fig 7 The chromium content (μg g^{-1}) in the geological matrices related to the geological background and samples from River Bílina sediments (R001–R020). The individual river stretches indicated in Fig. 1. are indicated by the line. Captions: Ptz, Proterozoic; Ngv, Neogene volcanics; Ngs, Neogene sediments; Ngc, Neogene coal; Ql, Quaternary loess

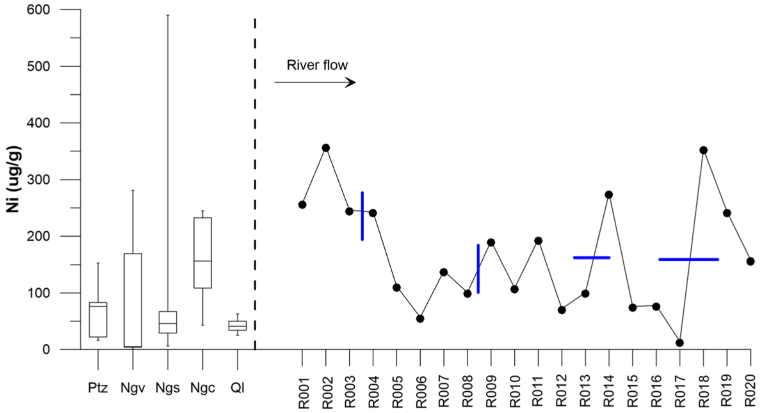

Fig 8 The nickel content (μg g^{-1}) in the geological matrices related to the geological background and samples from River Bílina sediments (R001–R020). The individual river stretches indicated in Fig. 1 are indicated by the line. Captions: Ptz, Proterozoic; Ngv, Neogene volcanics; Ngs, Neogene sediments; Ngc, Neogene coal; Ql, Quaternary loess

Chromium

The content of chromium (Cr) in stream sediments (Fig. 7) highly increased in the upper reach (R002, 650 μg g^{-1}). As the river enters an artificial channel, amounts of chromium gradually fall to 116 μg g^{-1} (R007). In the subsequent river stretch, high Cr levels alternating low levels was an apparent feature with no direct link to the surrounding environment. After the river channel enters industrial premises, the content increased up to the maximum at R018 and R019 where the values reached concentrations 623 and 602 μg g^{-1}, respectively. Extreme Cr content was found in Neogene volcanics and sediments (Fig. 7, Table 2).

Nickel

The nickel (Ni) content was found to be highest in the upper reach (Fig. 8, R002, 358 μg g^{-1}). As the river enters the artificial channel, nickel decreases gradually to as little as 57 μg g^{-1} at point R006. In the following reach downstream, high and low levels take turn without any apparent relation to the environment. The overall pattern for Ni is the same as for Cr, indicating the same source. The median of Ni in the geological underlay ranged from 5 to 156 μg g^{-1} (Table 2). Any extreme amounts were established in Neogene sediments when they significantly exceeded the concentrations measured in stream sediments (Fig. 8).

Vanadium

The vanadium content was very low in sediments of the upstream part of the river (Fig. 9) between points R001 and R007 (61–182 μg g^{-1}). Subsequently, there is a sharp increase in the content (982 μg g^{-1}) at point R009, followed by high values alternating low values without any obvious trend. The highest vanadium content was found in coal with a median of 311 μg g^{-1}. In Neogene volcanic rocks, the vanadium content was below the limit of determination and in the Quaternary loess and Neogene sediments, it does not exceed 227 μg g^{-1} (Table 2).

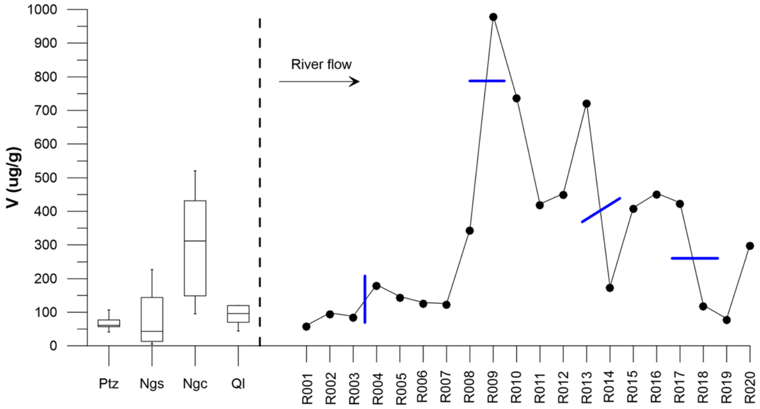

Fig 9 The vanadium content (μg g^{-1}) in the geological matrices related to the geological background and samples from River Bílina sediments (R001–R020). The individual river stretches indicated in Fig. 1 are indicated by the line. Captions: Ptz, Proterozoic; Ngv, Neogene volcanics; Ngs, Neogene sediments; Ngc, Neogene coal; Ql, Quaternary loess

Natural background levels

Ti and Al were applied as normalization elements for River Bílina sediments due to the following reasons: (1) the natural content of both elements tends to be stable; (2) Al and Ti oxides reflect the genetic ratio in the lithogenic basement of the study area; (3) Al and Ti are associated with fine solid materials and are resistant to weathering.

EF values were interpreted as suggested by Sakan et al. (2014), where EF < 1 indicates no enrichment, < 3 is minor enrichment;, 3–5 is moderate enrichment, 5–10 is moderately severe enrichment, 10–25 is severe enrichment, 25–50 is very severe enrichment, and > 50 is extreme enrichment. The contamination degrees are indicated by the line in Fig. 10.

Enrichment factor values of the studied elements in stream sediments using the average values of EF_{Al} varied from extreme severe to minor enrichment and decreased in the following order: As > Pb > V > Cu > Ni > Cr > Zn (Fig. 10). The same order of elements was

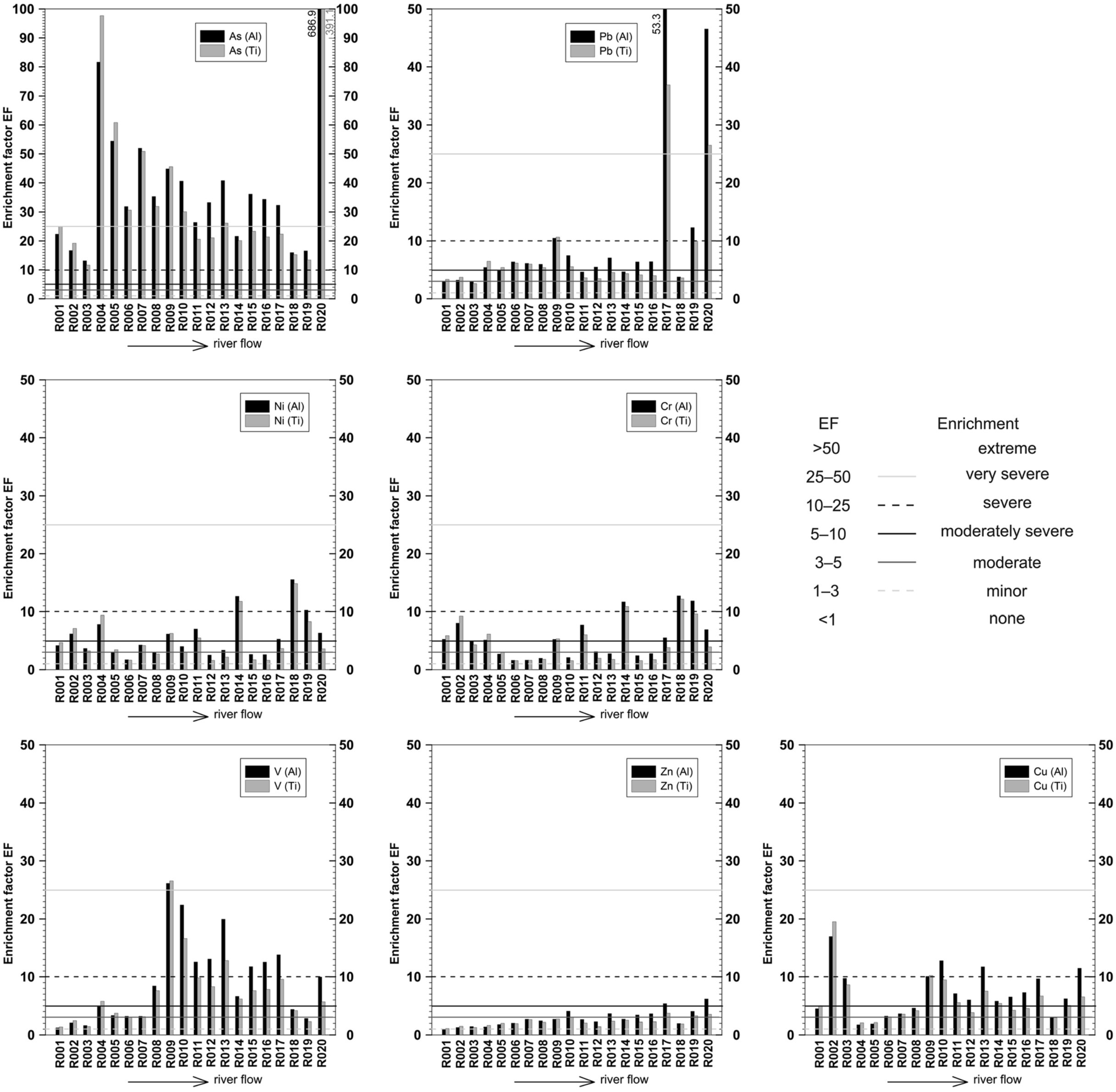

Fig. 10 Enrichment factor (EF) values calculated for the content of As, Pb, V, Cu, Ni, Cr, and Zn in River Bílina stream sediments relative to Al and Ti as standardization elements

obtained when Ti was used as a normalization factor for EF_{Ti}, i.e., As > Pb > V > Cu > Ni = Cr > Zn. Since the river reach between the towns of Most and Bílina passes in the close vicinity of mine tailings and coal-storing premises and is therefore directly affected by mining (Kaiglová et al. 2015a), it can be assumed that coal and coal-bearing sediments present an important input into the River Bílina system and coal can be expected to be a source of element enrichment. The increased amounts of Pb and As seemed not to be consistent with the natural background conditions. Therefore, it is possible to assume their anthropogenic origin, which supports the conclusions reached by Kohušová et al. (2011).

Conclusion

The present study of chemical composition of River Bílina sediments and the surrounding rocks from geological units demonstrated the importance of a comprehensive approach in areas heavily affected by anthropogenic activity. Open-cast brown-coal mines and the related activities have changed the overall character of the landscape not only in terms of morphology but also from the aspect of the quantity of the material entering into the river setting. It involves defunct tailings that contain Neogene sediments, i.e., gangue and a small proportion of coal mass, and are subject to intense weathering on contact with precipitation. As a result, the Neogene sediments are supposed to be the main natural source for assessing environmental pollution in the area. For these sediments, median values of evaluated elements are 2.5 $\mu g\ g^{-1}$ for As, 25.5 $\mu g\ g^{-1}$ for Cu, 199.0 $\mu g\ g^{-1}$ for Zn, 14.0 $\mu g\ g^{-1}$ for Pb, 94.5 $\mu g\ g^{-1}$ for Cr, 44.0 $\mu g\ g^{-1}$ for Ni, and 53.5 $\mu g\ g^{-1}$ for V. Due to high percentage of organic matter and reduction conditions, there is enhanced content of the elements in the fluvial environment of the River Bílina.

Since in industrial processes other than coal processing activity As is not present at any larger scale, Ng sediments can be considered a primary source of increased levels of this element in river sediments. Industrial sources of the study elements unrelated to coal mining and processing can be assumed only for Cu, Zn, and Pb.

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References

Bábek, O., Grygar, T. M., Faměra, M., Hron, K., Nováková, T., & Sedláček, J. (2015). Geochemical background in polluted river sediments: How to separate the effects of sediment provenance and grain size with statistical rigour? *Catena, 135*, 240–253. https://doi.org/10.1016/j.catena.2015.07.003.

Blahová, J., Schandlová, L., Grabic, R., Fedorová, G., Randák, T., & Svobodová, Z. (2012). Assessment of polycyclic aromatic hydrocarbon contamination of the Bílina River (Czech Republic) using passive water samplers and fish biliary metabolites. *Acta Veterinaria, 2011*(80), 353–357. https://doi.org/10.2754/avb201180040353.

Bouška, V., & Pešek, J. (1999). Quality parameters of lignite of the North Bohemian Basin in the Czech Republic in comparison with the world average lignite. *International Journal of Coal Geology, 40*, 211–235. https://doi.org/10.1016/S0166-5162(98)00070-6.

Brügman, L. (1995). Metals in sediments and suspended matter of the Elbe River. *Science of the Total Environment, 159*, 53–65. https://doi.org/10.1016/0048-9697(94)04252-i.

Cajz, V., Vokurka, K., Balogh, K., Lang, M., & Ulrych, J. (1999). The České středohoří Mts.: Volcanostratigraphy and geochemistry. *Geolines, 9*, 21–28.

Caracciolo, L., Le Pera, E., Muto, F., & Perri, F. (2011). Sandstone petrology and mudstone geochemistry of the Peruc–Korycany Formation (Bohemian Cretaceous Basin, Czech Republic). *International Geology Review, 53*(9), 1003–1031. https://doi.org/10.1080/00206810903429011.

Doležalová Weismannová, H., Pavlovský, J., & Chovanec, P. (2015). Heavy metal contaminations of urban soils in Ostrava Czech Republic: assessment of metal pollution and using principal component analysis. *International Journal of Environmental Research, 9*, 683–696.

Famera, M., Babek, O., Matys Grygar, T., & Nováková, T. (2013). Distribution of heavy-metal contamination in regulated river-channel deposits: a magnetic susceptibility and grain-size approach; River Morava, Czech Republic. *Water, Air, and Soil Pollution, 224*, 1525–1542. https://doi.org/10.1007/s11270-013-1525-1.

Fojtík, S., Voroš, D., & Geršlová, E. (2018). Distribution of trace elements in the lower and upper benches of the main coal seam in the Most Basin. *Geoscience Research Reports, 51*(1), 43–45.

Grba, N., Neubauer, F., Šajnovič, A., Stojanovič, K., & Jovančičevič, B. (2015). Heavy metals in Neogene sedimentary rocks as a potential geogenic hazard for sediment, soil, and surface and groundwater contamination (eastern

Posavina and the Lopare Basin, Bosnia and Herzegovina). *Journal of the Serbian Chemical Society, 80*(6), 827–838.

Jurajda, P., Adámek, Z., Janáč, M., & Valová, Z. (2010). Longitudinal patterns in fish and macrozoobenthos assemblages reflect degradation of water quality and physical habitat in the Bilina river basin. *Czech J. Anim. Sci., 3*, 123–136.

Kaiglová, J., Jiřinec, P., Langhammer, J., Ingeduldová, E., Chalupová, D., Ferenčík, M., & Jánský, B. (2015a). Numerical modelling of heavily polluted fine-grained sediments remobilization in northern Czech Republic. *Ecohydrology and Hydrobiology, 15*, 111–124. https://doi.org/10.1016/j.ecohyd.2015.02.001.

Kaiglová, J., Langhammer, J., Jiřinec, P., Janský, B., & Chalupová, D. (2015b). Numerical simulations of heavily polluted fine-grained sediment remobilization using 1D, 1D+ and 2D channel schematization. *Environmental Monitoring and Assessment, 187*(3), 115. https://doi.org/10.1007/s10661-015-4339-3.

Ketris, M., & Yudowich, Y. (2009). Estimations of clarkes for carbonaceous biolithes: world averages for trace element contents in black shales and coals. *International Journal of Coal Geology, 78*, 135–148. https://doi.org/10.1016/j.coal.2009.01.002.

Kohušová, K., Havel, L., Vlasák, P., & Tonika, J. (2011). A long-term survey of heavy metals and specific organic compounds in biofilms, sediments, and surface water in a heavily affected river in the Czech Republic. *Environmental Monitoring Assessment, 174*, 555–572. https://doi.org/10.1007/s10661-010-1478-4.

Kružíková, K., & Svobodová, Z. (2012). Assessment of mercury contamination in the Bílina River (Czech Republic) using indicator fish. *Acta Veterinaria, 81*, 63–68. https://doi.org/10.2754/avb201281010063.

Langedal, M. (1997). Dispersion of tailings in the Knabena—Kvina drainage basin, Norway, 1: Evaluation of overbank sediments as sampling medium for regional geochemical mapping. *Journal of Geochemical Exploration, 58*, 2–3. https://doi.org/10.1016/S0375-6742(96)00069-6.

Nováková, T., Matys Grygar, T., Kotková, K., Elznicová, J., Strnad, L., & Mihaljevič, M. (2015). Pollution assessment using local enrichment factors: the Berounka River (Czech Republic). *Journal of Soils and Sediments, 16*, 1081–1092. https://doi.org/10.1007/s11368-015-1315-z.

Orendt, C., Wolfram, G., Adámek, Z., Jurajda, P., & Schmitt-Jansen, M. (2012). The response of macroinvertebrate community taxa and functional groups to pollution along a heavily impacted river in Central Europe (Bilina River, Czech Republic). *Biologia, 67*, 180–199.

Pešek, J., & Sivek, M. (2016). *Coal-bearing basins and coal deposits of the Czech Republic*. Prague: Czech Geology Survey http://unicat.nalis.bg/Record/BAS.000521302#description.

Pešek, J., Bencko, V., Sýkorová, I., Vašíček, M., Michna, O., & Martinek, K. (2005). Some trace elements in coal of the Czech Republic, environment and health protection implications. *Central European Journal of Public Health, 13*, 153–158.

Pribylova, P., Klanova, J., & Holoubek, I. (2006). Contamination of the Czech aquatic environment by short and medium chain chlorinated paraffin's. *Environmental Pollution, 144*(1), 248–254. https://doi.org/10.1016/j.envpol.2005.12.020.

Rieder, M., Crelling, J. C., Sustai, O., Drábek, M., Weiss, Z., & Klementová, M. (2007). Arsenic in iron disulfides in a brown coal from the North Bohemian Basin, Czech Republic. *International Journal of Coal Geology, 71*, 115–121. https://doi.org/10.1016/j.coal.2006.07.003.

Rieuwerts, J., & Farago, M. (1996). Heavy metal pollution in the vicinity of a secondary lead smelter in the Czech Republic. *Applied Geochemistry, 11*, 17–23. https://doi.org/10.1016/0883-2927(95)00050-X.

Sakan, S., Dević, G., Relić, D., Anđelković, I., Sakan, N., & Đorđević, D. (2014). Evaluation of sediment contamination with heavy metals: the importance of determining appropriate background content and suitable element for normalization. *Environmental Geochemistry and Health, 67*, 97–113. https://doi.org/10.1007/s10653-014-9633-4.

Schäfer, S., Buchmeier, G., Claus, E., Duester, L., Heininger, P., Körner, P., Mayer, P., Paschke, A., Rauert, C., Reifferscheid, G., Rüdel, H., Schlechtriem, C., Schröter-Kermani, C., Schudoma, D., Smedes, F., Steffen, D., & Vietoris, F. (2015). Bioaccumulation in aquatic systems: methodological approaches, monitoring and assessment. *Environmental Sciences Europe, 27*, 5. https://doi.org/10.1186/s12302-014-0036-z.

Sindern, S., Tremöhlen, M., Dsikowitzky, L., Gronen, L., Schwarzbauer, J., Siregar, T. H., Ariyani, F., & Irianto, H. E. (2016). Heavy metals in river and coast sediments of the Jakarta Bay region (Indonesia)—Geogenic versus anthropogenic sources. *Marine Pollution Bulletin, 110*(2, 30 September 2016), 624–633. https://doi.org/10.1016/j.marpolbul.2016.06.003.

Singh, M., Müller, G., & Singh, I. B. (2003). Geogenic distribution and baseline concentration of heavy metals in sediments of the Ganges River, India. *Journal of Geochemical Exploration., 80*(1), 1–17. https://doi.org/10.1016/S0375-6742(03)00016-5.

Vilímek, V., & Raška, P. (2016). The Krušné Hory Mts.—The longest mountain range of the Czech Republic. In T. Pánek & J. Hradecký (Eds.), *Landscapes and landforms of the Czech Republic. World Geomorphological Landscapes*. Springer. https://doi.org/10.1007/978-3-319-27537-6_10.

Voroš, D., Geršlová, E., Díaz-Somono, M., Sýkorová, I., Suárez-Ruizi, I., Havelcová, M., & Kuta, J. (2018). Distribution and mobility potential of trace elements in the main seam of the Most Coal Basin. *International Journal of Coal Geology, 196*, 139–147.

Vuković, D., Stankovič, S. J., Vukovič, Ž., & Jakkovič, K. (2014). Transport and storage of heavy metals in the Sava River Basin in Serbia. *Journal of the Serbian Chemical Society, 79*(3), 379–387.