

Geochemical and Pb isotopic evidence for sources and dispersal of metal contamination in stream sediments from the mining and smelting district of Příbram, Czech Republic

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Pb isotopes properly complete traditional investigations of metal sources and dispersal in contaminated stream sediments.

Abstract

Stream sediments from the mining and smelting district of Příbram, Czech Republic, were studied to determine the degree, sources and dispersal of metal contamination using a combination of bulk metal and mineralogical determinations, sequential extractions and Pb isotopic analyses. The highest metal concentrations were found 3–4 km downstream from the main polymetallic mining site (9800 mg Pb kg⁻¹, 26039 mg Zn kg⁻¹, 316.4 mg Cd kg⁻¹, 256.9 mg Cu kg⁻¹). The calculated enrichment factors (EFs) confirmed the extreme degree of contamination by Pb, Zn and Cd (EF > 40). Lead, Zn and Cd are bound mainly to Fe oxides and hydroxides. In the most contaminated samples Pb is also present as Pb carbonates and litharge (PbO). **Lead isotopic analysis indicates that the predominant source of stream sediment contamination is historic Pb–Ag mining and primary Pb smelting (²⁰⁶Pb/²⁰⁷Pb = 1.16), while the role of secondary smelting (car battery processing) is negligible.**

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1. Introduction

Mining and smelting constitute the principal sources of metals in the environment at a large number of sites (Hudson-Edwards et al., 1996; Miller, 1997; Monna et al., 2000; Hillier et al., 2001; MacKenzie and Pulford, 2002; Ettler et al., 2004, 2005). In the mining district of Příbram, Czech Republic, extensive Ag–Pb mining has occurred since Middle Ages up to the 1970s and U mining was practiced mainly in the second half of the 20th century. Furthermore, the Pb

smelter, which is in operation for over 200 years, constituted another significant source of pollution in the area. In the last few decades, a large number of studies have focused on the distribution of pollution of soils (Rieuwerts et al., 1999; Ettler et al., 2004, 2005), alluvial soils (Borůvka et al., 1996) and mosses (Sucharová and Suchara, 2004) by metals.

Stream sediments are believed to record the environmental impact on fluvial systems over time and are often studied to determine the overall pollution in an area (Hillier et al., 2001). However, information on the bulk concentration of a contaminant alone is not sufficient to assess the fate or potential mobility of contaminants and must be combined with other, more precise mineralogical or chemical techniques

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(Hudson-Edwards et al., 1996; Hillier et al., 2001). The purpose of this article is to provide a complete image of the metal contamination in the bed sediments of two major streams draining the mining and smelting district of Příbram. Investigation of the Pb, Zn, Cu, Cd, Fe, Mn, Ni and Cr concentrations in stream sediments was coupled with sequential extraction analyses (SEA), detailed investigation of physico-chemical parameters, mineralogical analysis by X-ray diffraction analysis (XRD) and identification of Fe and Mn oxides and hydroxides by voltammetry of microparticles and UV–Vis spectroscopy. In addition, the Pb isotopic composition was used to trace possible sources of contamination and metal dispersal at different levels of the stream, using the data on historic pollution sources in the area obtained by Ettler et al. (2004).

2. Materials and methods

2.1. Study area

The mining and smelting district of Příbram is located approximately 60 km SW of Prague, the capital of the Czech Republic (Fig. 1). The geology of the area is dominated by two Upper Proterozoic belts (volcano-sedimentary rocks), located within the Cambrian geological units (greywackes and conglomerates) and accompanied by the Variscan intrusions of Bohutín (diorite; SW of Příbram) and the Central Bohemian Pluton (granites and granodiorites; SE of Příbram) (Vlašimský, 1982) (Fig. 1). The mineralization is related to the

Variscan intrusions and occurs as two types of deposits: (i) polymetallic ore veins (Pb–Ag–Zn) located at Bohutín and Březové Hory, SW of Příbram (left Proterozoic belt dipping to the SE); and (ii) uranium deposits located in the contact aureole of the Upper Proterozoic rocks and the Central Bohemian Pluton, SE of Příbram (right Proterozoic belt dipping to the NW) (Vlašimský, 1982). The polymetallic ore deposits are mainly composed of Ag-bearing galena (PbS), sphalerite (ZnS), antimonite (Sb_2S_3) and various sulphosalts in the gangue formed especially by siderite ($FeCO_3$) (Bambas, 1990; Vlašimský, 1982). The U deposits are mainly formed by uraninite (UO_2) within the mixed carbonate gangue minerals (Vlašimský, 1982).

The Příbram district has a long history of Pb–Ag mining, probably dating from the time of the Celtic civilisation, 6th–1st century B.C. (Ettler et al., 2001). The mining activity in the polymetallic ore district peaked between 1850 and 1950 (Bambas, 1990). About 3500 t Ag, 480 000 t Pb and 260 000 t Zn were mined in the polymetallic ore district at Bohutín and Březové Hory (Bambas, 1990; Vlašimský, 1982). From 1786 to the 1970s, the smelter located 4 km NW of Příbram processed the Pb–Ag ores mined in the area (Ettler et al., 2001) and since 1972, secondary scrap, mainly car batteries, has been processed. A description of the smelter technology is given elsewhere (Ettler, 2000; Ettler et al., 2001). The peak of mining activity in the U district occurred from the 1950s until it was terminated in 1989; the ore was processed outside the studied area.

The Příbram district is drained by two principal perennial streams: the Litavka and the Příbramský streams (Fig. 1). The Litavka springs out W of Láz and flows through the area of the historical mining sites at Bohutín and Březové Hory and the smelter area at Lhota (total length 56 km, total drainage basin approximately 200 km², channel and alluvium widths at Trhové Dušníky 4 m and 20 m, respectively). The stream sediments were sampled along the first 18 km downstream to the confluence with the right-hand tributary of the Příbramský stream. The Příbramský stream is formed by several small

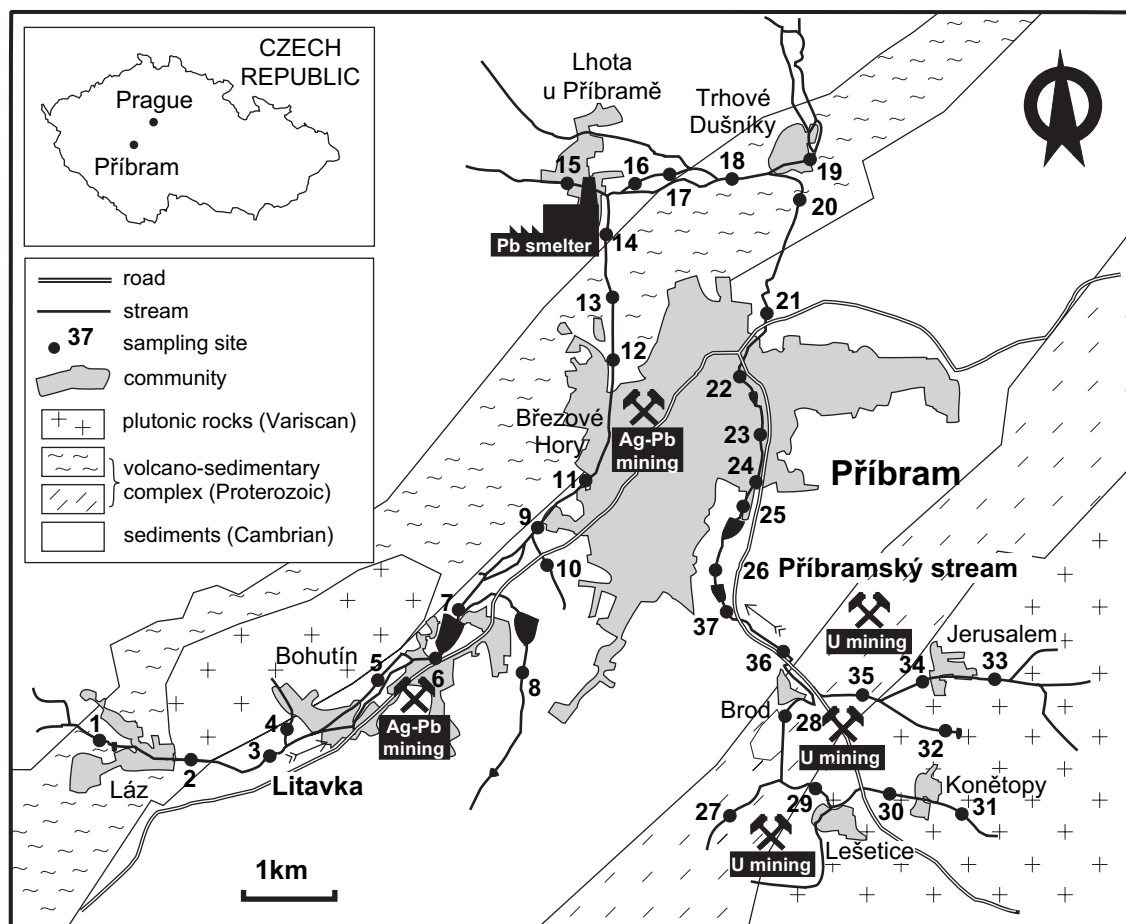


Fig. 1. Location of stream sediment samples, historic mining and smelting areas and geology of the Příbram district.

tributaries springing out in the area of the U mining district. It flows through the centre of Příbram and is connected to the Litavka near Trhové Dušňky (total length 11 km, channel and alluvium widths at the confluence with the Litavka are 4 m and 5 m, respectively). The discharge of both streams at their confluence is approximately the same, varying from 0.25 to 0.30 m³ s⁻¹. The caliber of the material transported by both streams varies mainly from silt to coarse sand fraction, with gravel fraction transported only during spring floods.

2.2. Sampling and preparation of stream sediments and other materials

A total of 37 stream sediments were sampled in both streams (the Litavka and the Příbramský streams) in May 2003 in order to include both relatively pristine and highly polluted areas in the vicinity of potential pollution sources (mines, smelter) (Fig. 1). At each sampling site, the samples were taken using a plastic trowel near the middle of the flow of the stream. About 1 kg of sediment surface was collected into clean polyethylene (PE) bags and treated immediately on returning to the laboratory. The sediment samples were wet-sieved through an acid-cleaned 63- μ m mesh nylon sieve in order to obtain the chemically active material, dried at 40 °C to constant weight and ground in an agate mortar to ensure homogeneity. In order to obtain the geological background materials, about 3 kg of rock from each geological unit of the studied area were sampled and finely ground in an agate mortar.

2.3. Analytical procedure

2.3.1. Bulk concentrations

A mass of 1 g of dry sample was dissolved in 10 ml HF and 1 ml HClO₄ and evaporated to dryness. The procedure was repeated with 10 ml HF and 1 ml HClO₄ in order to remove total silica, was again evaporated, and the residue was dissolved in 10 ml 10% (v/v) HCl and diluted to 50 ml with deionised water (MilliQ+). All the acids used in the dissolution procedure were reagent grade (Merck, Germany and Lachema, Czech Republic). The same dissolution procedure was used for the decomposition of bedrock samples. The concentrations of Pb, Zn, Cu, Cd, Fe, Mn, Al, Cr, Co and Ni were determined on a Varian SpectrAA 200 HT flame absorption atomic spectrometer (FAAS) under standard analytical conditions. The analytical precision and accuracy of sample decompositions and metal concentrations' measurements were controlled by AGV-2 (andesite) reference material certified by USGS and an internal laboratory sediment standard with high trace element concentrations (the accuracy was better than 5%). In addition, the relative standard deviations (RSDs) for duplicate measurements of 10 randomly selected samples were generally better than 10%.

In order to assess the degree of stream sediment contamination, the enrichment factors (EF) were calculated with respect to the normalized value of Al using the formula (Andrews and Sutherland, 2004):

$$EF = \frac{\left(\frac{X_i}{Al_i}\right)}{\left(\frac{X_0}{Al_0}\right)} \quad (1)$$

where X_i and X_0 are the concentrations of the individual metals in the sample and in the background, respectively, and Al_i and Al_0 are the concentrations of Al in the sample and in the background, respectively. Aluminium is widely used as a conservative element for normalization. The background values corresponded to the element concentrations in the sampled bedrocks of the geological units at each sampling site or were taken from the literature (Vlašimský, 1982; Ettler et al., 2004). The five-category pollution index (Andrews and Sutherland, 2004) has been used for the pollution assessment: EF < 2, minimal pollution; EF 2–5, moderate pollution; EF 5–20, significant pollution; EF 20–40, high pollution; EF > 40, extreme pollution.

2.3.2. Sequential extraction analysis (SEA)

Selected samples of sediments from the Litavka stream ($n = 8$) were submitted to sequential extraction analysis (SEA) according to Tessier et al. (1979) in order to determine the chemical fractionation of Pb, Zn, Cu and Cd.

These samples corresponded to the least and most contaminated stream sediments from the areas affected by mining of polymetallic ores and smelting activities. The detailed SEA procedure is described elsewhere (Tessier et al., 1979; Gleyzes et al., 2002). Each SEA fraction was operationally defined as (i) exchangeable/salt-displaceable (fraction A); (ii) acid extractable/bound to carbonates or specifically sorbed (fraction B); (iii) reducible/bound to Fe and Mn oxides and hydroxides (fraction C); (iv) oxidisable/bound to organic matter (OM) and sulphides (fraction D); and (v) residual/silicate (fraction E). A procedural blank was run for each extraction step and the standard deviation of duplicate analysis was <10% RSD for the individual SEA step. The sum of the individual fractions corresponded well to the concentration obtained by total dissolution of the sample. The agreement was very good for Cu ($r^2 = 0.9973$), Zn ($r^2 = 0.9957$) and Cd ($r^2 = 0.9950$) and relatively good for Pb ($r^2 = 0.9831$).

2.3.3. Physico-chemical properties and mineralogy of stream sediments

The measurements of the sediment pH, total content of organic and inorganic carbon (TOC and TIC) and sulphur (S), cation exchange capacity (CEC) and oxalate-extractable Fe, Al and Mn were analogous to those used for smelter-impacted soils as described in Ettler et al. (2005). The heavy mineral fraction of eight samples selected for SEA was submitted to X-ray diffraction (XRD) analysis following a 24-h separation of a 0.2-g aliquot part of sediment in 10 ml of bromoform in a 15-ml glass tube placed in a sonication bath. A PAN-Analytical X'Pert Pro diffractometer equipped with a diffracted-beam monochromator was used for XRD analyses. The analyses were performed using a CuK α radiation (40 kV, 30 mA) in the range of 3–80° 2 θ (step size 0.02, counting time 150 s per step using an X'Celerator multichannel detector). Qualitative analysis was performed with the X'Pert HighScore software, version 1.0d (PANalytical, the Netherlands), equipped with the JCPDS PDF-2 database (ICDD, 2002). Samples selected for SEA were also studied by UV–Vis diffuse reflectance spectroscopy (DRS) and voltammetry of microparticles (VMP) in order to confirm the presence of Fe, Mn (and possibly other free metal) oxides and hydroxides in the samples. The DRS and VMP analyses were performed according to Grygar and van Oorschot (2002) and Grygar et al. (2003).

2.3.4. Pb isotopic analysis

An aliquot part of the dry sample (stream sediments, rocks) was dissolved in reagent grade double-distilled mineral acids (HF–HClO₄–HNO₃). The sample diluted to 25 \pm 5 μ g l⁻¹ was purified using an anion exchange resin (Bio-Rad AG1X8) and analysed using a VG Elemental PQ3 quadrupole-based inductively coupled plasma mass spectrometer (ICP-MS) as described in Ettler et al. (2004). Calibration against a common Pb isotopic standard (NIST SRM 981) was used after each sample measurement to correct mass bias and dead time effects. The standard error for both ratios ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb was <0.4% RSD for the stream sediments and <0.5% RSD for the bedrocks.

3. Results and discussion

3.1. Stream sediment properties and mineralogy

The sediment pH values ranged from 5.0 to 7.4. The most acid pH of 5.0 was found in sample 14 from the vicinity of the smelter, but pH values of >7.0 were commonly observed in samples from the Příbramský stream. Interestingly, the pH values in the mining areas were not acidic, but near-neutral, probably as a result of the strong buffering capacity of the carbonates in the gangue of the mined ores. The concentration of TOC in stream sediments varied from 3.55 to 6.38%. In samples 11 and 12 in the vicinity of the Březové Hory mining area, TIC was detected analytically with values of 0.13 and 0.06%, respectively (the detection limit was 0.05%). This observation may also be related to the presence of gangue-derived carbonate minerals in the sediments, detected by XRD analysis (see below). Sulphur was detected in samples from the vicinity of

the Březové Hory mines (up to 0.33%, sample 12) and Pb smelter (0.66%, sample 14) (the detection limit was 0.02%). The CEC of the samples was relatively high, ranging from 12.3 to 26.8 cmol kg⁻¹. The oxalate-extractable Fe, Mn and Al varied significantly as follows: Fe: 7.6–44.8 g kg⁻¹, Mn: 0.4–4.9 g kg⁻¹, Al: 1.8–4.9 g kg⁻¹. An increase in oxalate-extractable Fe to values >12 g kg⁻¹ was observed in the mining and smelting areas, attaining 44.8 g kg⁻¹ in sample 14.

XRD indicated the substantial amounts of metal-bearing phases within the heavy mineral fraction of the most contaminated samples from the Litavka stream. In addition to the commonly found Fe(III) oxides and hydroxides, the presence of sphalerite (ZnS), litharge (PbO), cerussite (PbCO₃), hydrocerussite (Pb₃(CO₃)₂(OH)) and wulfenite (PbMoO₄) was observed (Table 1). Goethite (FeOOH), lepidocrocite (FeOOH), hematite (Fe₂O₃) and free Pb oxides were also confirmed by VMP and DRS (Table 1). The presence of Fe(III) oxides and hydroxides is consistent with high oxalate-extractable Fe contents. The observed Fe(III) oxides and hydroxides replace or precipitate as the alteration products of primary phases, here probably siderite or Fe hornblende, as it has been observed at other sites (Hudson-Edwards et al., 1996). No Mn oxides or hydroxides were detected in the studied samples by XRD, VMP and DRS.

3.2. Bulk metal contamination

The spatial variation of bulk concentrations of Pb, Zn, Cd and Cu is shown in Fig. 2. The concentrations of these elements in the Litavka stream sediments significantly increase in the mining district of Březové Hory (samples 11 and 12) and reach the highest values in the vicinity of the Pb smelter (samples 14 and 16) up to 9805 mg Pb kg⁻¹, 26 039 mg Zn kg⁻¹, 316.4 mg Cu kg⁻¹, and 256.9 mg Cd kg⁻¹ (Fig. 2). For Pb, the

first important increase in the concentrations occurs in the proximity of the historic mining area of Bohutín (samples 5 and 6) (Fig. 2). The spatial variations of the bulk concentrations of Pb, Zn, Cd and Cu in the stream sediments of the Příbramský stream all have similar patterns and are significantly lower than in the Litavka stream. The highest concentrations were observed in the vicinity of the confluence with the Litavka stream (sample 20) and in the inhabited area of Příbram (samples 21–24).

The calculated enrichment factors (EFs) for the individual samples are given in Table 2. A large number of samples of both streams exhibit EF values in the category of “extreme” pollution (EF > 40). The EFs for Pb indicate that all the samples from the Litavka stream are extremely polluted especially in the mining areas (Bohutín and Březové Hory) and in the vicinity of the smelter. Extreme pollution of the Litavka stream sediments has also been observed for Zn and Cd, especially in the vicinity of Březové Hory and the Pb smelter. In contrast, the Cu pollution is relatively low (Table 2).

For the Příbramský stream, extreme contamination by Pb, Zn and Cd was observed close to the confluence with the Litavka stream (sample 20) and SE from the smelter stack (Table 2). Very high pollution has also been observed for Pb and Zn in the Příbram town area (Table 2). Copper exhibits low EF values corresponding to minimal or moderate pollution.

The concentrations of the other analysed elements are scattered, without any significant trend, exhibiting the following concentration ranges: Mn: 0.9–9.4 g kg⁻¹, Fe: 24–93 g kg⁻¹, Co: 12.6–56.9 mg kg⁻¹, Ni: 21.1–77.5 mg kg⁻¹, Cr: 28.2–137.6 mg kg⁻¹. No significant pollution was observed for these elements using the EF approach. It is important to note that no statistically significant relationship between the physico-chemical properties (pH, CEC, TOC) and bulk metal (Pb, Zn, Cd, Cu) concentrations was observed. This observation is probably related to the fact that the pool of metals in the system is extremely large and will be related rather to the specific mineralogical composition (e.g., the presence of Fe(III) oxides and hydroxides) and mineralogy-related chemical fractionation of individual contaminant metals.

3.3. Chemical fractionation and metal mobility

The chemical fractionation of Pb, Zn, Cd and Cu in selected stream sediments is depicted in Fig. 3. Zinc, Cd and Pb show similar chemical fractionations with a predominant reducible fraction (corresponding to the operationally defined fraction bound to Fe and Mn oxides and hydroxides) (up to 84% Cd, 71% Pb and 61% Zn of the total speciation) (Fig. 3). This observation is consistent with the mineralogical analysis confirming the presence of Fe(III) oxyhydroxides, in particular goethite or lepidocrocite (FeOOH) (Table 3). Chemisorption or co-precipitation with these crystallised Fe(III) oxyhydroxides may constitute an important sink mechanism for metals present in extremely high concentrations under the near-neutral pH conditions observed in our system. The acid-extractable fraction, operationally defined as bound to carbonates,

Table 1
Mineralogy of the heavy mineral fraction of selected stream sediment samples from the Litavka stream

Mineral	Formula	Sample		
		11	14	16
		Location		
		Mining area	Smelter area	Dowstream from the smelter
Hornblend	Ca ₂ (Mg, Fe ²⁺ , Al) ₅ (Si, Al) ₈ O ₂₂ (OH) ₂	***	***	***
Rutile/anatase	TiO ₂		**	*
Goethite	FeOOH	** ^a		* ^a
Lepidocrocite	FeOOH		** ^a	
Hematite	Fe ₂ O ₃		*	** ^a
Siderite	FeCO ₃	***	**	**
Sphalerite	ZnS	*	*	*
Cerussite	PbCO ₃		*	*
Hydrocerussite	Pb ₃ (CO ₃) ₂ (OH)		*	*
Litharge	PbO		* ^a	* ^a
Wulfenite	PbMoO ₄	*		

Description: ***abundant, **common, *present.

^a Detected by XRD, VMP and DRS.

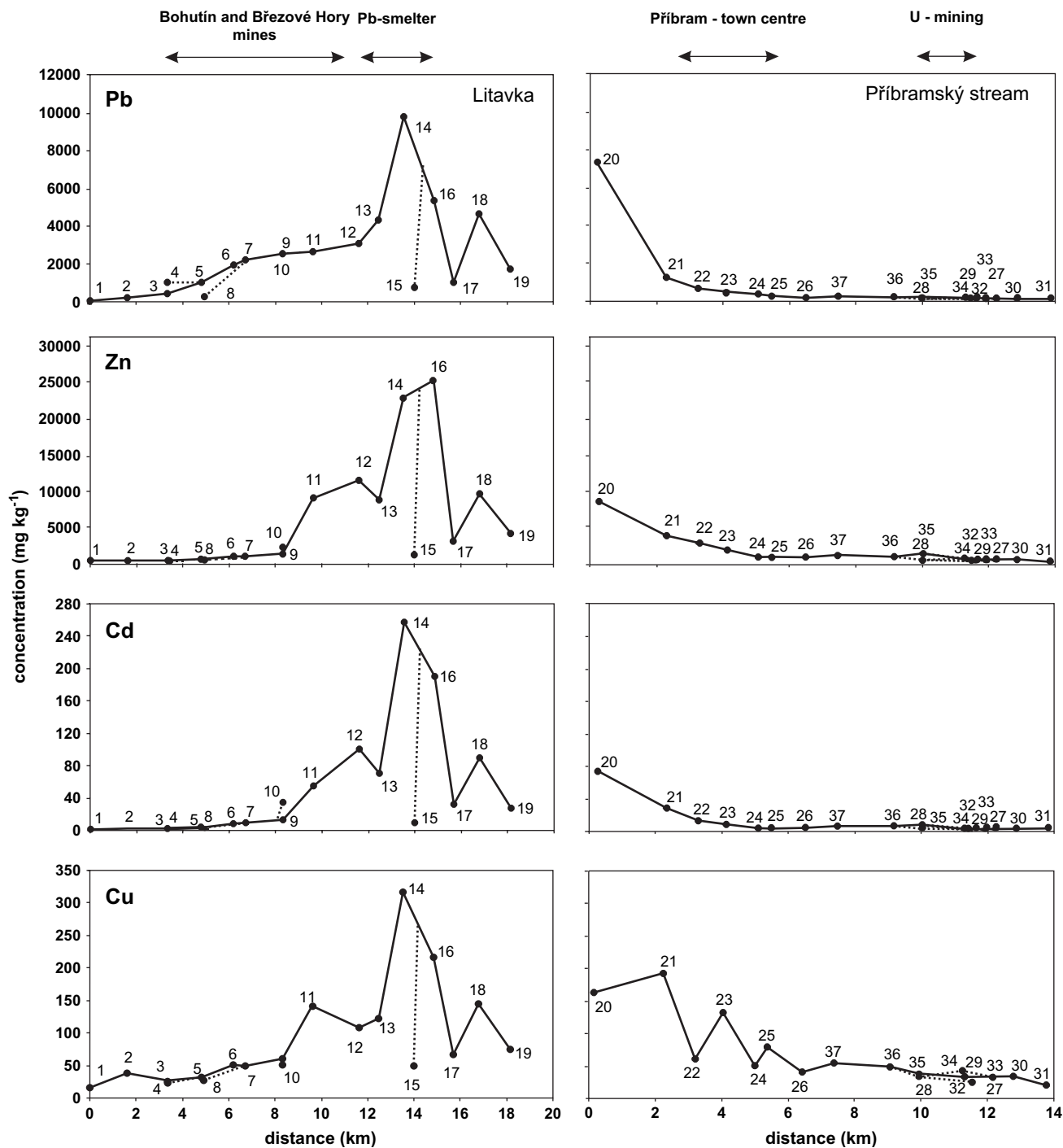


Fig. 2. The spatial variation of bulk concentrations of Pb, Zn, Cd and Cu in stream sediments from the Litavka and Příbramský streams.

is important especially for Pb (up to 39%) and Zn (up to 30% of total speciation). These data are also supported by mineralogical analysis of the sediments, indicating the presence of Pb carbonates (cerussite and hydrocerussite) in the heavy mineral fraction of the sediment (Table 1). Zinc may be present in this fraction as co-precipitated with other isostructural carbonates (Speer, 1990), e.g., siderite (FeCO₃) commonly found in the ore gangue. The oxidisable fraction was typically dominant for Cu (up to 85%) and was more pronounced in heavily contaminated samples (Fig. 3). This observation is not surprising

while the preferential binding of Cu to organic matter is connected with a strong affinity for complexation of Cu²⁺ ions by humic substances even at low concentrations (Stumm and Morgan, 1981). Cadmium also exhibits an important binding in the oxidisable fraction (up to 46% especially in heavily contaminated samples) (Fig. 3). The oxidisable fraction accounts for 12–42% of the Pb and 8–19% of the Zn, and can correspond to binding to either organic matter or sulphides, as sphalerite (ZnS) was confirmed in the heavy mineral fraction. The presence of sphalerite may also be responsible for an

Table 2

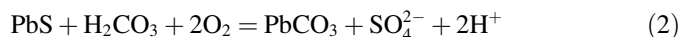
Calculated enrichment factors (EFs^a) for Pb, Zn, Cd and Cu for stream sediments of the Litavka and Příbramský streams

EF – Litavka stream					EF – Příbramský stream				
Sample	Pb	Zn	Cd	Cu	Sample	Pb	Zn	Cd	Cu
1	3	2	1	0	20	265	39	45	2
2	13	5	3	1	21	51	42	13	6
3	22	3	1	0	22	21	25	5	1
4	29	3	1	0	23	21	21	4	4
5	57	5	3	1	24	18	11	2	2
6	112	10	7	1	25	11	10	2	2
7	112	9	6	1	26	10	13	3	2
8	16	3	2	1	27	4	2	2	0
9	136	12	9	1	28	14	11	7	0
10	141	21	24	1	29	3	21	2	1
11	193	111	51	4	30	2	25	2	1
12	165	73	91	2	31	5	3	1	0
13	198	47	55	1	32	4	3	1	0
14	544	333	157	13	33	6	5	2	1
15	42	13	5	2	34	3	22	2	1
16	198	164	91	3	35	7	4	3	0
17	34	18	14	1	36	9	8	4	1
18	265	65	86	2	37	11	10	4	1
19	110	31	30	1					

^a EF > 40, extreme pollution (the values given in *italics* correspond to extreme pollution); EF 20–40, high pollution; EF 5–20, significant pollution; EF 2–5, moderate pollution; EF < 2, minimal pollution.

important recovery of Cd in the oxidisable fraction; Bambas (1990) stated that Cd was commonly associated with ZnS in the ores mined at Bohutín and Březové Hory (up to 1.46 wt.% Cd).

In oxidised and moist environments, primary metal-bearing minerals (galena, Cd-bearing sphalerite) commonly undergo physico-chemical transformation (dissolution, oxidation and precipitation of secondary phases) (Hudson-Edwards et al., 1996). The absence of primary galena in the heavy mineral fraction of stream sediments suggests its complete dissolution, partial binding of Pb on newly formed Fe(III) oxides and hydroxides or transformation to Pb carbonates under high pH/pCO₂ (Hudson-Edwards et al., 1996):



Under oxidised near-neutral conditions, litharge (PbO) could be another oxidation product, as was confirmed by the mineralogical investigation in the stream sediment downstream from the mining area (Table 1). Primary sphalerite behaves differently and seems to be only partially dissolved (because detected by XRD), and oxidises to yield a dissolved

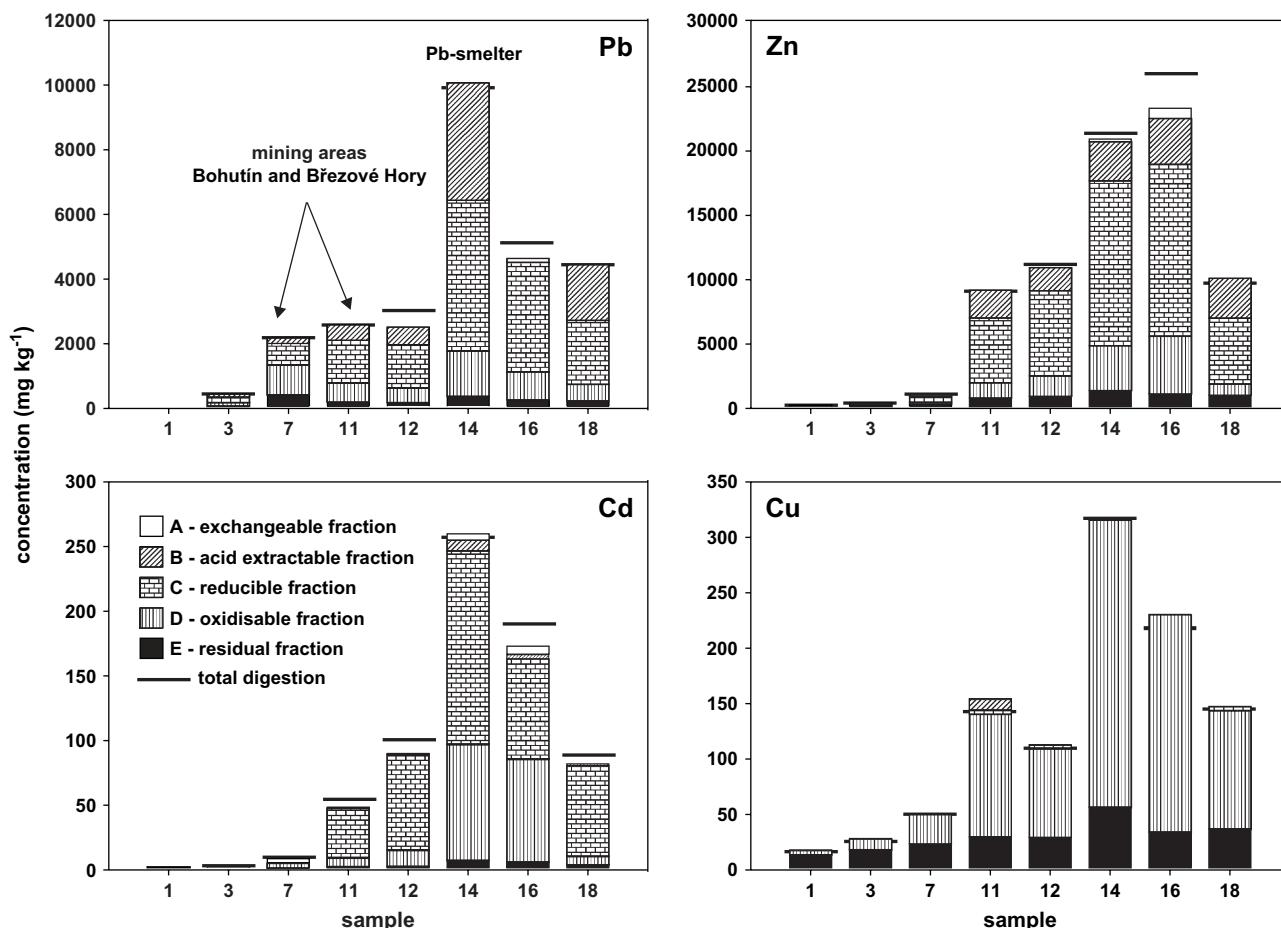


Fig. 3. Chemical fractionation of Pb, Zn, Cd and Cu in selected stream sediments of the Litavka obtained by SEA.

Table 3

Lead isotopic compositions (mean values and standard deviations) and total Pb contents in the bedrocks of the main geological units and waste materials from Pb metallurgy in the Příbram district

Bedrock	Sampling location	$^{206}\text{Pb}/^{207}\text{Pb}$		$^{208}\text{Pb}/^{206}\text{Pb}$		Pb (mg kg ⁻¹)
		Value	1 σ	Value	1 σ	
Proterozoic						
Siltstone	Březové Hory – Pb–Ag–Zn mining dumps	1.160	0.005	2.111	0.008	35.0
Shale	Březové Hory – Pb–Ag–Zn mining dumps	1.161	0.004	2.109	0.011	19.6
Siltstone ^a	Bedrock from smelter-polluted soil profile (1 km SE of smelter)	1.166	0.003	2.101	0.008	96.7
Siltstone	Lešetice – uranium mining dumps	1.178	0.004	2.090	0.007	6.0
Cambrian						
Greywacke/conglomerate ^a	Bedrock from smelter-polluted soil profile (3 km NW of smelter)	1.220	0.003	2.032	0.003	2.5
Greywacke	NW Cambrian belt – 2 km N of Láz	1.185	0.003	2.087	0.010	1.75
Greywacke	Březové Hory bedrock	1.182	0.004	2.086	0.011	1.1
Arcose	Central Cambrian belt – 3 km W of Lešetice	1.171	0.003	2.098	0.007	8.45
Conglomerate	Central Cambrian belt – 3 km W of Lešetice	1.201	0.005	2.056	0.010	0.65
Plutonic rocks (Variscan)						
Granite	Lešetice – uranium mining dumps	1.189	0.003	2.078	0.005	6.5
Q diorite	Bohutín old dumps	1.177	0.006	2.089	0.010	1.6
Waste materials ^a						
Old metallurgical slag ^a	Metallurgical dumps – ore processing slag	1.165	0.004	2.104	0.005	2.50% ^b
Recent metallurgical slag ^a	The Příbram smelter – car battery processing slag	1.169	0.004	2.100	0.007	0.79% ^b
Recent fly ash ^a	The Příbram smelter – fly ash from car battery processing	1.177	0.003	2.081	0.004	60.5% ^b
Galena from Příbram ^a	Mineralogical collections of Charles University	1.164	0.002	2.099	0.006	86.6% ^b

^a Values from Ettler et al. (2004).

^b Concentration values (in wt.%) obtained from Ettler (2000).

species that may be adsorbed on the surface of Fe(III) oxides and hydroxides (Hudson-Edwards et al., 1996):



The adsorption of Zn on Fe(III) oxides and hydroxides is also consistent with the observed chemical fractionation of Zn (Fig. 3). The formation of secondary smithsonite (ZnCO₃), commonly observed at other sites, does not occur in our system, but zinc could possibly be co-precipitated with predominant FeCO₃, detected by XRD in samples. It is, however, important to note that newly formed carbonate minerals (cerussite, hydrocerussite) can easily break down under acidic conditions and similarly, in acid and/or reducing environments, metals bound in the reducible fraction may be liberated into the solution due to dissolution of Fe(III) oxides and hydroxides (Hudson-Edwards et al., 1996).

3.4. Pb isotopic composition and tracing of pollution sources

A strong variation has been observed in the Pb isotopic composition of the stream sediments and bedrocks ($^{206}\text{Pb}/^{207}\text{Pb} = 1.159\text{--}1.220$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.031\text{--}2.113$). The Pb isotopic compositions and bulk Pb contents in selected bedrocks and waste materials from Pb metallurgy in the Příbram area are given in Table 3. Fig. 4a represents a three-isotope graph ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$) showing the isotopic composition of sediments from the Litavka and Příbramský streams, bedrocks and waste materials (slag, fly ash) from Pb metallurgy in the Příbram district (Ettler et al., 2004).

The isotopic signature of the Cambrian bedrocks was significantly more radiogenic ($^{206}\text{Pb}/^{207}\text{Pb}$ up to 1.22) (Table 3, Fig. 4a). Interestingly, the arcose, the principal unit located in the central Cambrian belt between the town of Příbram and the U deposits, exhibits a less radiogenic Pb signature (Table 3). In contrast, the Proterozoic rocks of the Pb–Ag–Zn mining district exhibit higher Pb concentrations (up to 96.7 mg kg⁻¹) and form a distinct population at the other end of the Pb isotopic mixing line ($^{206}\text{Pb}/^{207}\text{Pb}$ equals approximately 1.16) (Table 3, Fig. 4a). In contrast to the Pb–Ag–Zn mining district, the isotopic composition of bedrocks of the SE Proterozoic belt (uranium deposits) is more radiogenic ($^{206}\text{Pb}/^{207}\text{Pb} = 1.178$), and also exhibits significantly lower bulk Pb contents (Table 3, Fig. 4a).

The isotopic composition of almost all the stream sediments from the Litavka corresponds to the isotopic signature of polymetallic mining activities at Bohutín and Březové Hory ($^{206}\text{Pb}/^{207}\text{Pb} = 1.159\text{--}1.167$). Sample 1 represents the only exception, with a $^{206}\text{Pb}/^{207}\text{Pb}$ value of 1.176 closer to the isotopic signature of the Bohutín diorite intrusion (Fig. 4a, Table 3). Fig. 4b depicts the relationship between the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and the bulk Pb content expressed as Al-normalized values. This diagram indicates high Pb contamination of the Litavka stream sediments, originating from the metalliferous Proterozoic rocks with the corresponding isotopic signature. As a result, this contamination is probably related either (i) to mining activities and dispersal of metal contaminants from Bohutín and Březové Hory or (ii) to historical emissions from ore processing in the smelter exhibiting a similar isotopic signature. The latter source would correspond rather to flushing of contaminated material from smelter-impacted soils and its settling/deposition in the channel bed of the stream during strong rain events. However,

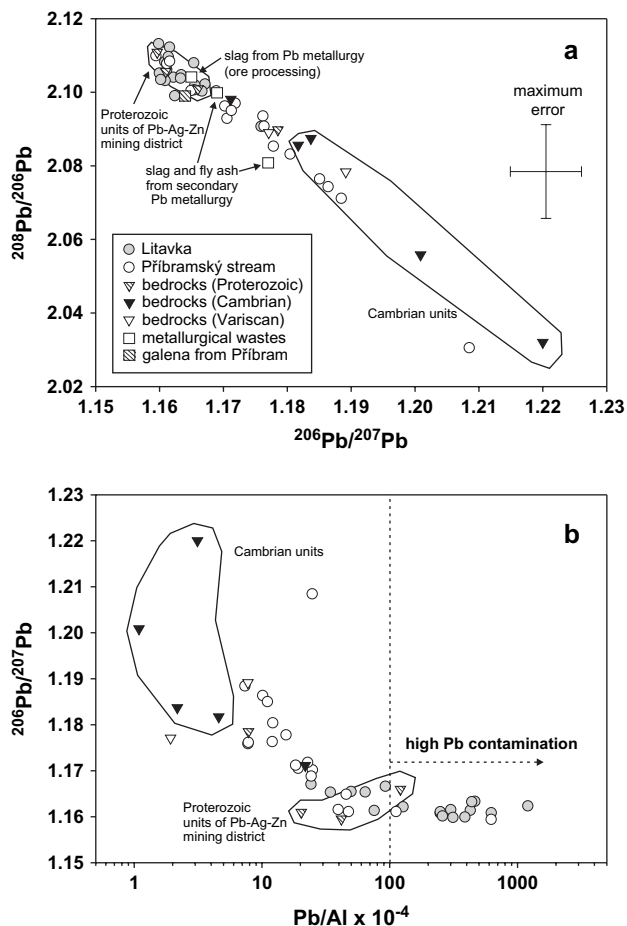


Fig. 4. (a) Three-isotope plot ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$) showing the distribution of the isotopic compositions of stream sediments and bedrocks from the Příbram district and the isotopic signatures of some waste materials from Pb metallurgy obtained from Ettler et al. (2004). (b) Diagram $^{206}\text{Pb}/^{207}\text{Pb}$ versus $\text{Pb}/\text{Al} \times 10^{-4}$ showing the sources and degrees of contamination of the stream sediments.

this source will probably be minor and cannot be isotopically clearly distinguished from the mining-derived contamination. In contrast to soil environments (Ettler et al., 2004), no contribution of Pb derived from secondary Pb smelting (car battery processing) was observed. Such a source is probably negligible because of the efficient flue-gas cleaning procedure in place for over past 10–15 years; in addition, no significant shift in the isotopic composition towards more radiogenic values typical for secondary Pb smelting was found (Table 3, Fig. 4a).

The isotopic compositions of sediments from the Příbramský stream are more variable due to the much more complex geological situation. The isotopic compositions of the upper stream samples (26–37) correspond to the signatures of background granite ($^{206}\text{Pb}/^{207}\text{Pb} = 1.189$), siltstones of the SE Proterozoic belt ($^{206}\text{Pb}/^{207}\text{Pb} = 1.178$) and Cambrian arcose with relatively low isotopic ratio values ($^{206}\text{Pb}/^{207}\text{Pb} = 1.171$) (Fig. 4a,b, Table 3). The very different isotopic composition of sample 28 ($^{206}\text{Pb}/^{207}\text{Pb} = 1.208$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.031$, Fig. 4) probably corresponds to Cambrian andesite intrusion in the close vicinity of the stream (Fig. 1). As the Pb content increases from sample 25 downstream, where the Příbramský

stream penetrates into the town of Příbram, the Pb isotopic compositions decrease from 1.170 to 1.160. Such a phenomenon unequivocally shows that the Pb input is related to the Pb–Ag–Zn mining area and/or primary Pb metallurgy. As a result, three possible transport mechanisms of Pb contamination may be proposed for stream sediments in the centre of Příbram: (i) aerial transport of fine dust from mining area (dumps, flotation sites) at Březové Hory located approximately 1.5 km E of the centre of Příbram; (ii) historical use of gangue material from old mining dumps for civil engineering purposes in the town centre; and (iii) historic long-term smelter emissions from ore processing. The latter source is consistent with the prevailing wind direction (NW) and significantly higher air-borne contamination of soils SE of the smelter stack (Rieuwerts et al., 1999; Ettler et al., 2004, 2005). The mechanism of highly contaminated surface soil and material transport into the stream during the rain events will be the same as described above. Furthermore, the contamination of sample 20 might be linked to the deposition of mining-related material in the area of the confluence of the two streams during extreme flood events (see the confluence shape in Fig. 1).

4. Conclusions

Lead isotopic tracing of possible sources of stream sediment pollution in the Příbram district indicates a distinct role of mining activities and, to a lesser extent, of primary Pb metallurgy (ore processing) ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.16$). In contrast to soil systems in the Příbram area (Ettler et al., 2004), the influence of recent secondary Pb smelting (processing of car batteries) on stream sediment contamination is considered to be negligible. The evolution of the concentration gradient shows a strong effect of the metal works, especially on the overall contamination of the stream sediments from the Litavka stream, which flows through the Pb–Ag–Zn mining district. Interestingly, a concentration peak and the presence of metal-bearing minerals (sphalerite, cerussite, hydrocerussite, PbO) were observed 3–4 km downstream from the main mining area, indicating contaminant dispersal via fluvial transport. The dense material (heavy mineral fraction enriched in metallic elements) travels in the stream bed at a slower rate and remains generally closer to the source site (Miller, 1997). A significant redistribution of the contamination can occur during the flood events and, in contrast to the heavy mineral fraction, metals bound to Fe oxides and organic matter may travel further (Miller, 1997). The SEA results reveal that, under near-neutral conditions, metals trapped by stream sediment constituents (carbonates, oxides, organic matter) exhibit relatively low mobility. However, a change in the Eh/pH conditions could induce the dissolution of secondary carbonate minerals (cerussite, hydrocerussite) and Fe(III) oxides and hydroxides, followed by a significant release of metal contaminants into the water. This study confirms that combined geochemical/mineralogical and isotopic investigation of the stream sediments is extremely useful in determining the pollution sources and degree of contamination compared to the regional background values.

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