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Pollutant dispersal and stability in a severely polluted floodplain: A case study in the Litavka River, Czech Republic

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Abstract

The fluvial system of the Litavka River in the Czech Republic has been severely polluted by polymetallic ore mining and smelting that occurred mainly between the 1780s and 1970s. To decipher the mechanisms of the pollution transport pathways, we analysed river valley sediments from river headwaters upstream from the ore district through mining and smelting areas to downstream sites. We sampled recently inundated areas as well as sites just outside 100-year (Q100) inundation. In the river valley, it was necessary to distinguish anthropogenic alluvium (AA) floodplain sediments produced due to ore mining and processing. AA had changed K/Rb signal ratios (measured by energy dispersive X-ray fluorescence, ED XRF); Pb and Zn pollution; and ^{206}Pb/^{207}Pb isotope ratios. The main part of the primary pollution of the river system was deposited in 19th century and during the first half of the 20th century, a few km far downstream from the primary pollution sources (waste deposits of ore mining processing and the smelter). AA has a Zn/Pb ratio of ~ 1.5 and a local enrichment factor (LEF) of up to ~160 for Pb and up to ~130 for Zn. The floodplain further downstream has received diluted primary pollution with the same Zn/Pb ratio and a LEF of ~ up to 80 for Pb and up to 50 for Zn. Much less severe pollution is recognized in fallout-polluted soils at the river valley edges outside Q100 (Zn/Pb~0.9, LEF~ 7 for Pb and LEF~2 for Zn). The secondary pollution currently exported from the watershed and floodplain is substantially enriched in Zn (Zn/Pb ~ 1.5-6). That is obviously a consequence of the higher mobility of Zn in the temporary reservoirs in the mining and smelting area and floodplain. We demonstrate that simple element ratios obtained by convenient laboratory XRF spectrometry can considerably help in deciphering the complex structure of floodplain fill as well as pollution transport routes because that method allows us to adequately process a large number of samples to characterize the complexity of the pollutant distribution in floodplains.

Keywords

Anthropogenic alluvium • Fluvial sediments • Heavy metals • Secondary pollution from mining

Introduction

The soils around the city of Příbram in the Czech Republic and particularly the alluvium of the Litavka River have been polluted by Ag, Pb, and Znmining, ore processing and smelting, mainlyfrom the 18th to 20th centuries (Ettler et al., 2001, 2006; Mihaljevič et al., 2006; Vaněk et al., 2005, 2008; Žák et al., 2009). The Litavka is therefore one of numerous European river systems affected by a lack of environmental concern in the early periods of the industrial revolution. The soils and sediments in the close vicinity of the mining and smelting area have already been subjected to mineralogical analysis (Ettler et al., 2001, 2005c; Vaněk et al., 2005, 2008) and chemical fractionation studies (e.g., Ettler at el., 2005a; Vaněk et al., 2005) as well as analyses of stable isotopes of lead (Ettler et al., 2004, 2006) and magnetic susceptibility (Dlouhá et al., 2013; Petrovský et al., 2001). The concentrations of Cd, Pb and Zn in the floodplain of the Litavka exceed the limits for soils by a substantial margin, which devalues the floodplain estates (Janků, 2009). The river system is now among the largest secondary pollution sources in the Czech Republic (Žák et al., 2009). Long-range atmospheric transport of Pb from the smelter has been demonstrated by Suchara and Suchová (2004) and Mihaljevič et al. (2006). The mechanisms of pollutant transport by the fluvial system of the Litavka and secondary pollution has been evaluated by Žák et al. (2009). However, we lack a deeper understanding of the pollution fates in the Litavka river alluvium as related to its fluvial style.

In most of the research of the last decade and perhaps in all practical contemporary chemical-analytical studies, pollution has been evaluated by comparison of the risk element concentrations with legislative limits or other predefined values. That approach neglects the lithological variability inherent to fluvial sediments and soils (Dung et al., 2013; Majerová et al., 2013; Matys Grygar et al., 2013, 2014; Reimann and de Caritat, 2005); it cannot readily decipher the pollutants’ fate in the environment. In fluvial systems, where sediments have been hydraulically sorted, the target element concentrations must be grain-size corrected, which is most easily achieved by geochemical background functions (a geochemical baseline, meaning a line, not a value). Perhaps the simplest grain-size correction is the use of normalisation functions to describe the local geological background (Vijver et al., 2008; Majerová et al., 2013; Matys Grygar et al., 2013; Nováková et al., 2013; Matys

Grygar et al., 2014). The implementation of background functions and the enrichment factor concept is still insufficient in spite of their long history (Reimann and de Caritat 2005; Dung et al., 2013) and how efficient they are for fluvial (Nováková et al., 2013; Vijver et al., 2008), estuarine (Hanson et al., 1993; Newman and Watling, 2007) and shallow sea deposits (Covelli and Fontolan, 1997). Another useful tool to study pollutant fates in dynamic environments is the ratio of target elements (Devesa Rey et al., 2013; Weng et al., 2003).

The aim of this paper was to better describe the spatial distribution of Cu, Pb and Zn in the floodplain of the Litavka River. In previous works, channel sediments of the Litavka (Ettler et al., 2006), floodplain surface (top decimetres of fluvisols) (Vaněk et al., 2005, 2008) and erosion banks (Žák et al., 2009) were analysed. In contrast to previous works, we analysed densely sampled cores in the floodplain at variable positions with respect to the river channel and at varying distances from the pollution source. We then applied a methodology that was developed recently for data processing based on chemostratigraphic correlation and the local enrichment factor concept (Majerová et al., 2013; Matys Grygar et al., 2013) Local enrichment factors (LEF) principally differ from conventional enrichment factors (EF) for which average shale or average crust values were originally used as background (e.g., Beck et al. 2013; Reiman and de Caritat, 2005). In this report, we also sampled the sediments from the river valley edges because the pristine sediments in the Litavka floodplain floor close to the pollution source are covered by a too thick and severely polluted layer. The floodplain fill was described using a simple and economic method - laboratory XRF with energy dispersive detector and approaches of applied fluvial sedimentology and geographic information systems.

Study area and methods

Mining, ore processing and pollution

Mining in the Příbram area has a very long history. In the Příbram ore district, Ag-Pb-Zn (-Sb) minerals have been extracted, mainly sulphides in veins of Paleozioc rocks (Figure 1).

Veins at the Březové Hory deposit are contained mainly in crosscut of diabase dykes in Cambrian sediments and also in Variscian diorite. The first mining was likely performed since medieval times. More detailed information about geology and ore deposit characteristic can be found elsewhere (Bambas, 1990; Vurm, 2001; Kafka, 2003; Žák et al., 2009).

Since the 16th century, mainly Ag and some Pb were produced; ore was mined from depths down to 100-250 m in the Bohutín area, where old mining dumps are located. Ore processing was performed in the Březové Hory area, where waste was also deposited in historical tailing ponds that were repeatedly destroyed during large flood events, e.g. in 1932 and 1952 (Vaněk et al., 2008; Žák 2009; Žák et al., 2009; Sýkorová, 2014).

The amount of ore processed the 16th and 17th centuries was only a few percent of the more modern production (Ettler et al., 2001). In the second half of 18th century, new mines in Březové Hory deposit were opened (more information are given e.g., in Bambas, 1990)and a modern smelter was built in Lhota u Příbramě, 4 km NW from the city of Příbram. The modern technology of the smelter, as described by Ettler et al. (2001), allowed for production of not only Ag and Pb but also Zn. Slag from waste dumps near Lhota u Příbramě (Ettler et al., 2001, 2004a, 2009) and fly ash from the smelter (e.g., Ettler et al., 2005b, 2005c) contain rather reactive forms of heavy metals, that is, forms not very stable under ambient temperature and humidity. Primary smelting of local ores was terminated in 1970s then the smelter in Lhota was used to reprocess Pb wastes, mainly spent car batteries (Ettler et al., 2005c).

The smelter produced considerable pollution in sites 9 km WSW from Příbram, as shown by Pb concentrations in peat profiles (Mihaljevič et al., 2006) and pollution mapping in moss (Suchara and Sucharová, 2004). Atmospheric pollution from the smelter has substantially decreased in the late 20th century thanks to technological improvements in Pb waste processing (Ettler et al. 2005a).

The Litavka alluvium has been severe polluted, mainly by solid wastes from ore processing deposited in Březové Hory (Vaněk et al., 2008, Žák et al., 2009, Žák, 2009). According to previous works conducted within this study area (Ettler et al., 2006; Vaněk et al., 2008), chemical fractionation showed that Cd, Pb and Zn are mainly present in the most mobile fractions (ion-exchangeable and soluble by weak acids) and bound to Fe and Mn oxides. Only a minor or negligible part of their distribution is in primary sulphide ores (the amount of total S and fraction of metals in oxidisable fraction are negligible) (Vaněk et al., 2005). Ion-exchangeable and the weak acid-soluble forms of metals have a great potential for mobility, especially in deeper floodplain sediments exposed to redox processes and transport by the fluctuating water table inherent to floodplains. Magnetic susceptibility (MS) measurements revealed not only a clear association with heavy metal pollution but also the importance of the gleying processes (reductive dissolution of magnetic Fe oxides) from depths of 15-20 cm (Dlouhá et al., 2013).

Pollution is still exported from the Příbram area, although mining was terminated in 1978, and the smelter has modern technology preventing the emission of fly ash (Ettler et al., 2005b, 2005c). Žák et al. (2009) summarized the analyses of suspended particulate matter in the Litavka River channel obtained in the last decade. The authors assumed that the main source of current pollution is the physical erosion of severely polluted alluvium downstream from Lhota. As follows from the review of results in Žák et al. (2009), the ratio of Pb and Zn in the suspended particulate matter of the Litavka has a considerable scatter and, additionally, it is enriched by Zn compared to the alluvium composition. That misfit indicates that some geochemical processes in alluvium and/or sequestration of pollutants in the river system affect the secondary pollution pattern in matter currently still exported from the Litavka fluvial system.

Sampling, analyses and data processing

The Litavka River (total length ~56km, mean discharge ~ 2.6 m^3/s, watershed ~ 630 km^2) channel has been affected only by moderate engineering in larger cities. The river channel was subjected to channelization inside cities (Příbram, Beroun and Zdice) and also in several villages (Žák et al., 2009), except for the lowermost reach not studied in this work, where the Litavka River discharges the Berounka River and the entire last part of the river before the confluence is also channelized (Figure 1). Most parts of the river channel also contain flood preventing barriers built up within the years 2013-2014.

The positions of sampling sites are shown in Figures 1 and 2. Floodplain sediments were obtained from cores and, in one case (TNL3), from an erosion bank. Hand-drill coring of floodplain fines was performed by a groove corer by Eijkelkamp (the Netherlands) with an internal diameter of 2 or 3 cm. The maximal accessible depth for that groove corer was limited by presence of too coarse sediments (pebble-size or coarser). Sediments were sampled continuously in 2-5 cm long segments.

Sediments were air dried and directly subjected to mass magnetic susceptibility (MS) measurement using KappaBridge KLY-2 (Agico; Institute of Geology AS CR, v.v.i., Prague). After the measurement of magnetic susceptibility, samples were milled using an automatic planetary ball mill (Fritsch, Germany). The resulting powders were poured into measuring cells with Mylar foil bottoms with a diameter of 2.7 cm of ED XRF spectrometer MiniPal 4.0 (PanAnalytical, the Netherlands; Institute of Inorganic Chemistry AS CR, v.v.i., Řež), as described previously (Grygar et al., 2010; Matys Grygar et al., 2012; Majerová et al., 2013; Nováková et al., 2013). Analytical signals of Al, Si, Fe, Mn, Ti, Rb, Pb, Zn and Cu were obtained (reproducibility of the ED XRF signals was from 1 to 4 rel. %). The spectral signals of individual target elements were calibrated by ICP-MS analyses of 73 selected specimens (Table 1). Calibration equations of K and Al are listed e.g. in the work of Matys Grygar and Mach (2013). Multi-element analyses and analyses of the ratios of stable isotopes of Pb were undertaken using ICP analysis after acid digestion of samples ($HF+HClO_4$), as described previously (e.g., Grygar et al., 2010; Strnad et al., 2005), using an inductively coupled plasma mass spectrometer X Series 2 (ThermoScientific, Germany; Laboratories of the Geological Institutes, Charles University in Prague).

The detailed analytical parameters are given elsewhere (e.g., Strnad et al., 2005). The number of replicate analyses in ICP-MS was 3 for element concentrations and 5 for stable Pb isotopes; in each series of sample processing, one sub-sample of reference materials was digested and 3 replicates of their ICP-MS analyses were performed. The analytical precision of the ICP-MS data for all of the analysed elements ranged from 0.5 to 4 relative %. The accuracy of this analytical method was controlled using the SRM 2709a (NIST, USA) and BCR-2 reference materials (USGS, USA).

The Pb isotopic measurement was performed using the same ICP MS instrument, and a correction for mass bias was performed using SRM NIST 981. The standard errors for measurements of ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb were below 0.3 % (1 σ). The accuracy of the measurements was verified by repeated analyses of the AGV-2 reference material (USGS, USA; ^{206}Pb/^{207}Pb = 1.2086 ±0.0007, ^{208}Pb/^{206}Pb =2.0411 ± 0.0015).

Calibrated ED XRF results allowed us to establish the local background functions of Pb, Zn and Cu (see Table 2 and also Fig. 6C and D). Local background functions were further used for the calculation of local enrichment factors (LEF), where the LEFs of individual elements are calculated as a ratio between the actual element concentration (M) and its predicted background concentration (M_{gbf}), which is calculated using the local background function,

$$LEF = M/M_{gbf}$$

where LEF is dimensionless for M and M_{gbf} are in the same units, as is described in previous works (e.g., Matys Grygar et al, 2014).

Selected representative sub-samples were also subjected to grain size analysis. Sample preparation included organic matter removal using peroxide and 3% hydrochloric acid (Blanck, 1976). The grain size distribution of 26 samples selected from all present sedimentary facies was performed by laser diffraction method using Sympatec HELOS system with QUIXEL dispersing unit (Laboratory of Physical Geography, Charles University in Prague).

Dating of recent floodplain sediments (profile TNL16) in Trhové Dušníky was performed by ^{137}Cs and ^{210}Pb dating methods. The samples were sealed for three weeks in measurement vessels for establishment of radioactive equilibrium in samples. Activities of ^{137}Cs and ^{210}Pb were measured directly in selected samples from upper part of profile TNL16 using a gamma spectrometer REGe(n) equipped with GR3018 detector (CANBERRA Industries, USA; T. G. Masaryk Water Research Institute, Prague). Isotope ratios of ^{226}Ra and ^{228}Ra were obtain to evaluate a possible influence on ^{210}Pb systematic due to the past U-mining activities east of the Příbram area.

Activities of unsupported ^{210}Pb were obtained as a result of the subtraction of the mean activities of ^{214}Pb from the total measured activities of ^{210}Pb. Unsupported activities of ^{210}Pb, according to the CRS dating model (Appleby and Oldfield, 1978), were further used for estimation for deposition rate, as described previously (Matys Grygar et al., 2012).

The radiocarbon dating method was used for dating the charcoal sample (dendrologically identified as a spruce sample) that was found at a depth of 117.5 cm in the erosion bank profile TNL3. Analysis of ^{14}C was performed using AMS spectrometer in Poznań Radiocarbon Laboratory (Poland).

Analyses of historical maps (GIS)

River dynamics were evaluated by comparing historical maps (the 2nd Military Survey, from the first half of the 19th century) and orthophotomaps (1953, 2011 and 2013).

The 2nd Military Survey map (1836 – 1852) was georeferenced by Geoinformatics Laboratory, J.E. Purkyně University from map copies of the Austrian State Archive/Military Archive in Vienna.

Scanned Imperial Obligatory Imprints of the Stable Cadastre (1839), orthophotomaps from 2011, 2013 and laser scanning dataset DMR 4G (Digital Terrain Model of the 4th generation) were purchased from the Czech Office for Surveying, Mapping and Cadastre (© ČÚZK).

The historical orthophotomap from 1953 was created within the National Inventory of Contaminated Sites project, and source aerial images were provided by the Military Geographic and

Hydrometeorology Office (© MO ČR). Data sources were processed using ArcGIS 10.2 for Desktop software.

These maps were used to study the channel migration of the Litavka River within the Trhové Dušníky area, and the lateral shifts of the channel during the last 150 years. The inundated floodplain areas were visualized by Q100 shape files provided by the T. G. Masaryk Water Research Institute.

Results

Channel dynamics and the character of floodplain sediments

Over the last 150 years (from the 2nd Military Survey to the present), the total length of the river channel was shortened due to lateral shifts of the channel position (with estimated map uncertainty ±5 m). The total length of the Litavka River channel has decreased by ~ 5%. The river channel length changes have occurred mainly near towns and villages, where the river flow is artificially regulated.

The historical development of the Litavka River channel downstream from Trhové Dušníky is shown in Figure 2. The river by several km downstream from Trhové Dušníky was meandering according to the historical map (1843), which shows a typical wavy channel pattern. Active channel shifts are apparent also from the existence of steep erosion banks and pieces of turf fallen into the river channel (this is shown in Figure 6 in Žák et al., 2009). Rather than the continuous meander evolution typical of actively meandering rivers, channel avulsions occurred in the past 150 years – points of avulsions are shown by arrows in Figures 2C and 3B. An example of such abrupt channel shifts is near sampling site TNL3 (Figure 3, just south of TNL3): the channel shifted westward between the first half of the 19th century and 2013, while after a 2013 flood, it shifted back eastward toward the previous historical position. The shifts left a large sandy gravel bar within the channel in the point of avulsion (Figure 3, aerial photograph taken in 2013). There is obviously a depression at the western edge of the floodplain (between sampling sites TNL24 and TNL25, see Figure 3A) of a width and shape very similar to the current channel belt in that area – probably a remnant of even older river channel.

The Litavka River has a coarse-grained channel bed and fine silty-clayey floodplain downstream from Příbram (see also Table 3). The lithology of sediments in Trhové Dušníky shows none of the systematic vertical facies changes that are typical for rivers with shifting channels. Most of the analysed sediments were floodplain fines with major clay + silt fractions and minor sand (Table 3). Sediment coarseness in depth profiles is shown in Figure 4 (TNL3 profile with Al/Si signal ratio used as a grain size “proxy”, see also Figure 5, which shows the Al and Ti relation to the content of the clay-size fraction). Granulometry analysis was done from selected sub-samples and results were used for confirmation that Al/Si ratio could be used as a grain-size proxy within depth profiles. The profiles from floodplain have a nearly constant Al/Si ratio, with occasional minima in layers with coarser sediments. These individual coarser strata also contain pebbles and/or more sand; they are horizontally stable over the floodplain, obviously as a result of aggradation. One such prominent layer was found at a depth of ~ 55 cm in the TNL3 profile from the erosion bank (Figure 4), 50 cm in TNL4, ~45 cm in TNL5 and ~40 cm in TNL16. The cobble layers were attributed to single extreme floods. Visual signs of gleying (layers enriched with Fe-oxide concretions and irregular stains) were in most core sections apparent at the depth ~0.2 m. The top strata of floodplain sediments were densely rooted by plants to the depths of approx. 0.1-0.15 m.

Sediment pollution

Examples of element depth profiles and magnetic susceptibility (MS) in Trhové Dušníky are shown in Figure 6. Both heavy metals (Cu, Pb and Zn) and MS have broadly similar depth patterns. This finding is consistent with previous studies (Dlouhá et al., 2013; Petrovský et al., 2001). There is an obvious correlation between pollution by magnetic particles and heavy metals in the Litavka floodplain, which is discussed in more details further in Results.

In Figure 6A, the depth profiles of local enrichment factors of Pb and Zn are shown together with the K/Rb (ED XRF signal ratio), magnetic susceptibility (MS) values and Fe concentrations in the Trhové Dušníky floodplain. The profiles are shown from right to left, with a growing distance from the main channel. Profile TNL3 was obtained from erosion bank, TNL6 and TNL25 represent floodplain profiles, TNL24 was sampled from floodplain close to the current Q100 inundation area and TNL26 was obtained at the valley edge outside the current Q100. TNL26 was sampled to check the expected atmospheric pollution. All of the sampled profiles were more polluted on top, with lower concentrations of heavy metals at depths of more than 30-50 cm for the profiles close to the valley edge and more than 80-120 cm for profiles in the proximal floodplain and the erosion bank. Local enrichment factors for Pb and Zn in floodplain are up to ~160 for Pb and up to ~130 for Zn. Pollution in TNL24 was most distal to the current active channel and in TNL26; the valley edge pollution (outside Q100) is two orders of magnitude smaller than in the floodplain floor (see Figure 6A).

The maximal pollution of floodplain sediments substantially decreased downstream from the Příbram area (Figure 6B). The floodplain further downstream from Trhové Dušníky has local enrichment factors up to ~ 80 for Pb and of up to ~ 50 for Zn. This implies the considerable dilution of the primary pollution by recycled older fluvial sediments; however, the pollution is still obvious as enrichment with respect to background even in the most remote profiles in the lowermost reach. Much less severe pollution downstream from Trhové Dušníky was recognized in fallout-polluted soils at the river valley edges outside Q100 (LEF ~ 7 for Pb and LEF ~ 2 for Zn in TNL26).

In Figure 7A and in detail in Figure 7B, Pb and Zn concentrations in all of the analysed samples are plotted together with the results from previous studies. There are obviously three branches in this plot, marked by Roman numerals: Pb-rich (I), medium with Pb~Zn (II) and Zn-rich (III). The Pb rich and medium branches are each nearly linear and cross only in the area of unpolluted sediments, which points to two distinct pollution sources or transport mechanisms. The Pb-rich branch consists of sediments upstream from the mining area, where fluvial pollution by ore-processing wastes is impossible; from the Bohutín area; and from the valley edge above Q100 inundation area in Trhové Dušníky (TNL26). The sediments with that pollution pattern are spatially stable and correlateable.

The medium branch II in Figure 7A consists of polluted samples from an inundated floodplain in the medium and lower reaches of the Litavka, i.e., sites more remote from the Příbram area but within the extent of fluvial transport from ore-processing and waste dumping areas (Březové Hory and

Lhota). The sediments with the pollution pattern of the medium branch in Figure 7A are also spatially stable and correlateable. In Figure 7A and B, these strata are in nearly all polluted sediments from the inundated floodplain in Trhové Dušníky and in all of the profiles further downstream.

The Zn-rich branch (III in Figure 7A) is convex and merges with medium branch II at higher concentrations of metals. This branch consists only of sediments from Trhové Dušníky from relatively thin strata just below the most severely polluted sediments. No such Zn-rich polluted strata were found elsewhere in the Litavka floodplain. Such lack of spatial correlation points to a specific situation in Trhové Dušníky rather than to any specific historical primary pollution signal. The fact that the Zn-rich pollution can only be found in one place and below the most severely polluted sediments, invokes a hypothesis that it is a consequence of post-depositional migration of heavy metals.

Post-depositional migrations and local background functions

The usual way to acquire local background functions is to take lithogenic background values from pristine sediment, located just under the polluted layer (e.g., Covelli and Fontolan, 1997; Matys Grygar et al., 2013). In the floodplain of the Litavka, in particular in Trhové Dušníky, it is not as simple (see also Figure 7A, III – Zn rich branch) due to the severe pollution of the entire area and presence of pollutants in labile forms (Ettler et al., 2006; Vaněk et al., 2008). To evaluate the possible migrations of pollutants from the most polluted strata, we searched for discrepancies in individual pollution characteristics.

We found distinct ratios of some “lithogenic” elements (elements not produced in the Příbram area), namely, K and Rb and the Rb ratio to Al in the most severely polluted strata, that is, mainly in Trhové Dušníky. This difference is demonstrated in Figures 7C and D. In Figure 7C, the non-calibrated EDXRF signal ratios of K vs. Rb are plotted. The ratio of the two alkaline metals is low and practically constant in unpolluted sediments and sediments with a Pb-rich pollution pattern (branch I in Figure 7A), while much less Rb at a given K (larger K/Rb) was found in sediments severely polluted by Pb and Zn (branches denoted by Roman numerals II and III in Figure 7A). The sediments for which the analyses are plotted between these two branches have weak or medium pollution. The

K/Rb signal ratio of unpolluted alluvium is close to 13.4, which is shown as a line in the main branch in Figure 7C and as vertical lines in the K/Rb panel in Figure 6. The main branch in Figure 7C represents this value in normal alluvium, which includes mainly sediments from three locations: upstream from the mining area (in headwaters of the Litavka south of the city of Příbram), from deeper strata at the valley edges in Trhové Dušníky, and from deeper strata in the lower river reach profiles. The coincidence between the switch from “normal” to “anthropogenic alluvium” is apparent in Figure 6 as a coincident increase of Pb and Zn content and K/Rb ratio, with only minor misfit of the Zn depth profile. In Figure 7D, this interrelation is shown for all sediment profiles in Trhové Dušníky. Pb pollution is clearly found mainly in sediments with an increased K/Rb ratio. Similar dependence was also found in profiles downstream from Trhové Dušníky (Figure 6B). A different situation occurs in sediments from Litavka headwaters and from the Bohutín area, where Pb-rich pollution is not accompanied by comparable substantial increase of K/Rb.

Pristine sediments (unpolluted and not affected by element migration driven by redox variations, or caused by water table level fluctuations), of which identification is essential for establishing local background functions, cannot easily be found in the vicinity of the river channel and the frequently inundated floodplain in the most polluted areas. Such pristine (pre-industrial) floodplain sediments in Trhové Dušníky are covered by more than one meter thick of severely polluted sediments (Figure 6A) and are hence at such large depths that they have been exposed to element mobilization by the fluctuating water table. Pristine sediment samples in the middle river reach were therefore searched for at the valley edges, e.g., in Trhové Dušníky, in profiles TNL24 and TNL26 (Figure 6A, depths with lithogenic background values in pristine sediments are highlighted in Pb and Zn LEF panels in TNL26 profile).

Isotopic ratios of ^{206}Pb/^{207}Pb also serve for tracing pollution sources and for distinguishing the anthropogenically polluted sediments in the Trhové Dušníky floodplain. The source of pollution by Pb in the Litavka River sediments has a single ^{206}Pb/^{207}Pb ratio ~1.16, while that ratio is ~1.19 in unpolluted sediments. The former value is in agreement with the mean composition of the local Pb ores processed in the smelter in Lhota and resulting pollution (Ettler et al, 2004b, 2006; Mihaljevič et al., 2006). According to Vaněček et al. (1985), ores from the Březové Hory area have ^{206}Pb/^{207}Pb ratio

~ 1.160, whereas ores form the Bohutín area have ^{206}Pb/^{207}Pb ratio ~ 1.157. The ratio ~1.19 in unpolluted sediments is within the interval obtained experimentally from various rocks of the area by Ettler et al. (2004b) and Ettler et al. (2006) and from lithogenic Pb in peat cores in nearby site in the Brdy Mts. (Mihaljevič et al., 2006).

The isotope ratio of ^{206}Pb/^{207}Pb was used for pollution tracing independent of actual Pb concentrations in sediments. From Figure 8A, it is clear that pollution produces a decrease of the^{206}Pb/^{207}Pb ratio, from 1.19-1.20 in pristine sediments to values down to 1.16. The ^{206}Pb/^{207}Pb ratio below 1.18 in analysed sediments hence indicates the anthropogenic pollution (Figure 8A), which allowed us to distinguish the lithogenic part of sediments from anthropogenically polluted sediments (see also Figure 6A).

Post-depositional migration of Pb was then revealed by finding low ^{206}Pb/^{207}Pb isotopic ratios, which are typical of pollution, already in some of the lowermost part of the polluted strata, where other features did not point to primary pollution. Such was the case of Zn-rich pollution (branch III in Figures 6A and B) below the main polluted strata in Trhové Dušníky. For example, in the lower parts of the TNL24 profile, the total concentrations of Pb seemed not to be enriched in concentrations but the isotopic ratios of ^{206}Pb/^{207}Pb were too low to be pristine: only ~ 1.178.. These layers were, hence, excluded from the establishment of local enrichment background functions (LEF). The post-depositional migration of Pb was revealed by Sb/Pb ratios (see Figure 8B), where Sb is considered to be rather immobile in sediments. In the Příbram area, Sb and Pb pollution are statistically interrelated (Suchara and Sucharová, 2004). Most samples with lower Sb/Pb ratio and simultaneously with higher Pb and Sb values (the lower branch in Figure 8B) are from the lower parts of "anthropogenic alluvium" layers in Figure 6A and B and/or from layers with Zn-rich pollution (branch III in Figure 7A). Unfortunately, we are unable to distinguish whether this is the authentic sedimentary signal of contamination character changes (e.g., processing of low-level Sb-ores at the beginning of mining in the past) or if these concentrations are a result of post-depositional migration of Pb from upper parts of anthropogenically alluvium strata (or increase of Pb concentrations due to the migration caused by water table level changes) without simultaneous changes of naturally less mobile Sb concentrations.

Post-depositional migration of Zn in the lower parts of profiles in Trhové Dušníky floodplain was confirmed by the misfit of its depth profiles with magnetic susceptibility. Interrelations between pollutants and magnetic susceptibility (MS) are shown in Figure 8C and D. Samples with increased Zn concentrations and low MS values are shown as black circles in Figure 8D. Actually, these black circles belong to the Zn-rich branch III in Figures 6A and B.

Local background functions were calculated only from pristine samples with no above described indications of post-depositional migrations. All sediments used for local background functions were overbank fines without minor sand fractions – Table 3, as it is known that sandy strata are too permeable to preserve the primary pollution signal. The resulting local background functions for Pb normalized by Ti and Zn normalized by Al, empirically found as the most suitable normalising elements (predictors), are shown in Figure 8E and F. The resulting background functions allow calculation of local enrichment factors (LEFs, see also Figure 6AB).

Sediment dating

Sediment from the upper part of the TNL16 profile in the Trhové Dušníky floodplain was subjected to gamma spectrometric analysis of ^{210}Pb and ^{137}Cs activities, of which the results are summarized in Table 4. Unsupported ^{210}Pb was found in sediments from the top 11 cm, and its activity in the lower parts of profile was below uncertainty of the measurement (the activity of total ^{210}Pb was roughly equal to the activity of its parent isotopes ^{214}Pb and ^{214}Bi). Activities of ^{226}Ra in the sediments are similar to background values in Czech rivers not impacted by U mining (Hanslik et al., 2005). The mean sedimentation rate in the top 11 cm (~ 0.15 cm/year) was calculated using the depth profiles of the activities of unsupported ^{210}Pb.

The activity of ^{137}Cs has a maximum near the surface, which can conventionally be attributed to the accident in the Chernobyl nuclear power plant in 1986. Certain activities of ^{137}Cs were found at considerable depths of 19 cm, even at depths where no unsupported ^{210}Pb was present. This can be explained by the downward migration of a part of Chernobyl ^{137}Cs, as has been reported to occur in floodplain sediments (Matys Grygar et al., 2012; Nováková et al., 2013). The presence of the ^{137}Cs maximum on the top of TNL16 shows that the youngest sediments have been preserved in the floodplain and together with results of ^{210}Pb dating method confirmed constant sedimentation of top strata.

Charcoal taken from the TNL3 profile in the current erosion bank was dated using ^{14}C method and results produced the age estimates shown in Table 5. The age of the charcoal is within the uncertainty interval due to equivocal calibration curve between 17th and early 20th century that corresponds to the previous set of results from the same place published by Žák et al. (2009). All of the data demonstrate a rather rapid deposition of nearly 1 m of the most severely polluted anthropogenic alluvium in Trhové Dušníky. On the other hand medieval charcoal (Žák et al., 2009) was also found under the anthropogenic alluvium sediment at a depth of ~120 cm.

Discussion

Background functions in strongly polluted floodplains

The determination of the local geochemical background in fluvial systems that is strongly impacted by historical mining is complicated by the widespread massive pollution of the fluvial systems and frequently by anthropogenic changes of the fluvial style related to mining (e.g., Ciszewski et al., 2012; Heim and Schwarzbauer, 2013; Hudson-Edwards et al., 1998; Hürkamp et al., 2009). In addition to the normal dynamics of fluvial deposition, mining and ore processing commonly change the flow regime and introduce extra particulates, commonly resulting from failures of settling ponds. As a consequence, pristine fluvial sediments may be covered by excessively thick polluted deposits that endanger the post-depositional stability of the pollution record, such as in the studied case in the Litavka River. Without knowledge of the actual local geochemical background, it is hardly possible to realistically evaluate both the historical impact of mining and the effect of recovery and remediation of the river system after disasters (Bird et al., 2008; Turner et al., 2008).

To obtain background functions for the Litavka fluvial sediments, we sampled not only at the proximal floodplain but also at the river valley edges near the edge of the Q100 inundation area. In these marginal floodplain sites, we found sediments with the same lithology and geochemistry as in the weakly polluted parts of floodplain (upstream from the main pollution source in Březové Hory and Lhota) and farther downstream from the pollution sources (in lower reach of the Litavka River). The sediments outside the Q100 area were processed in the same manner as sediments from the active floodplain (within Q100): pristine sediments were found below top strata polluted mainly by atmospheric fallout from the local metallurgy. We have recently used a similar approach (use of sediments from active floodplain and sediments outside the Q100 area in the valley of the Ploučnice River (Matys Grygar et al., 2014). In such a way, we assembled sufficient number of pristine sediments to establish the local background functions of Pb and Zn for the Litavka (Figure 8E,F) and to assess the pollution level using local enrichment factors.

Such marginal floodplain sites may hypothetically include older fluvial deposits (e.g., Pleistocene or Early Holocene), loess deposits and loess-derived loess, and/or colluvial deposits. Loess would, however, have a different appearance and coarseness (lack of clay fraction), while colluvium would be poorly sorted with rock fragments. In fact, the sediments that we used as pristine in this study have the same lithology and appearance as deposits in the Litavka River floodplain and have had the same major element patterns. We hence consider all of them to be Litavka fluvial sediments.

Element ratios for pollution tracing

The risk element ratios can help to distinguish the pollution of sediments and soils. Such use of the ratio of Cu, Pb and Zn for soils has recently been proposed by Weng et al. (2003) and Devesa Rey et al. (2013). Although the original substantiation by Weng et al. (2003) and Devesa Rey et al. (2013) that these ratios in mature soils should be homogeneous due to biogeochemical processes may be simplistic, the idea is inspiring. In sediment profiles, both sorting and certain post-depositional processes should similarly affect all heavy metals with a similar behaviour, such as Pb and Zn. Their ratios should, hence, vary either if there are specific pollution sources in the study area or if the pollutant fates in the sediments are element-specific. We found very distinct ratios of Zn and Pb in the Litavka fluvial system (Figure 6AB), which clearly points to variation in both pollution sources and pollutant fates in the Litavka fluvial system.

The plot of the Zn to Pb ratio in the floodplain of the Litavka in all sampled sediments (Figure 7A) shows three clearly distinguished branches. Pb-rich pollution is typical for the uppermost course (headwaters) of the Litavka River and the Bohutín area, that is, upstream from the ore processing in Březové Hory and the smelter in Lhota. The finding of Pb-rich pollution (Pb>>Zn) in these areas is consistent with previous analyses of the Litavka stream (Ettler et al., 2006) and floodplain sediments (Vaněk et al., 2008). We newly found a Pb>>Zn pollution pattern (with Zn/Pb ratio ~ 0.9) in sediments in Trhové Dušníky close to or above the Q100 inundation area (Figure 6A, profile and TNL26). The only possible mechanism that could have spread the Pb-rich pollution over such remote places is atmospheric transport, probably from the finest particles emitted from the smelter in Lhota (with possible contribution from some older lead-silver smelters in Příbram). The efficiency of such long-distance pollution by Pb from the Příbram area was demonstrated by the analysis of moss in large-area mapping (Suchara and Suchová, 2004) as well as by the analysis of the peat profile 9 km west of Příbram (Mihaljevič et al., 2006). Lead as a volatile metal is known to form extremely fine particles by high-temperature processes; global pollution by Pb is attributed actually to this feature of Pb (Shotyk et al., 2002).

The sediment with the pollution pattern belonging to the main Pb~Zn branch in Figure 7A (with a Zn/Pb ratio nearly constant ~1 – 2, irrespective of the pollution level) can be found in the vast majority of severely polluted anthropogenic alluvium in the area downstream of Příbram. The Zn/Pb ratio in this branch is coincident with the pollution pattern in dust and topsoils (outside the floodplain) in places a few hundred metres far from the smelter in Lhota (Rieuwerts and Farago; 1996, their mean Zn/Pb ratio is shown by solid line in Figure 7A). We hence attribute the pollution pattern in the medium branch in Figure 7A to ore-processing pollution transported atmospherically for short distances (as dust, a few hundred metres) from Lhota and fluvially for much longer distances.

Downstream from the Lhota area, the pollution in the floodplain profiles was stepwise diluted, but the Zn/Pb ratio remained constant, as shown in Figures 6A and in detail in Figure 7B.

The third pollution pattern, the Zn-rich branch in Figure 7A, is typical for the alluvium from the deeper layers in the floodplain near Trhové Dušníky. Žák et al. (2009) also found Zn-rich pollution on average samples from the top 120 cm of the surface of erosion banks in Trhové Dušníky. Vaněk et al. (2008) assumed that this Zn-rich pollution is a result of the early periods of mining when only Pb and Ag was extracted while Zn accompanying those target elements could have passed to the tailings. That explanation is unlikely from the stratigraphic point of view: Zn-rich strata are not present in other sites than in Trhové Dušníky floodplain, for example, there is no such sediment in the profiles in Čenkov (Figure 6B).

Interestingly, the current secondary pollution exported from the Litavka River system, that is, suspended particulate matter transported by the Litavka in its lowermost course, actually has a Zn-rich pollution pattern with a Zn/Pb ratio of ~ 1.5 – 6 and values of up to ~ 1332 ppm Pb and ~ 4512 ppm Zn (Žák et al., 2009).The representative analyses are shown in Figure 7A and in Figure 9 (showing Zn/Pb ratios in SPM in the water flow, taken from Žák et al., 2009, in comparison with our Zn/Pb results). The Zn enrichment therefore needs some additional explanation: it simply cannot originate from mere physical erosion of the existing polluted alluvium because the current deposits in the floodplain have relatively less content of Zn.

Anthropogenic alluvium downstream from Příbram

The most polluted fluvial strata in the Trhové Dušníky area are 0.8 - 1.2 m thick, further downstream the pollution level and thickness of polluted strata is only slowly decreasing. The onset of fluvial pollution is clearly visualized by the nearly coincident onset of Pb and Zn enrichment, with only a minor misfit in the lowermost decimetres of the polluted profiles. Radiocarbon dating of charcoals from the erosion bank indicates that this sediment unit has been deposited very quickly. The strata were surely deposited vertically: they evenly cover the entire floodplain width and they are intercalated by laterally stable horizontal layers of cobbles/pebbles, such as a prominent layer at the depth of 0.4 - 0.5 m (in profiles TNL3, TNL4 and TNL5). Such coarse clastics in the Litavka floodplain are deposited only by extreme river discharges during the largest floods (Žák et al., 2009). The collapses of the historical tailing ponds from ore processing during large floods (Sýkorová, 2014; Vaněk et al., 2008; Žák, 2009; Žák et al., 2009) definitely contributed to that sedimentation pattern.

We hence suppose that the most polluted strata in Trhové Dušníky are genetically different than “normal”, pre-mining alluvium of the Litavka. It has not only contains severe pollution but also a different matrix, as shown by different K/Rb ratios (Figure 7C). These most polluted strata of the Litavka alluvium therefore meet the definition of “legacy sediments” (James, 2013) and “anthropogenic alluvium” (Macklin et al., 2014): they are anthropogenic by their physical nature, they were formed by the artificial introduction of a large amount of particulate load to the fluvial system and they can also be clearly distinguished by polymetallic pollution.

The introduction of anthropogenic alluvium apparently enhanced the Litavka channel dynamics. While a wavy channel typical for actively meandering rivers is shown in historical map downstream from the Trhové Dušníky (Figure 2A), several avulsions (and no meander loop development) has occurred since then (Figure 2C). Avulsions within channel belt and channel instability are obvious by existence of steep erosion banks and contributes to secondary pollution (Žák et al., 2009). Another consequence of existence of so thick polluted strata in the floodplain is that the polluted sediments are exposed to fluctuating water table and hence endangered by chemical remobilization.

Post-depositional migration of risk elements and secondary pollution

Risk elements in historically polluted alluvium are generally prone to post-depositional migration, that is, chemical remobilization. This phenomenon was first systematically addressed in mining-polluted deposits of UK rivers (Hudson-Edwards et al., 1998). Later it was concluded that PbS and ZnS are relatively stable in floodplain fill. In contrast, Hürkamp et al. (2009) gave an example of pollutant depth profiles in mining-impacted alluvium affected mostly by post-depositional migrations in floodplain of the Vils in Germany - nearly all Pb in overbank fines is now accumulated in the organic-rich topmost strata of otherwise coarse deposits. Aleksander-Kwaterczak and Ciszewski (2012) and Cizewski et al. (2012) showed the effects of post-depositional migrations of heavy metals in mining-polluted alluvium. Also in the Litavka alluvium, post-depositional migrations have obviously also taken part – the pollutants are not presented in the original sulphidic form. Chemical fractionation (speciation) studies showed that Litavka alluvium mostly contains much more reactive species: a considerable percentage of risk elements is in easily soluble/leachable forms (e.g., Vaněk et al., 2008). While the chemical fractionation shows mainly actual potential for mobility, the stratigraphic correlation of element depth profiles should demonstrate its consequences, that is, proof of whether the elements were actually translocated in the sediment profiles irrespective of their current forms. Chemostratigraphic correlation is a well-established tool of sedimentary studies, but in environmental geochemistry it is rarely used.

Using correlation of sediment profiles, we observed Pb- and Zn-depletion in the deeper strata of floodplain sediments at the level of fluctuating water table in several previously studied floodplains (Grygar et al., 2010; Majerová et al., 2013; Matys Grygar et al., 2013; Matys Grygar et al., 2014; Nováková et al., 2013). That migration is a consequence of fact that a considerable fraction of heavy metals in both pristine and polluted sediments is bound to Mn (III,IV) and Fe(III) oxides. Redox-driven dissolution/re-precipitation of Fe(III) oxides (short-range migration) at depths of the fluctuating water table is either visible by the naked eye as a colour change (rusty stains or reddish brown concretions in discoloured, greyish matrix) or as significant changes and systematic depletion in Mn and Fe depth profiles (also shown by Richardson et al. 2014). We observed such changes in the Fe depth profiles at a 20 cm depth in the TNL3 profile; these alterations of Fe oxides cause erratic changes in the magnetic susceptibility depth profiles, as reported for the Litavka alluvium by Dlouhá et al. (2013). However, these trivial (expected) changes in Fe oxides proceeded within the severely polluted strata (anthropogenic alluvium) and did not significantly change the pollutant depth profiles. On the other hand, the Litavka alluvium is impacted by further and more relevant processes at larger depths of the alluvium.

We concluded above that Zn-rich pollution (branch III in Figures 7A and B and the corresponding chemostratigraphic unit in Figure 6A) is a consequence of the migration of heavy metals in the alluvium in Trhové Dušníky. Obviously, Zn is more vertically mobile with respect to Pb, which is in agreement with the higher percentage of Zn in most mobile chemical fractions than Pb (Vaněk et al., 2008).

The varying Zn/Pb ratio in the alluvium of the Litavka (Figures 6A,B) and the different post-depositional stability of these metals discussed above are relevant to rationalize the Zn/Pb ratios in the suspended particulate matter (SPM) carried by the river water in the lowermost course of the Litavka, that is, for pollution continuously exported from the Litavka to the Berounka River. The results of the SPM analyses at varying river discharge summarized in Žák et al. (2009) are plotted in Figure 9 together with the results of alluvium analyses that we obtained. At lower river discharges, the Zn/Pb ratios in SPM are high (Zn-enriched with respect to Pb pollution) and correspond to the Zn-rich branch in Figures 7A and B, that is to the Zn/Pb ratio, which we interpret as controlled by higher post-depositional migration (secondary remobilization) of Zn. Only at growing river discharges, when physical erosion of river banks can grow, the Zn/Pb ratio asymptotically decreases towards the values typical for the anthropogenic alluvium downstream from Trhové Dušníky. Simple element ratio of pollutants hence prove an extra source of Zn in low river discharges – and we hypothesise “leaching” of the thick layer of anthropogenic alluvium is responsible for that situation.

Conclusions

Analyses of floodplain sediments using simple ED XRF element analysis, stratigraphic correlation and a basic description of the fluvial (depositional) style were used to create a chemostratigraphic description of the polluted alluvium of the Litavka. We obtained the primary pollution pattern and revealed post-depositional effects, interpretable as a consequence of faster migration of Zn. Simple Zn vs. Pb scatterplots revealed Pb-rich pollution transported mainly by atmosphere and Pb~Zn pollution transported by the river flow. For the contamination of the Litavka River by risk elements from mining and ore processing and metallurgical processes has been known for a long time, this work shows new approach when anthropogenic alluvium was identified in the river system by using chemostratigraphic correlation of profiles taken across the floodplain and hypothesized to represent quickly deposited layer of extra sediment artificially added to the river system during the extensive development of mining and ore processing. The strata below the most polluted anthropogenic alluvium are specifically enriched by Zn in excess with pollution by Pb and magnetic particles, probably due to Zn migration by chemical mobilization, possibly enhanced by the large thickness of the polluted floodplain sediments.

The effective secondary pollution, that is, suspended particulate matter exported from the entire river system of the Litavka, is derived from the episodic physical remobilization that occurs during extreme river discharges, when lateral erosion and/or channel avulsions occur. At lower discharges, preferential chemical mobilization of Zn from the polluted alluvium seems to be involved.

Our study demonstrates the power of the multidisciplinary approach integrating geochemical analysis, stratigraphic correlations adopted from fluvial sedimentology, and evaluation of historical maps and aerial photographs using geoinformatic systems (GIS).

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Table 1. Results of correlation of ED XRF signals of Ti, Rb, Zn, Pb, Cu and Fe with ICP MS results of selected samples analyses, further used for calibration.

Table 2 Correlation of ICP MS and ED XRF lithogenic background values of Zn with Al, Pb with Ti and Cu with Rb, further used as local lithogenic background functions.

Table 3. Grain size analyses, position in floodplain, pollution status and K/Rb signal ratio of selected sediments.

Table 4. Dating of floodplain sedimentary profile TNL16 using ^{210}Pb and ^{137}Cs activities.

Table 5. Radiocarbon dating of erosion bank (profile TNL3).

Table 1. Results of correlation of ED XRF signals of Ti, Rb, Zn, Pb, Cu and Fe with ICP MS results of selected samples analyses, further used for calibration.

ED XRF signal	**Callibration equations**	**Number of samples**	**r^2**
Ti	Ti (ppm) = 7.2057 *Ti(c.p.s.)	71	0.829
Rb	Rb (ppm) = 0.9567*Rb(c.p.s.) + 21,218	71	0.815
Zn	Zn (ppm) = 0.0000485*(Zn (c.p.s)) ^{2}+ 2.3607977*Zn (c.p.s.)	71	0.994
Pb	Pb (ppm) = 5.3632*Pb (c.p.s.)	71	0.986
Cu	Cu (ppm) = 2.5443*Cu (c.p.s.)	70	0.926
Fe	Fe (ppm) = 5.4705*Fe (c.p.s.)	58	0.829

Table 2. Correlation of ICP MS and ED XRF lithogenic background values of Zn with Al, Pb with Ti and Cu with Rb, further used as local lithogenic background functions

.

ED XRF signal	**Normalisation equations**	**Number of samples**	**r^2**
Pb/Ti	Pb(ppm)= 0.011*Ti(ppm) – 9.0203	22	0.514
Zn/Al	Zn(ppm)=0.0396*(Al(c.p.s.))^2+3.4948*Al(c.p.s.)	57	0.568
Cu/Rb	Cu(ppm)= 0.1538*Rb(ppm) + 7.8559	55	0.303

Table 3. Grain size analyses, position in floodplain, pollution status and K/Rb signal ratio of selected sediments.

Sample	Core position and pollution status	Pb (ppm)	K/Rb (c.p.s./c.p.s.)	Clay-silt-sand (%)
TNL21 65-70	Floodplain edge, weakly polluted	62	13	50-48-2
TNL17 15-20	Floodplain, weakly polluted	130	12	27-63-10
TNL17 30-35	Floodplain, weakly polluted	74	13	30-50-20
TNL3 3-6	Erosion bank, strongly polluted (AA)	1305	23	34-27-39
TNL3 155-160	Erosion bank, strongly polluted (AA)	86	14	33-18-49
TNL6 20-25	Floodplain, strongly polluted (AA)	3170	30	14-51-35
TNL24 25-30	Floodplain edge, weakly polluted	368	15	33-60-7
TNL24 130-135	Floodplain edge, weakly polluted	60	15	27-48-25
TNL26 40-45	Valley edge, weakly polluted	93	13	33-57-10
TNL26 55-60	Valley edge, weakly polluted	60	14	25-41-34
TNL7 30-35	Floodplain, strongly polluted	2057	27	26-58-16
TNL9 10-15	Floodplain, polluted	1163	19	16-40-44
TNL9 135 - 140	Floodplain, polluted	38	12	28-34-38
BTN14 90-95	Floodplain edge, weakly polluted	48	20	56-20-24

Table 4. Dating of floodplain sedimentary profile TNL16 using ^{210}Pb and ^{137}Cs activities.

Depth (cm)	**^{210}Pb Bg/kg**	**Uncert. (±)**	**^{214}Pb Bg/kg**	**Uncert. (±)**	**^{137}Cs Bg/kg**	**Uncert. (±)**	**^{226}Ra Bg/kg**	**Uncert. (±)**	**^{228}Ra Bg/kg**	**Uncert. (±)**
2-4	236	24	53.1	2.6	15.6	1.3	50.6	2.9	20.1	2
4-6	110	8	58.0	1.9	49.1	1.7	56.5	2	23.3	1.1
6-8	95.7	7.9	56.8	1.9	86.9	2.7	55.4	1.9	21.9	1.1
8-10	77.8	9.2	52.7	2.1	64.9	2.4	52.4	2.4	20.9	1.1
10-12	44.2	4.7	50.9	1.6	32.4	1.1	50.7	1.6	21	0.8
14-16	45.5	5.4	54.6	1.8	16.1	0.8	53.7	1.8	25	1
18-20	39.9	4.8	55.1	1.7	14.8	0.7	53.7	1.7	25.6	0.9

Table 5. Radiocarbon dating of erosion bank (profile TNL3).

Sample	**Depth (cm)**	**Lab. no.**	**Age ^{14}C (years)**	**Calibrated age AD (years)**	**Probability (%)**
Profile TNL3	117.5	Poz-57059	165 ± 3	1662 - 1706	16.9
				1720 - 1819	49.3
				1832 - 1880	10
				1915	19.2

Figure 1. Geological map with marked positions of all sediment profiles.

Figure 2. Detailed map of the Trhové Dušníky area: the 2nd Military Survey Survey (A), 2011 (B), river dynamics displayed on DEM model; orthophotomaps from 1953 (D), 2011 (E) and 2013 with marked Q100 range (F).

Figure 3. Detail of DEM model in the Trhové Dušníky area (A). Paleochannel in the first half of 19th century (B) and examples of avulsions in Trhové Dušníky area.

Figure 4. Typical profile from erosion bank (TNL3) in the Trhové Dušníky area with following sections: Results of 14C charcoal dating (A), profile description (B) and depth profiles of Al/Si (c.p.s./c.p.s.) as a proxy of a grain size, Fe (c.p.s.) and Mn (c.p.s.) and Pb/Ti and Zn/Al (both c.p.s./c.p.s.) (C).

Figure 5. Calibration of Al (A), Ti(B) and Al/Si ratio (C) as a “proxy” of clay fraction.Linear regression of Al (c.p.s), Ti (c.p.s) and Al/Si signals (c.p.s/c.p.s.) measured by ED XRF and percentage of clay fraction (grain size analyses of selected sediment samples).

Figure 6. A: Depth profiles of LEFs of Pb, with 206Pb/207Pb isotopic ratios, LEFs of Zn and depth profiles of K/Rb, with K/Rb line of pristine sediments (~13.4) shown for illustration, MS and Fe in Trhové Dušníky area, and also distinguished types of sediments according the type of contamination (I-III) with marked post depositional migration zones. B: The decrease of sediments pollution in profiles downstream from the Příbram area.

Figure 7. A: Concentration of Zn vs. Pb for all sampled sediments with three branches, indicated by Roman numerals (I-III): Pb-rich branch (I), medium (Pb~Zn) branch (II) and Zn-rich branch (III). B: The detail of the beginning of the plot shown in Figure 7A. C: Uncalibrated EDXRF signal ratios of K vs. Rb in all sampled sediments, with K/Rb=13.4 line shown for description of “normal alluvium”. D: Relation between Pb concentrations a K/Rb ratio in Trhové Dušníky area.

Figure 8. A: 206Pb/207Pb ratio vs. Pb concentration. B: Sb (ppm) plotted against Pb (ppm) concentrations in selected samples. C: Magnetic susceptibility values vs. Pb and Zn (D) concentrations within the entire study area. Linear regressions of Zn to Al (E), and Pb to Ti (F) with their local lithogenic background functions.

Figure 9. Zn/Pb ratios in SPM (wt. ratio) vs. the Litavka River water flow. Results were taken over from Table 2 in Žák et al. (2009). Our results are shown using grey rectangle for Pb~Zn branch (II) pollution and white rectangle for Zn-rich branch (III).

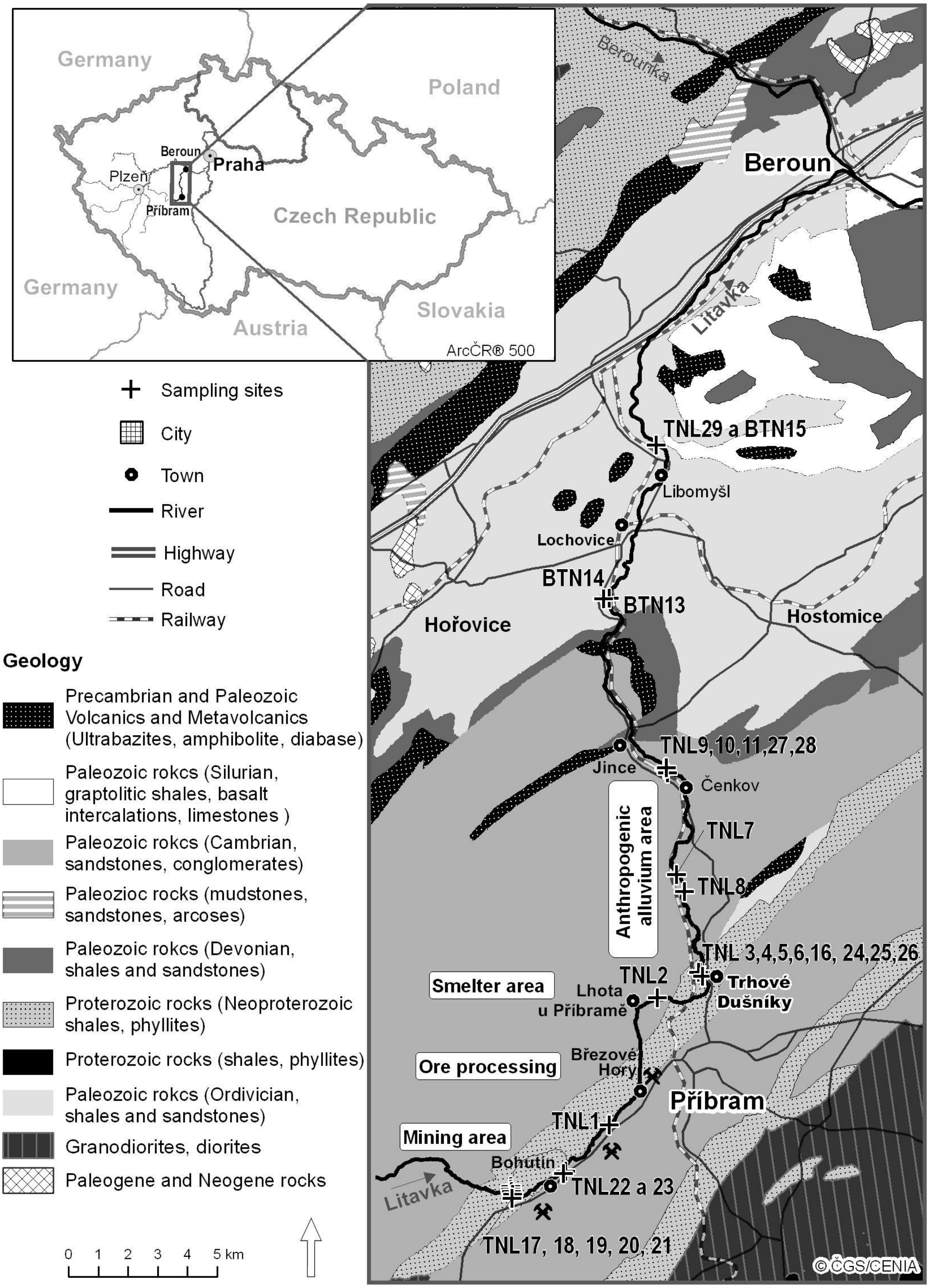
Germany
Poland
Beroun
Praha
Plzeň
Příbram
Czech Republic
Germany
Slovakia
Austria
ArcČR® 500
Sampling sites
City
Town
River
Highway
Road
Railway
Geology
Precambrian and Paleozoic Volcanics and Metavolcanics (Ultrabazites, amphibolite, diabase)
Paleozoic rokcs (Silurian, graptolitic shales, basalt intercalations, limestones)
Paleozoic rokcs (Cambrian, sandstones, conglomerates)
Paleozioc rocks (mudstones, sandstones, arcoses)
Paleozoic rokcs (Devonian, shales and sandstones)
Proterozoic rocks (Neoproterozoic shales, phyllites)
Proterozoic rocks (shales, phyllites)
Paleozoic rokcs (Ordivician, shales and sandstones)
Granodiorites, diorites
Paleogene and Neogene rocks
0 1 2 3 4 5 km
Berounka
Beroun
Litavka
TNL29 a BTN15
Libomyšl
Lochovice
BTN14
BTN13
Hořovice
Hostomice
TNL9,10,11,27,28
Jince
Čenkov
Anthropogenic alluvium area
TNL7
TNL8
TNL 3,4,5,6,16, 24,25,26
TNL2
Smelter area
Lhota u Příbramě
Trhové Dušníky
Ore processing
Březové Hory
Příbram
TNL1
Mining area
Bohutín
TNL22 a 23
Litavka
TNL17, 18, 19, 20, 21
©ČGS/CENIA

Figure 1

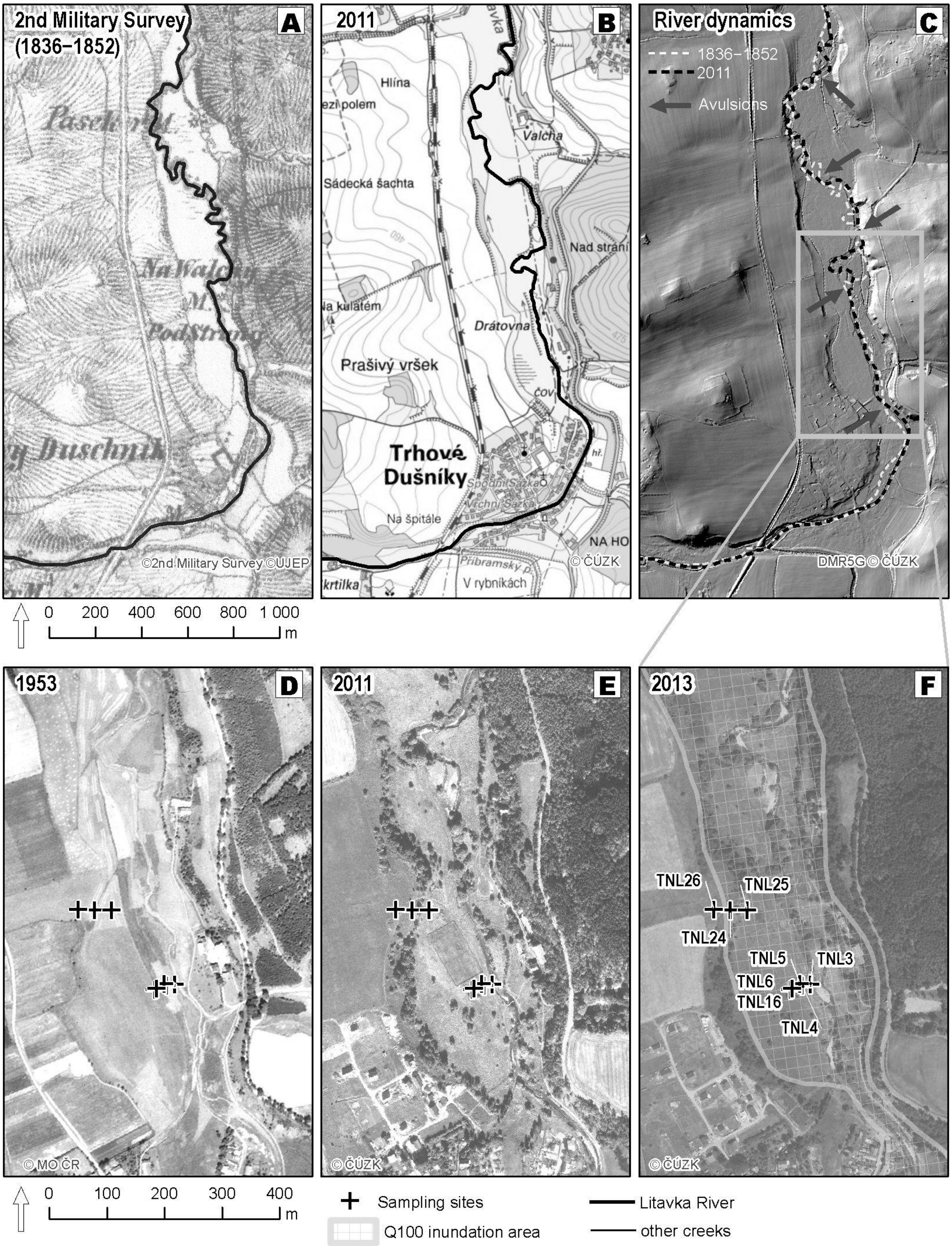
2nd Military Survey (1836–1852)
A
Paseka
Na Walcha
M.
Pod Strani
Duschnik
©2nd Military Survey ©UJEP
2011
B
Litavka
Hlína
Mezi polem
Valcha
Sádecká šachta
Nad strání
Na kulatém
Drátovna
Prašivý vršek
čov
Trhové Dušníky
Spodní Sázka
Vrchní Sázka
Na špitále
Příbramský p.
V rybníkách
Krtilka
NA HO
© ČÚZK
River dynamics
C
1836–1852
2011
Avulsions
DMR5G © ČÚZK
0 200 400 600 800 1 000 m
1953
D
© MO ČR
2011
E
© ČÚZK
2013
F
TNL26
TNL25
TNL24
TNL5
TNL3
TNL6
TNL16
TNL4
© ČÚZK
0 100 200 300 400 m
Sampling sites
Q100 inundation area
Litavka River
other creeks

Figure 2

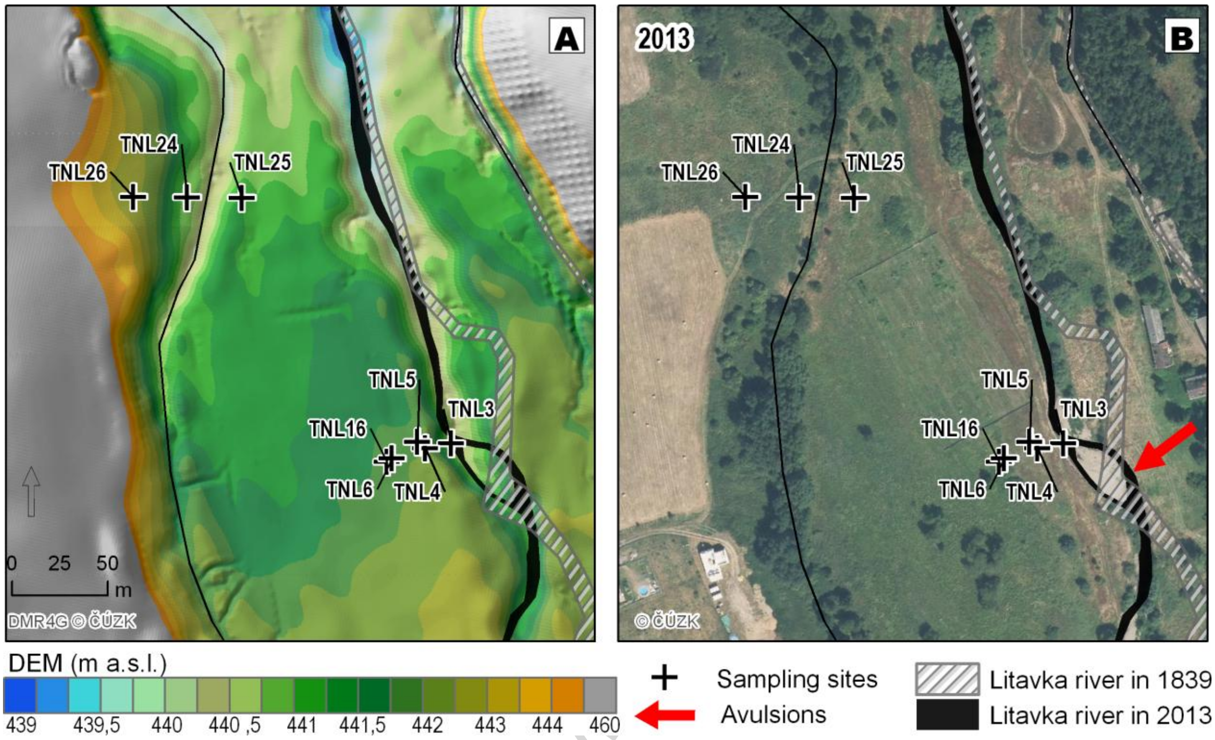
A
2013
B
TNL24
TNL26
TNL25
TNL5
TNL3
TNL16
TNL6
TNL4
0 25 50
m
DMR4G © ČÚZK
© ČÚZK
DEM (m a.s.l.)
439
439,5
440
440 ,5
441
441,5
442
443
444
460
Sampling sites
Avulsions
Litavka river in 1839
Litavka river in 2013

Figure 3

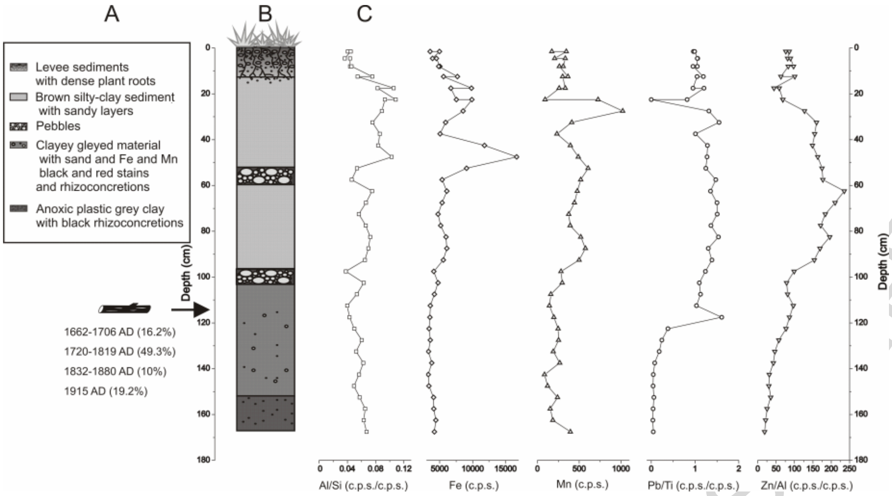
A
B
C
Levee sediments with dense plant roots
Brown silty-clay sediment with sandy layers
Pebbles
Clayey gleyed material with sand and Fe and Mn black and red stains and rhizoconcretions
Anoxic plastic grey clay with black rhizoconcretions
1662-1706 AD (16.2%)
1720-1819 AD (49.3%)
1832-1880 AD (10%)
1915 AD (19.2%)
Depth (cm)
0
20
40
60
80
100
120
140
160
180
0
0.04
0.08
0.12
Al/Si (c.p.s./c.p.s.)
5000
10000
15000
Fe (c.p.s.)
0
500
1000
Mn (c.p.s.)
0
1
2
Pb/Ti (c.p.s./c.p.s.)
0
50
100
150
200
250
Zn/Al (c.p.s./c.p.s.)

Figure 4

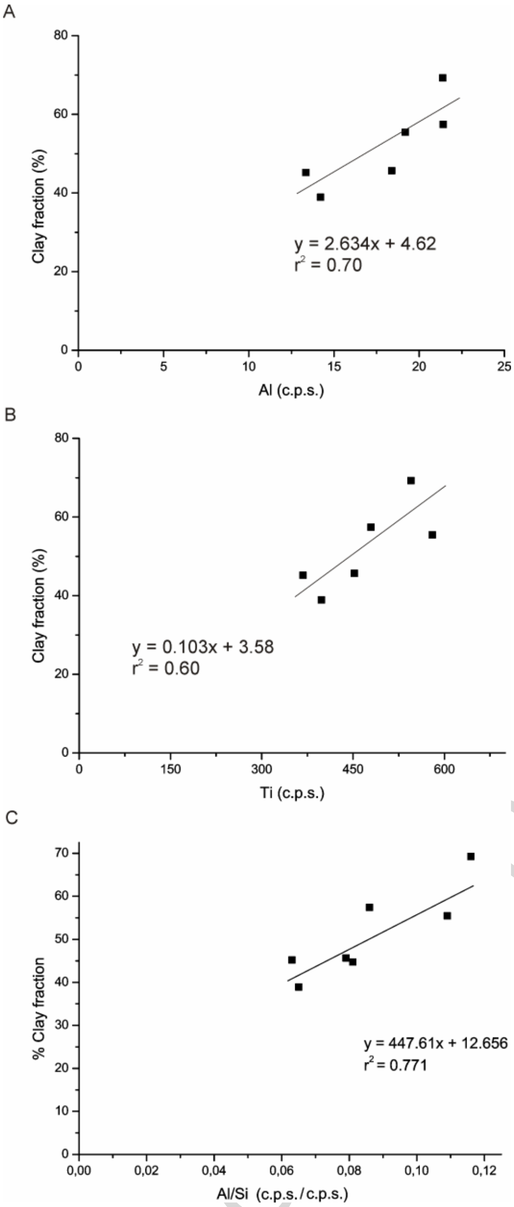
A
Clay fraction (%)
0
20
40
60
80
Al (c.p.s.)
0
5
10
15
20
25
y = 2.634x + 4.62
r^2 = 0.70
B
Clay fraction (%)
0
20
40
60
80
Ti (c.p.s.)
0
150
300
450
600
y = 0.103x + 3.58
r^2 = 0.60
C
% Clay fraction
0
10
20
30
40
50
60
70
Al/Si (c.p.s./c.p.s.)
0,00
0,02
0,04
0,06
0,08
0,10
0,12
y = 447.61x + 12.656
r^2 = 0.771

Figure 5

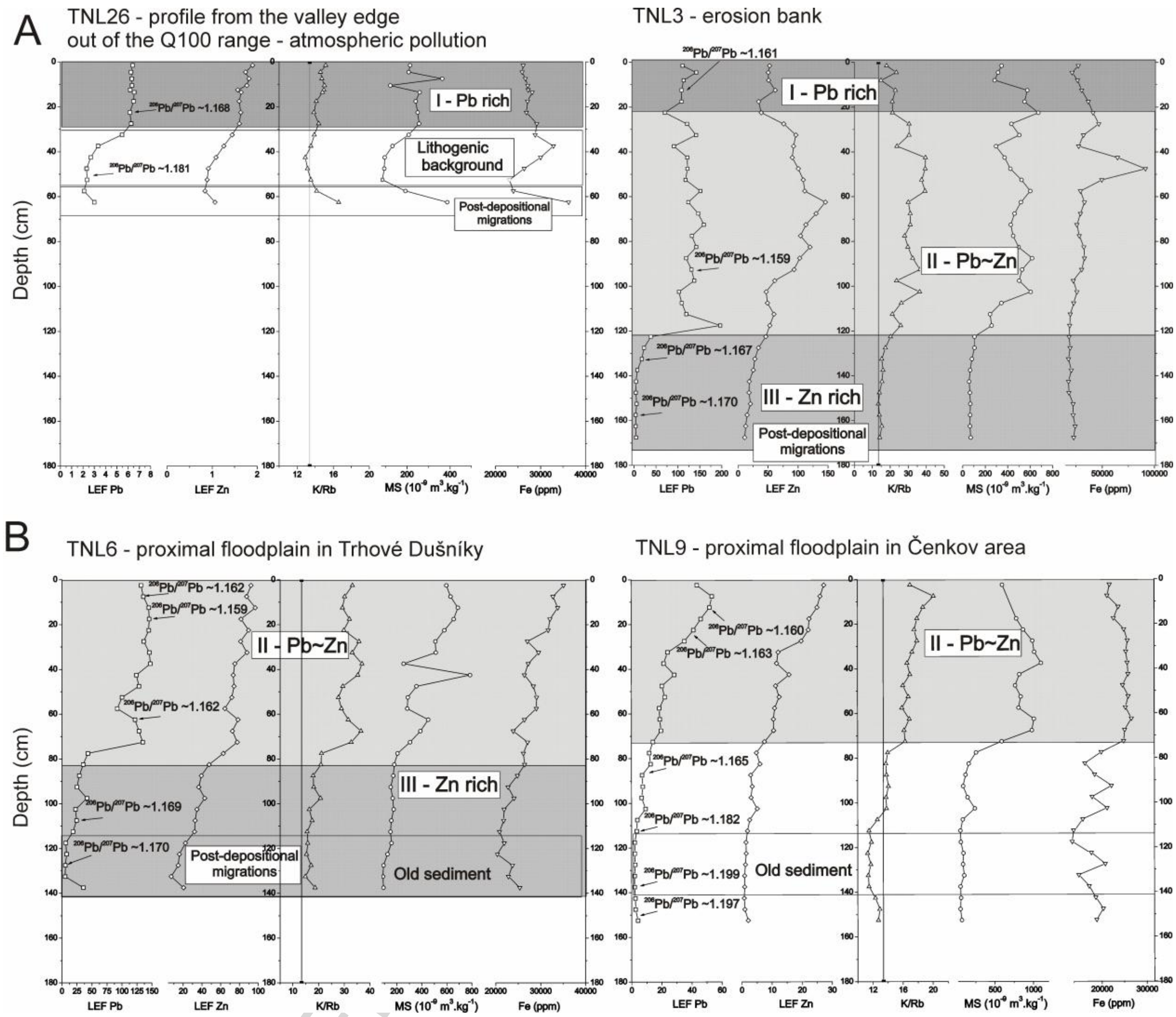
A
TNL26 - profile from the valley edge
out of the Q100 range - atmospheric pollution
TNL3 - erosion bank
Depth (cm)
^{206}Pb/^{207}Pb ~1.168
^{206}Pb/^{207}Pb ~1.181
I - Pb rich
Lithogenic background
Post-depositional migrations
^{206}Pb/^{207}Pb ~1.161
^{206}Pb/^{207}Pb ~1.159
^{206}Pb/^{207}Pb ~1.167
^{206}Pb/^{207}Pb ~1.170
II - Pb~Zn
III - Zn rich
LEF Pb
LEF Zn
K/Rb
MS (10^{-9} m^3.kg^{-1})
Fe (ppm)
B
TNL6 - proximal floodplain in Trhové Dušníky
TNL9 - proximal floodplain in Čenkov area
^{206}Pb/^{207}Pb ~1.162
^{206}Pb/^{207}Pb ~1.159
^{206}Pb/^{207}Pb ~1.162
^{206}Pb/^{207}Pb ~1.169
^{206}Pb/^{207}Pb ~1.170
Old sediment
^{206}Pb/^{207}Pb ~1.160
^{206}Pb/^{207}Pb ~1.163
^{206}Pb/^{207}Pb ~1.165
^{206}Pb/^{207}Pb ~1.182
^{206}Pb/^{207}Pb ~1.199
^{206}Pb/^{207}Pb ~1.197

Figure 6

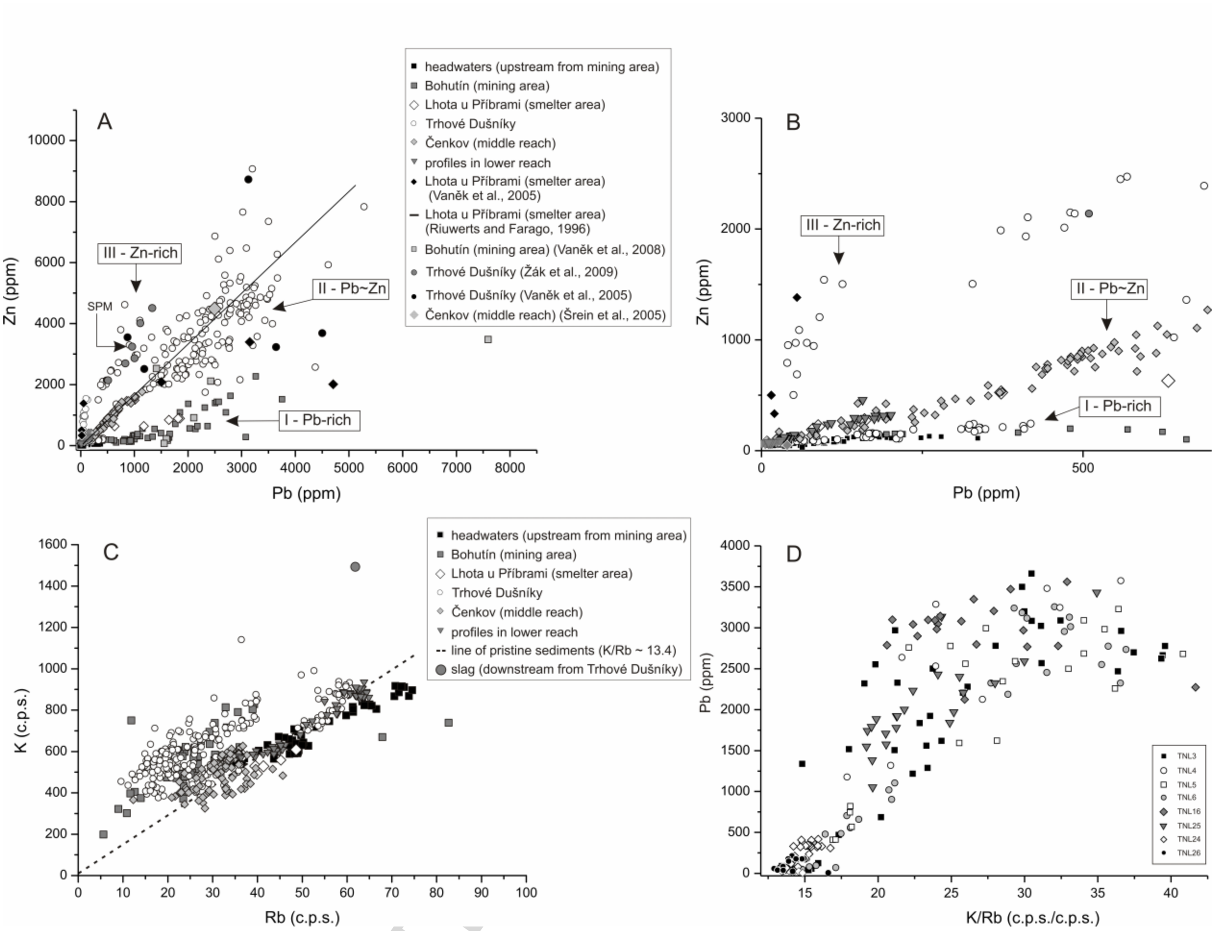
A
Zn (ppm)
Pb (ppm)
III - Zn-rich
II - Pb~Zn
I - Pb-rich
SPM
■ headwaters (upstream from mining area)
■ Bohutín (mining area)
◇ Lhota u Příbrami (smelter area)
○ Trhové Dušníky
◆ Čenkov (middle reach)
▼ profiles in lower reach
◆ Lhota u Příbrami (smelter area) (Vaněk et al., 2005)
— Lhota u Příbrami (smelter area) (Riuwerts and Farago, 1996)
■ Bohutín (mining area) (Vaněk et al., 2008)
● Trhové Dušníky (Žák et al., 2009)
● Trhové Dušníky (Vaněk et al., 2005)
◆ Čenkov (middle reach) (Šrein et al., 2005)
B
Zn (ppm)
Pb (ppm)
III - Zn-rich
II - Pb~Zn
I - Pb-rich
C
K (c.p.s.)
Rb (c.p.s.)
■ headwaters (upstream from mining area)
■ Bohutín (mining area)
◇ Lhota u Příbrami (smelter area)
○ Trhové Dušníky
◆ Čenkov (middle reach)
▼ profiles in lower reach
-- line of pristine sediments (K/Rb ~ 13.4)
● slag (downstream from Trhové Dušníky)
D
Pb (ppm)
K/Rb (c.p.s./c.p.s.)
■ TNL3
○ TNL4
□ TNL5
● TNL6
◆ TNL16
▼ TNL25
◇ TNL24
● TNL26

Figure 7

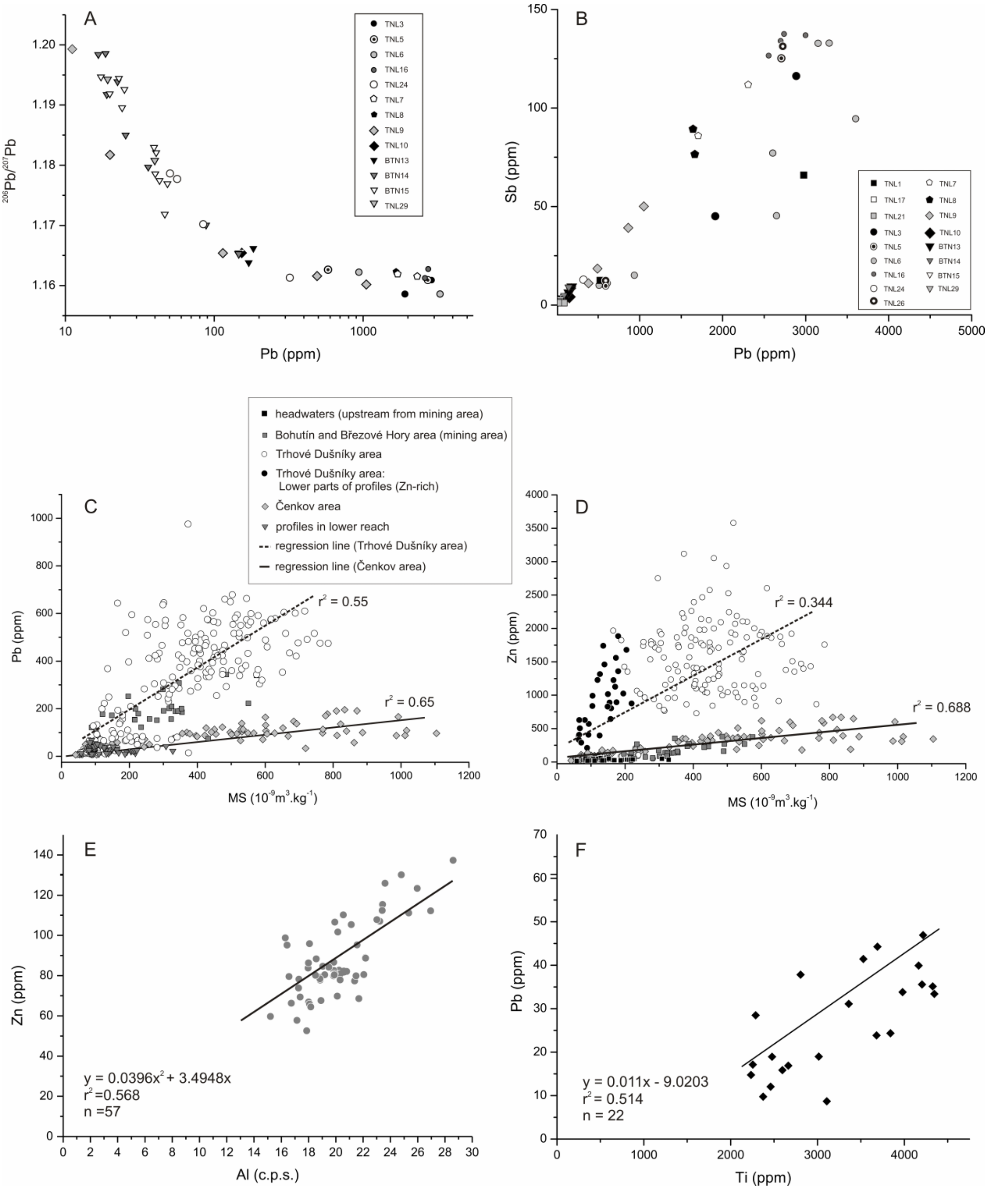
A
^{206}Pb/^{207}Pb
1.20
1.19
1.18
1.17
1.16
10
100
1000
Pb (ppm)
TNL3
TNL5
TNL6
TNL16
TNL24
TNL7
TNL8
TNL9
TNL10
BTN13
BTN14
BTN15
TNL29
B
Sb (ppm)
150
100
50
0
1000
2000
3000
4000
5000
Pb (ppm)
TNL1
TNL17
TNL21
TNL3
TNL5
TNL6
TNL16
TNL24
TNL26
TNL7
TNL8
TNL9
TNL10
BTN13
BTN14
BTN15
TNL29
headwaters (upstream from mining area)
Bohutín and Březové Hory area (mining area)
Trhové Dušníky area
Trhové Dušníky area: Lower parts of profiles (Zn-rich)
Čenkov area
profiles in lower reach
regression line (Trhové Dušníky area)
regression line (Čenkov area)
C
Pb (ppm)
1000
800
600
400
200
0
r^2 = 0.55
r^2 = 0.65
0
200
400
600
800
1000
1200
MS (10^{-9}m^3.kg^{-1})
D
Zn (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
r^2 = 0.344
r^2 = 0.688
0
200
400
600
800
1000
1200
MS (10^{-9}m^3.kg^{-1})
E
Zn (ppm)
140
120
100
80
60
40
20
0
y = 0.0396x^2 + 3.4948x
r^2 =0.568
n =57
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
Al (c.p.s.)
F
Pb (ppm)
70
60
50
40
30
20
10
0
y = 0.011x - 9.0203
r^2 = 0.514
n = 22
0
1000
2000
3000
4000
Ti (ppm)

Figure 8

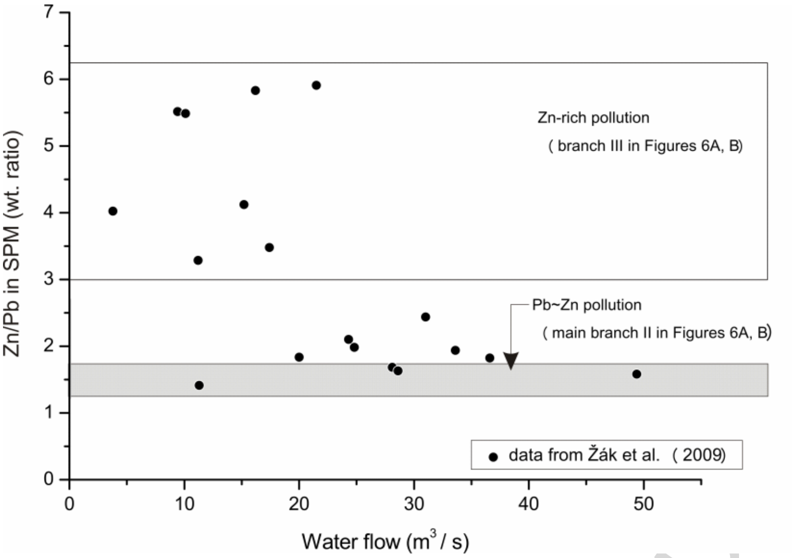
Zn/Pb in SPM (wt. ratio)
0
1
2
3
4
5
6
7
Water flow (m³ / s)
0
10
20
30
40
50
Zn-rich pollution
(branch III in Figures 6A, B)
Pb~Zn pollution
(main branch II in Figures 6A, B)
● data from Žák et al. (2009)

Figure 9

Research highlights:

- Secondary pollution of a fluvial system from polymetallic ore-mining and processing
- Tracing the presence of anthropogenic alluvium sediments in a fluvial system
- Revealing preferential chemical mobilization of Zn compared to Pb