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Obtaining isochrones from pollution signals in a fluvial sediment record: A case study in a uranium-polluted floodplain of the Ploučnice River, Czech Republic

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Research highlights:

- integrated approach to assess pollutant distribution in floodplain
- natural background concentration is a function and not a value
- concept of local enrichment factors based on local background functions
- secondary pollution from transient fluvial deposits

Uranium mining and processing in the watershed of the Ploučnice River in the Czech Republic during a well-defined time interval (1969-1989) allowed for a study of pollutant fates in sediments of a meandering river that is otherwise in a nearly natural state. A considerable part of the primary pollution is present in hotspots in the floodplain 10-15 km downstream from the mining district. One of the hotspots was characterised using geoinformatic, geophysical and geochemical means. The floodplain geomorphology and architecture and river channel dynamics were studied to develop an understanding of the formation of the hotspot and evaluate further movement of pollutants in the river system. Local background functions (with Rb or Ti as a predictor) and local enrichment factors (LEFs) were obtained for Ba, Ni, Pb, U and Zn concentrations in unpolluted sediments from the deeper strata of the active floodplain, an abandoned floodplain and an ancient terrace. The most recent (2013) overbank fines in the study area are still considerably enriched in Ni, U and Zn (LEF 3, 6 and 8, respectively), and thus pollution by heavy metals several km downstream of the hotspots continuously increases even though the primary source of pollution was terminated more than 20 years ago. The onset of the primary pollution (the base of the polluted strata) is hence clearly identified in the distal floodplain sediments as persistent and a potentially isochronous pollution signal in the fluvial record, whereas a secondary pollution signal

overwrites the expected “primary pollution climax” and “pollution improvement” signals. That inertia of the fluvial system can also be expected in other river systems with both laterally and vertically deposited sediments. The Ploučnice case study allowed for further elaboration of the concept of local enrichment factors in pollution assessment of fluvial sediments, which efficiently reduces the grain-size effects (the impact of hydraulic sorting) and hence allows for reconstruction of the pollution history.

## 1. Introduction

Knowledge of the manner in which pollution is distributed in a fluvial sediment record and how it behaves there helps in developing a better understanding of fluvial systems. The value of such approach has recently been demonstrated by the huge impact of methods based on the purely anthropogenic unstable isotope  $^{137}\text{Cs}$ , whose presence can provide isochrones in sediment bodies (Walling and He 1998). Chemical pollution of fluvial systems can also yield such isochrones, and its experimental characterisation can be less experimentally demanding than that of  $^{137}\text{Cs}$ . Chemical pollution can thus provide additional isochrones in sediment bodies. Certain pollutants may be more stable in sediment profiles than  $^{137}\text{Cs}$ , which migrates through coarser sediments with a low illite content. The pollution-based isochrones have been proven relevant for practical fluvial geomorphology and *vice versa*: the contaminant distribution in floodplains is a function of geomorphologic evolution (Macklin et al. 1994, Hudson-Edwards et al. 1999, Notebaert et al. 2011, Matys Grygar et al. 2011). The use of floodplain sediments for reconstructing the development of historical pollution has already demonstrated its potential in influential case studies of long-term historical pollution of European rivers (Hudson-Edwards et al. 1999, Swennen and Van der Sluys 2002). That approach has been developed further for evaluating pollution changes during the 20th century (Meybeck et al. 2007, Nguyen et al. 2009, Grosbois et al. 2012, Matys Grygar et al. 2012, Zachmann et al. 2013, Majerová et al. 2013). For each such sedimentary record, possible lags or other anomalies in the primary pollution signal are of crucial importance. Knowledge of the dynamics of the pollutant transport through the fluvial system with good temporal resolution is particularly important when the impacts of catastrophic pollution events and subsequent remediation measures are evaluated (Fleit and Lakatos 2003, Osán et al. 2007, Turner et al. 2008, Bird et al. 2008, Nguyen et al. 2009).

The aim of this study was to decipher the processes relevant to the deposition and fates of pollutants in floodplain sediments of the Ploučnice River, the Czech Republic. In a well-constrained

period of uranium mining in the 1970s and 1980s, that river system received a considerable load of pollutants (Hanslík et al. 1990, Kühn 1996, 1997, Kafka 2003, Majerová et al. 2013). One of our aims was to explain the presence of localised hotspots 10-15 km downstream from the mining area (Hanslík et al. 1990, Dědáček et al. 1991, Gnojek et al. 2005) and their consequences for the present-day situation. The pollution of Ploučnice sediments allows for insight into the processes of storage and future fates of sediments. Natural concentrations and the relative ratios of these actual concentrations to predicted natural concentrations (enrichment factors, EFs) were used while giving consideration to the known pitfalls of that approach (Reimann and de Caritat 2000, 2005, Desaulles 2012, Matys Grygar et al. 2013). We used EFs because they can substantially limit grain size effects on the actual contaminant concentrations in fluvial sediments (Matys Grygar et al. 2013, Nováková et al. 2013, Bednářová et al. 2013). EFs, if based on well selected on-site references, also best distinguish anthropogenic pollution from natural geogenic variability (Desaulles 2012, Majerová et al. 2013). The depth profiles of elements in floodplain fines may be affected by post-depositional migrations (Hudson-Edwards et al. 1998, Cappuyns and Swennen 2004), but if the normalising element is immobile, the migration of target elements is clear from “erratic” EF variations and their decrease at depths where reductimorphic processes affect also Fe depth profiles (Grygar et al. 2010, Matys Grygar et al. 2011, 2012, 2013, Nováková et al. 2013). EFs are hence efficient for constructing element depth profiles and then identifying possible pollution isochrones in sediment bodies. Our goal in this case study was thus to further improve the methodology of modelling fluvial records of pollution by introducing newly defined local enrichment factors.

## 2. Study area

### 2.1. Ploučnice River

The Ploučnice River (Figure 1) is a right-side tributary of the Labe/Elbe River (length: 106 km; catchment area: 1194 km<sup>2</sup>). The mean annual discharge at Mimoň is 2.30 m<sup>3</sup>/s, and the channel slope is approximately 0.6‰. It is a medium-energy meandering river in a confined valley with medium-grained cohesive to noncohesive floodplain sediments. The area (ca. 100x400 m) studied in detail is located south of the village of Boreček, alongside the middle reach of the river. In this area, the active floodplain is narrow (100-150 m), as the river is located in a valley bounded by Turonian to Coniacian sandstones (Kühn 1996) and Late Glacial/early Holocene fluvial deposits (Sádlo et al. 2013). The Ploučnice River has a meandering and anastomosing pattern on the floodplain, and the channel is ca. 5 m wide on average.

The entire active floodplain is inundated by Q5 discharges (Figure 2), but the lowest lying areas of the floodplain may be flooded annually during intense summer rainfalls. In the last decades, there were several overbank floods (1995, 1999, 2000, 2001, 2005, 2006, 2010, 2013) caused by the studied reach of river. Due to the narrow valley and the considerable slope, the flood flows are rapid. For example, on September 7-9, 2010, a flood with Q20-Q50 discharge (maximum 96 m<sup>3</sup>/s in Mimoň and 98 m<sup>3</sup>/s in Boreček) occurred in the study area (Figures 2 and 3), although the peak flood lasted only a few hours. The previous flood with a comparable magnitude was on July 18, 1981.

The middle reaches of the Ploučnice River (Figure 1) were affected by very different human impacts. Anthropogenic impact on the river system is clear in the maps of the 1st and 2nd Military Surveys (the second half of 18th and the first half of 19th century, respectively): there were several mills on the floodplain of the Ploučnice in the Boreček area. To provide the necessary amount of water and slope for the mills, artificial mill canals were built. In 1972-1986, the channel upstream of the studied area (Figure 1) was shortened and embanked (Kühn et al. 1996). The works started in Stráž pod Ralskem and ended south of the city of Mimoň (at the confluence of the Ploučnice River and Ploučnice Creek). The river in the area between Stráž pod Ralskem and Noviny pod Ralskem was engineered by the uranium mining company to prevent inundation and avoid polluting the cities just downstream of the mining areas (Figure 1).

Pollution of the Ploučnice River by heavy metals (Cd, Ni and Zn) and radioactive nuclides (<sup>226</sup>Ra, U) was first documented in 1978, and later studies confirmed downstream transport of pollution by the river system (Kühn 1996 and references therein). The primary pollution load was deposited in Boreček (Figure 1), an area just downstream of the end of the regulated river reach, where the natural meandering river channel and the wide inundated floodplain promote fluvial sediment deposition. The pollution in the Boreček area was confirmed by aerial and field gamma-spectrometric surveys in the latest 1980s and early 1990s (Hanslík et al. 1990, Kühn 1996) and chemical analyses (Kühn 1996). Hanslík et al. (1990) designated the area as the “central dump of radionuclides” due to very high gamma activity in three hotspots located along a reach approximately 2 km long near Boreček (Figure 1). For the current study, we choose the most downstream of the radioactivity hotspots in the Boreček area (Figure 2). The aerial gamma-spectrometric surveys in early 1990s and in 2005 (Dědáček et al. 1991, Gnojek et al. 2005) revealed uneven, highly localised deposition of gamma-emitting nuclides along nearly the entire reach of the Ploučnice River from Hamr na Jezeře and Stráž pod Ralskem (the areas of uranium industry) to the area of Česká Lípa. Laboratory gamma spectrometry analysis, particularly measurements of the <sup>226</sup>Ra/<sup>228</sup>Ra ratio (Hanslík et al. 2005), revealed pollution extending as far downstream as the confluence

of the Ploučnice and the Labe (the Elbe) Rivers.

## *2.2. Uranium mining and resulting pollution*

In the Stráž pod Ralskem area, uranium was mined by conventional methods (underground haulage) and by underground chemical leaching (Kafka 2003). Main U-bearing minerals are uraninite and hydrozircon; they occur in silty-sandy sediments. The conventional uranium mines were located in Hamr na Jezeře and Břevniště (Figure 1). They operated since the middle 1970s, with a peak in the 1980s (800-900 t/year). There was a decline after 1989, and the mining was terminated in 1994. Mine waters were the primary source of pollutants, which included heavy metals (particularly Ni and Zn),  $\text{SO}_4^{2-}$ , acid and radioactive nuclides (U,  $^{226}\text{Ra}$ ). The treating and cleaning of the polluted water were limited by its huge volume (Kafka 2003). At the beginning of the mining, the mine water was only treated by anion exchangers to remove U and by addition of  $\text{BaCl}_2$  to precipitate radiobarite  $(\text{Ra,Ba})\text{SO}_4$ . The primary pollution escaping to the Ploučnice system was minimised (terminated) at the end of the 1980s (Majerová et al. 2013), when, in 1989, a central waste-water management facility (“Central Decontamination Station” and settling reservoirs) was built (Kühn, 1996, Kühn 1997). Other possible sources of radioactive pollution of the Ploučnice system were tailing piles near mines at Hamr na Jezeře (Kühn 1997). The pollution of areas around such piles has recently been documented in other former U mining areas in the Czech Republic by Mihalík et al. (2011).

Chemical mining in the Stráž pod Ralskem area (Figure 1) started in 1969 by testing the underground leaching technology. This activity peaked in 1976 (800-900 t/year) and declined in the 1990s. The underground leaching consisted of pumping solutions of sulphuric acid (a total of 4.1 Mt of  $\text{H}_2\text{SO}_4$  was consumed) into U-bearing strata, extracting U from the leachate by anion exchangers and pumping the eluate back underground. Due to recycling of the acid solutions, this technology was reportedly nearly waste-free, except for a few spills of very limited spatial extent far from the Ploučnice River system. Chemical mining was thus most likely not responsible for the Ploučnice pollution (Kühn 1997, Kafka 2003).

## **3. Methods**

### *3.1. Geoinformatic and geophysical methods*

Datasets for GIS analysis were purchased from the Czech Office for Surveying, Mapping and Cadastre (ČÚZK) and Military Geographic and Hydrometeorology Office (VGHMÚř). For evaluation of channel avulsions aerial photographs from 1938, 1953, 1975, 1982, 1994, 1999, 2004, 2007, 2010 and 2013 were used. The historical photographs from 1938 were ortho-rectified using ERDAS 2013 LPS software. Actual and historical ortho-photos were used to study the channel migration of the Ploučnice River and characterise the morphological environment of the study area. Lateral shifts of the channel between 1938 and 2010 were analysed in ArcGIS 10.2 software. The laser scanning dataset from 2011 (DRM 5G) was used to create a detailed digital elevation model (DEM) and based on the DEM, a detailed geomorphologic analysis of the area was performed. Q5, Q20 and Q100 inundation areas were obtained from Povodí Ohře, a state enterprise responsible for the river management.

The subsurface architecture of the floodplain and distribution of the sediment bodies were studied using electrical resistivity tomography (ERT). Two ERT profiles, 175 and 103 m long (locations shown in Figure 2), with 1-m electrode spacing were developed using the automatic geoelectrical system ARES (GF Instruments, Czech Republic). The Wenner-Schlumberger method with 104 electrodes in a single array was used. The total 175-m length of profile 1 was measured using the roll-along method with a 24-electrode increment. Stacking of four pulses with a 0.5-s pulse time was used at each measurement point. The maximum depth of the apparent resistivity pseudosection was 15.2 m. An inverse model resistivity section was produced from the apparent resistivity pseudosection by the least-square inversion method using RES2DINV software (Geotomo Software, Malaysia).

### 3.2. Sampling

Sampling was performed as described in detail by Majerová et al. (2013). The sediments near the surface (0-30 cm) were sampled in shovel-dug pits. The deeper sediments (depths of 30 to 220 cm) were collected from drill cores in the bottoms of those pits using a manual groove corer with an inner diameter of 2 or 3 cm (Eijkelkamp, the Netherlands). Such coring cannot be used for coarse, wet sand and sediments with grains larger than the diameter of the groove. Sediment sampling for analyses was performed continuously to cover the entire depth profile at depth intervals (resolution) of 2 cm at the top, 3 to 5 cm at about 20-100 cm and 5 to 10 cm at the bottom of cores. In total, 516 sediment samples from 23 sampling sites were processed. The locations of the sampling sites are shown in Figures 1 and 2. The sediments from cores LMP3 and LMP12 had already been studied (Majerová et al. 2013), but their laboratory processing for XRF analysis was newly performed as part of the current study using different

sample processing (crushing by planetary mill instead of previous worse reproducible agate mortar & pestle), novel calibration of XRF analysis, much improved background functions and newly calculated enrichment factors. The deposits of a summer flood were sampled in locations shown in Figure 3 a few days after the overbank flood in summer 2013. That particular flood culminated between June 2 and June 3 at discharge of 37 m<sup>3</sup>/s.

### 3.3. Analytical methods

The sediment samples were air dried at ambient temperature (coarser sediments) or at 50 °C (finer sediments). Small stones (larger than ca. 5 mm) were manually removed before the sample processing. In sum 480 samples were analysed. The samples were crushed in a Pulverisette 6 (FRITSCH Germany). The XRF analysis was performed using a MiniPAL4.0 (PANalytical, the Netherlands) after placing the powder in the measuring cells with Mylar foil bottoms with a diameter of 2.7 cm, as described previously (Majerová et al. 2013, Matys Grygar et al. 2013). Reproducibility of the XRF analytical signal was 1 to 4 relative percent, Al, Si, Ti, Mn, Fe, Ni, Pb and U were obtained.

ICP-MS analysis of 12 samples was performed using an ICP-MS (X-Series II, Thermo Fisher) after acid digestion (HF+HClO<sub>4</sub>), as described previously (Strnad et al. 2005, Majerová et al. 2013). The analytical precision of the ICP-MS data for all the analyzed elements ranged from 0.5 to 5 relative %, the accuracy was controlled using the AGV-2 and BCR-2 reference materials (USGS, USA). Validation of results was performed as described previously (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 subsample of reference materials was digested and 2-3 replicates of their ICP-MS analyses were performed. The ICP analysis provided a dataset for calibration of the XRF signal (Table 1) and Pb stable isotope analyses.

Gamma spectrometry was performed with an REGe(n) GR3018 detector (CANBERRA Industries, Inc.). The samples were sealed in 450-ml Marinelli beakers for 30 days before measurement; this is a routine in gamma spectrometry to equilibrate isotopes in decay series.

The grain-size distribution of 12 samples of overbank fines was obtained by laser diffraction method using Sympatec HELOS system with QUIXEL dispersing unit. Organic matter was removed from the samples using peroxide and 3% hydrochloric acid (Blanck, 1976).

### 3.4. Background functions and local enrichment factors

The method of determining the natural concentrations was based on comparison of the target element concentrations and concentrations of a suitable, empirically selected element in unpolluted sediments not affected by post-depositional changes, called a normalisation or geochemical baseline (Covelli and Fontolan 1997, Vijver et al. 2008, Nováková et al. 2013, Matys Grygar et al. 2013, Dung et al. 2013). We prefer term "background functions" for that. The set of background (pristine) samples must not include sediments affected by post-depositional migration related to reductive dissolution and recrystallisation of Fe and Mn oxides driven by a varying water table, which is easily revealed by visual examination in the field and element analysis in the laboratory (Grygar et al. 2010, Matys Grygar et al. 2012, Nováková et al. 2013). The natural concentrations of target elements  $M_{\text{gbf}}$  are predicted by empirical functions of an appropriate element (predictor). We define local enrichment factors (LEFs) as the ratio of actual concentrations of metal  $M$  to its background concentration  $M_{\text{gbf}}$  predicted by the background function

$$\text{LEF} = M/M_{\text{gbf}} \quad (1)$$

LEF (as well as EF below) is dimensionless as  $M$  and  $M_{\text{gbf}}$  has the same concentrations units. For the first time we here use term LEF to stress that the definition (1) is different in principle from what is conventionally (historically) denoted the EF. Currently, the most widespread formula for the EF is

$$\text{EF} = (M/\text{Al})_{\text{sample}} / (M/\text{Al})_{\text{bg}} \quad (2)$$

where  $M$  and  $\text{Al}$  are concentrations of target element and  $\text{Al}$ , respectively. In eq. (2) the term  $(M/\text{Al})_{\text{bg}}$  is a single value of a reference sediment, traditionally that of type rocks prevailing in the watershed or even the mean ratio in the Earth's crust (the historical development of the EF concept was reviewed by Reimann and de Caritat (2000, 2005), Desaulles (2012) and Dung et al. (2013)). Formula (2) reduces to formula (1) only when  $M$  vs.  $\text{Al}$  (or other element predictor) is a linear function with a zero intercept, which is not always the best fitting function. Empirical functions best describing the relationship between the target and predicting elements may have a non-zero intercept (examples were presented by Covelli and Fontolan 1997, Vijver et al. 2008, Devesa-Rey et al. 2009, Majerová et al. 2013) or are non-linear (Majerová et al. 2013, Matys Grygar et al. 2013).

## 4. Results

### 4.1. River channel behaviour in Boreček

The channel in the study area exhibits lateral shifts within a ca. 10 m-wide channel belt between 1938 and

2010; thus, the rate of lateral erosion is 0-0.16 m/y (Figure 3). There is a common systematic development of meanders (increasing meander amplitude and general downstream channel shift). These features result from permanent deposition and erosion and reworking of the near-channel floodplain sediments by lateral channel shifts. Complete reworking of the active floodplain (including pollutants) most likely requires decades or centuries, as the width of the floodplain varies between 100 and 150 m in the studied hotspot.

Between 1994 and 1999, two meander cut offs or avulsions started to develop in the studied area according to aerial photographs, fully developed novel channels were apparent in 2007. That process produced two floodplain islands (Figures 2 and 3).

The field work during low-discharge periods indicated that the channel sediments consist of very fine (mud) to very coarse (gravel) deposits. The fine sediment is temporarily immobilised by woody debris and vegetation, and the coarser sediment is deposited in the form of bars in the over-widened sections with shoals. These sedimentary bodies can be reworked and thus remobilised by floods, and thus the pollutants contained within may be mobilised as well.

#### *4.2. Floodplain morphology and architecture at studied hotspot*

The floodplain surfaces in the study area may be divided into three geomorphic levels (Figure 2). The highest level (elevation of 268-269 m above sea level, m a.s.l., geomorphic unit C in interpreted DEM) is a terrace surface that could not be inundated even by Q100 discharges. Based on the ERT survey (Figure 4) and the lithological examination of the terrace material, the sedimentary structure of the terrace is strikingly different from that of other floodplain levels. The terrace surface consists of very poorly sorted, highly resistant and mechanically cohesive gravelly sediments with a thickness of ca. 5 m (see ERT profile 2 in Figure 4). Their matrix consists of mud and sand in variable proportions. The maximum grain size of the pebbles is 6 cm, and they are moderately rounded, indicating a short distance of fluvial transport.

The intermediate geomorphic level (267-268 m a.s.l., geomorphic unit D in interpreted DEM) is an abandoned floodplain segment. It could be inundated at discharges of over Q5 (both ERT profiles reach this surface, see Figure 2). In this floodplain section, the fragments of an abandoned channel were identified. This channel is nearly completely filled, and thus its present depth is just a few decimetres. The palaeo-channel is 10-15 m wide (approximately twice the width of the active channel) and its radius of curvature is several times larger than the active meanders). Consequently, the palaeo-channel developed

at a time when the Ploučnice River had a much higher discharge than currently. The palaeo-channel contains a few point bars, and it also displays evidence of erosion of the rims of the gravel terrace. This high floodplain section consists primarily of sand and silty sand to sandy silt with minor clay, and the thickness of the floodplain sediments according to ERT profile 2 is approximately 2-3 m. Finer, silty sediments are not common on this surface. This texture supports the conjecture that the palaeo-channel represents a time of larger discharge and higher-energy conditions.

The active floodplain represents the lowest (266.5-267.25 m a.s.l) geomorphic level, unit C in interpreted DEM. At this level, there are several meanders and a side channel of the meandering Ploučnice River. The channel is ca. 5 m wide, and its radius of curvature is ca. 20 m. The floodplain could be entirely inundated by Q5 floods (Figure 2), although its topographic lows could be flooded more frequently. There are a few decimetre-tall natural levees along the channel and crevasses connecting the channel with the distal floodplain depressions (Figure 2). A few remnants of an abandoned channel also were identified in the digital elevation model (Figure 2) and ERT profiles. The ERT survey revealed planar sedimentary structures of mud and sandy silt with uneven thicknesses (0.5-2 m), which is typical of meandering rivers with abandoned (buried) channel belts. Between stations 60 and 80 m along the ERT profile 1 there is a thick body of sandy sediments, which is probably a filled-in abandoned channel (Figure 2B). The ERT and field surveys revealed that much finer overbank sediment is deposited during floods than what has been deposited on the upper two geomorphological levels (i.e., former floodplain and terrace). Typical lithology of top 0.5 to 1 m of floodplain fill, i.e. typical overbank fines are silty clays to clayey silts with < 5 % sand.

The active floodplain in the studied hotspot is confined by the valley wall on the northwest and by the terrace and abandoned floodplain section on the southeast. Consequently, the width of the active floodplain tapers to a minimum of ca. 100 m. This width is considerably less than the width 300 to 500 m elsewhere in the Boreček area.

Immediately after the summer flood of 2013, we collected fresh overbank sediments from the active floodplain in the studied hotspot (sampling locations are shown in Figure 3). This sediment clearly indicates the presence of overbank aggradation in the current river system and valley; the thickness of the fresh sediment blanket was up to a few millimetres.

#### *4.3. Background functions of target elements*

Background functions are shown in Figure 5. They relate contents of target elements in pristine

(unpolluted) sediments to Rb or Ti, which produced better regressions than other elements tested (Al, K). That function for the given facies (overbank sediments) corrects for grain-size effects, as it is obvious from Figure 5. The sediment samples for the construction of background functions were selected using previously defined criteria of pristine sediments (i.e., from sufficient depths) not yet affected by redox changes caused by water table fluctuations (not from too great depths) (Grygar et al. 2010, Matys Grygar et al. 2011, 2012, 2013, Majerová et al. 2013, Nováková et al. 2013). Pristine samples were taken from all three geomorphic levels. Raw humus was not sampled, as it is geochemically disconnected from the mineral soil horizons below (Reimann and de Caritat 2000). For the Pb background functions, sediments from the surficial mineral strata along the terrace and the abandoned floodplain were excluded, as these were apparently affected by atmospheric fallout of Pb to LEFs of  $\sim 2$  (surficial 3-10 cm in the terrace and 40 cm in the abandoned floodplain). For other target elements, the surficial mineral strata in the abandoned floodplain, i.e., cores ŠTP1, ŠTP2, ŠTP5, ŠTP6 and ŠTP7, were not used because their uppermost 3-15 cm were clearly polluted. These profiles are located in the area inundated by Q20 and larger floods, at least two of which (1981 and 2010) occurred during and after the U mining. For the U, sediments that were too coarse (well sorted, gravelly sands with an Al/Si XRF signal ratio  $< 0.025$ ) were excluded from the background set due to their larger U contents. The resulting empirical background functions are shown in Figure 5, and their parameters are listed in Table 2. The decision to use Rb or Ti as the predictor (normalising element) was based on regression coefficients of the corresponding background functions.

The performance of the background functions is demonstrated also in Figure 6. It shows the actual U concentrations and ratios of actual U concentrations to the concentrations predicted for a given sample by the background functions ( $U/U_{\text{bgf}}$ ). The actual concentrations of U exhibit a broad polymodal distribution primarily due to the lithological variability of the pristine sediments. Regarding the lithology, there are two main populations of pristine samples: sandy-clayey silts from the abandoned floodplain and silt-clay mixtures typically with 30-60 % clay and  $< 5$  % sand from the active floodplain. This leads to two local maxima in U concentrations (Figure 6, left column). Properly chosen normalising element corrected this trivial grain-size effect and produced narrower and unimodal distribution function of  $U/U_{\text{bgf}}$ . A sediment sample can be considered polluted when its  $M/M_{\text{bgf}}$ , i.e., local enrichment factor, exceeds certain threshold values, which can be obtained from the empirical distribution functions of  $M/M_{\text{bgf}}$ , similar to what is shown for U in Figure 6. These threshold values are listed in Table 2 at the 95 and 99 % probability levels.

#### 4.4. Depth profiles of target elements in overbank fines downstream from Boreček

Depth profiles of Al/Si ratio and enrichment factors of Ba, Pb, U and Zn and Fe in cores ŠTP12, LMP12 and LMP3 are shown in Figure 7. Figure 8 shows the same element pollutants together with the  $^{137}\text{Cs}$  activity and  $^{226}\text{Ra}/^{228}\text{Ra}$  activity ratios from the gamma spectrometry and the  $^{206}\text{Pb}/^{207}\text{Pb}$  from ICP-MS for LMP12; from these values it is possible to infer an age model for the pollution (in Discussion). Isotope ratios of Ra and Pb were taken from our previous report (Majerová et al. 2013).

At depths greater than 45 cm, the overbank fines are sandy-silty or sandy, i.e., too coarse and too close to the fluctuating water table to prevent target elements from migrating associated with reductive dissolution and recrystallisation of Fe(III) oxides. Both phenomena are demonstrated by variable (scattered) LEFs of pollutants and Fe in Figure 7. The unpolluted sediment strata with Fe LEF ~1 ratio and target element concentrations are denoted “pristine” in Figure 7. Above, there is a layer approximately 10 cm thick with only Pb enrichment; this layer is associated with a slight shift in the  $^{206}\text{Pb}/^{207}\text{Pb}$ , designated “pre-U polluted” sediments in Figures 7 and 8. Overlying this layer there is a layer enriched in Zn, Ni, U and  $^{226}\text{Ra}$  (designated “U-polluted” sediments). Within this layer there is a horizon (an event layer) with a sharp maximum Ba enrichment (designated the “Ba event”). The top of the U-polluted strata displays stable or slightly declining Ni and U enrichment and stable or successively increasing Zn enrichment.

All three studied cores downstream of Boreček exhibit the same pattern of the pollution depth profiles (Figure 7). The same temporal shift of Pb (earlier) and Ni-U-Zn pollution has also been found in profiles LMP1 and LMP9 between core LMP12 and Česká Lípa (Majerová et al. 2013). In profile LMP3, most remote from the hotspot, there LEF of all U-related pollutants are smallest. On the other hand, LEF in LMP12 are higher than in ŠTP12 although the latter is closest to the hotspot, but polluted layer in LMP12 is thinner.

#### 4.5. Depth profiles of target elements in overbank fines in Boreček

The element depth profiles in selected cores in Boreček are shown in Figure 9. The difference between the excessively coarse sediments affected by Fe(III) dissolution and recrystallisation and target element migrations is visible as clearly as in the profiles downstream of the Boreček area. The pollution signal is, however, clearly different, and the chemostratigraphic correlation of the profiles from the Boreček area is much less straightforward, if possible at all. The “Ba-event” horizon, a layer with the highest

concentration of Ba (associated with Sr and U peaks), is present in all of the cores from the Boreček area, except for core MHP1. In cores MHP2, MHP4 and MHP9, the sediment in the top 5-10 cm is less polluted (but still exhibits considerable LEFs).

Core MHP1 is located on the southeastern edge of the active floodplain near a minor channel that is certainly active during floods. The core is situated in a thick unit of coarser, sandy silty overbank deposits, based on ERT profile 1 (Figure 4). Core MHP1 has the thickest sediment strata enriched by Pb and Zn, including the entire depth of the fine sediments (top 1 m), U and Ba (top 80 cm) (Figure 9). This remarkable thickness indicates very fast deposition in that part of the floodplain. There is no possible correlation of the MHP1 depth profiles of pollutants to that of any of the other studied cores.

Both Pb and U-associated elements are enriched in cores MHP2 and MHP4, and the pre-U polluted sediments (with only Pb enriched) are either missing or substantially condensed. In core MHP2 (Figure 9), the polluted sediments are underlain by coarser deposits, indicating that overbank fines from earlier periods are also missing.

Core MHP3 contained sandy sediment of the channel bank, with an elevated Pb concentration in the entire sampled thickness. At depths of 10-20 cm, there is a thin bed of a finer sediment (mud) with U-associated pollution (Ba, Ni, U, Zn).

The upper 18 cm of core MHP9 is polluted by all of the target elements. The “pre-U pollution” sediment only enriched in Pb may possibly be at a considerable depth (60-70 cm) or is missing. In contrast, nearby core MHP10 is polluted in the upper 50 cm. That latter site has stratified sediments (strata with alternating Al/Si, Figure 9), indicating the presence of alternating lower and higher energy flow regimes during deposition. The sediments from core MHP10 exhibit the largest LEFs among all of the sediments analysed.

Recent overbank fines (from the summer 2013 flood) are considerably enriched in heavy metals and U (Table 3). The LEFs of Ni, U and Zn are only slightly smaller than what is found in the uppermost centimetres of the sediment profiles in the Boreček area.

## **5. Discussion**

### *5.1. Background concentrations of target elements in sediments are functions, not values*

Sediment sorting is an inherent feature of fluvial deposition in floodplains. The contents of target elements including pollutants (like Pb) as well as “purely geogenic” elements (like Ti) in pristine

sediments hence inevitably vary with lithology; it ranges from sandy silt to silty clay in the studied Ploučnice floodplain. The reason is that generally each size fraction has a slightly different element composition and hence also background concentrations depend on lithology. Surprisingly the term "background" is mostly used by environmental geochemists for a value or a range. For a given watershed, a given river system and a given sedimentary facies it is hence possible to define empirical functions best relating target element concentrations with some grain-size proxy, such as Al, Ti or Rb, clay fraction or other easily accessible parameter (Vijver et al. 2008, Nováková et al. 2013, Matys Grygar et al. 2013, Dung et al. 2013). Use of background functions also called "normalisation" was most systematically corroborated in 1990s and early 2000s for estuarine and marine sediments, where the target elements are diluted mainly by autochthonous components (carbonates or organic debris, representative example is Covelli and Fontolan 1997). In fluvial domain, the diluting components are mainly quartz and further common minerals such as feldspars and muscovite. But while the use of normalization in near- and offshore marine sediments is so common that even reviewing it would be a demanding task, exceeding the scope of this paper, implementation of this concept in fluvial domain is quite underdeveloped.

The background functions (Figure 5, Table 3) obtained for the overbank fines in the studied reach of the Ploučnice allowed for processing a set of unpolluted sediment samples of varying grain size – both finer sediments from the active floodplain and coarser deposits of ancient floodplain surfaces. This provision supports the validity of the method of acquiring pre-industrial background functions (Matys Grygar et al. 2013, Nováková et al. 2013) used in this work. Although there are no firm independent time constraints on the background sediments from the active floodplain (they are "dated" merely by their lack of chemical pollution), the terrace and abandoned floodplain certainly predate any modern local and regional industrialisation. An abandoned floodplain with features (palaeo-channel and meander sizes, relative elevations above the active floodplain of 0.5-2 m) similar to those in the Boreček area but located 3.5 km downstream of our studied hotspot in Boreček was recently been studied by Sádlo et al. (2013). Pollen analysis indicated that the terrace and abandoned floodplain date to the Late Glacial or Preboreal periods.

The lithological variability in a large set of on-site reference samples produced very robust estimates of the background functions and hence robust calculations of the LEFs. This approach can allow for chemostratigraphic correlation of pollution signals unbiased by grain-size effects. Because the grain-size correction allowed for processing of sediments varying from silty sand to clayey silt, there was no need to decrease the element concentration variability by sieving as is otherwise common in environmental geochemistry. In fact, sieving introduces an unnecessary, artificial extra process of grain

size sorting, based on the not always substantiated idea that coarse grain-size fractions are not polluted.

### 5.2. Sedimentation patterns and age model for overbank fines

Deposits in the Ploučnice floodplain are mainly represented by coarse (gravelly sandy) channel sediments topped by sands from abandoned channel fills and/or point bars. These strata are shown on the ERT profiles in Figure 4 – they have resistivity 150-250  $\Omega\cdot\text{m}$ . On the top of those coarse sediments there are overbank fines, clayey silts to silty clays (resistivity  $<100 \Omega\cdot\text{m}$ ) – actually these are retrieved by the hand-drilled coring used in this study. The blanket of those overbank fines in the Ploučnice floodplain in the analysed cores downstream of Boreček has a thickness of approximately 50 cm (45 cm in ŠTP12, 50 cm in LMP12, 70 cm in LMP3). The accumulation of fine overbank deposits in the Ploučnice valley started before the period of industrial activity because sediments of greater depth on the active floodplain are not enriched in element pollutants (Figures 7 and 8, sediments denoted “pristine”). The uppermost sediments represent the time span of the industrialisation period to the present. Fine overbank deposits (muds) mostly originate as suspended sediment, which can be transported over very long distances during single flood events (Osán et al. 2007).

The stratigraphic correlation of pollutant depth profiles in the overbank fines (Figure 7) indicates that the Ploučnice floodplain contains a valuable sedimentary record. Direct dating of overbank deposits by  $^{137}\text{Cs}$  (Chernobyl accident) and indirect dating by assigning the pollution distribution to the industrial development, i.e. pollution chemostratigraphy for the given area is shown in Figure 8. In all profiles downstream from the hotspots there are pristine overbank fines at the base of the overbank fines (clayey silts to silty clays). Higher in the profiles there is the onset of Pb pollution (associated with the onset of Cu and Sb pollution) assigned roughly to 1900, an onset of modern industrial technologies, central European lead metallurgy and coal combustion (Zuna et al. 2011, Matys Grygar et al. 2012, Majerová et al. 2013). The Pb pollution in the Czech Republic peaked in the 1950s-1980s (Matys Grygar et al. 2012, Zuna et al. 2012), when the impact of leaded gasoline use contributed to both Pb enrichment and a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio decrease. The decrease in the  $^{206}\text{Pb}/^{207}\text{Pb}$  from the typical value in Czech soils and sediments (ca. 1.20) to approximately 1.17 in the uppermost sediments from the Ploučnice active floodplain is shown in Figures 8 and 10. In Figure 10, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of 25 samples of overbank fines is plotted against the Sb/Pb ratio. The stepwise decrease in the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in the background samples to the youngest sediments is clear and shows unequivocally diffuse pollution by Pb – there was no known Pb point pollution source in the Ploučnice watershed.

The onset of pollution related to the U industry may be dated to the early 1970s, and in the mid 1970s, the uranium mining grew most extensively (Kafka 2003). The beginning of radioactive pollution of the water of the Ploučnice River coincided with that period (early 1970s) and reached its maximum in the middle 1980s (results by Hanslík et al. cited by Majerová et al. 2013). In the sediment record, the onset of pollution related to the U industry is unequivocally marked by the onset of  $^{226}\text{Ra}$  and U as primary pollutants (Figure 8), coevally with onset of massive pollution by Ni and Zn. Nearly simultaneous growth of Ni, U and Zn is also apparent in the profiles in the studied hotspot (Figure 9).

In all profiles downstream from the hotspot there is only one sample (2-3 cm thick sediment layer) per a profile statistically significantly enriched in Ba (Figure 7 and 8, sediments denoted “Ba event”). That element is a very specific pollutant – it was introduced by the technology chosen for decontaminating the mine waters, from which  $^{226}\text{Ra}$  was co-precipitated in  $\text{BaSO}_4$  as radiobarite. That event layer with Ba was also found in the hotspot, where it is much thicker (MHP1 and MHP2) or where it is doubled (MHP10) (Figure 9). The association of that layer with the U-mining waste is also supported by a distinct  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in Ba-event layer in MHP10 core (Figure 10): it has the largest value due to the largest contribution by the  $^{206}\text{Pb}$  isotope having been created by the U decay series. These maximal values are 1.237 and 1.241 for samples MHP10 from depths of 16-19 cm and 45-50 cm, respectively. Notably, the uranium product (called “yellow cake”) from Stráž pod Ralskem contains Pb with a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of approximately 1.23 (Varga et al. 2009). According to Hanslík et al. (1990) and Kühn (1997), the reason for the primary input of pollution by the gamma emitting nuclides (mainly  $^{226}\text{Ra}$ ), to the Ploučnice River system was the extreme flood in 1981, i.e., in the period of very active U mining. For that reason, we attribute the Ba event horizon to the extreme 1981 flood.

The end of the 1980s was the period when pollutants largely stopped escaping from the U mining areas to the Ploučnice system. In LMP12 that period is marked by a  $^{137}\text{Cs}$  activity peak due to the accident in the Chernobyl nuclear power plant (Figure 8). However, the decline in pollution since the end of the 1980s is not apparent in the overbank sediments. Instead, the most recent floodplain sediments, collected in the area of the studied Boreček hotspot, are still considerably polluted (Table 3). Since the termination of the primary pollution more than 20 years ago, each profile shown in Figure 7 should have been capped by a 2-5 cm thick layer of unpolluted overbank sediment, assuming the age model of LMP12 shown in Figure 8. Clearly, secondary pollution has been important.

### *5.3. Hotspots in Boreček: causes, peculiarities and consequences*

All of the hotspots in the Ploučnice floodplain (Dědáček and Zabadal 1991, Gnojek et al. 2005; their locations are shown in Figure 1) are located in areas that were naturally inundated before 1981. Before 1981, the river channel was straightened and deepened in the section between the discharge points of the industrial solutions from the U mining in Stráž pod Ralskem and Noviny pod Ralskem. Between Noviny and Mimoň, the engineering works were not finished in 1981, when an extremely large flood transported pollution from the U industry to the Ploučnice floodplain and farther downstream (Kühn 1997). Hydrological extremes are known to enhance transport of sediments from temporary sinks in a river channel, valleys of higher-order tributaries and watersheds to the trunk river. Along the channelised section of the Ploučnice River, much less sediment was deposited due to an increased flow capacity of the artificial channel and reduced inundation; therefore, most of the particles containing waste from the U mining carried by the Ploučnice River were transported farther downstream. This explanation for the presence of hotspots in Boreček has already been proposed by J. Kühn (1996) and P. Kühn (1997).

The floodplain near Boreček has a highly variable width, which most likely determined the deposition pattern of the polluted suspended sediment, which therefore accumulated in a chain of hotspots instead of a single cover all over the active floodplain (Figure 1). The hotspot described in this paper (Figure 2) is located immediately downstream of a bridge built in the early 1980s, and it terminates where the active floodplain is extremely narrow (~100 m) due to the remnant of the old gravelly terrace. Such a geomorphological setting favours the formation of a “sediment plug”, such as where the valley widens between the two narrow sections and thus the energy of overbank flooding decreases, resulting in greater overbank deposition. The process is also enhanced by the dense herbaceous vegetation along this section of floodplain. The particularity of the studied hotspot is the relatively large pollutant concentrations in a relatively thick layer. The lack of chemostratigraphic correlation in the Boreček sediment cores shows spatially uneven deposition of the youngest sediments, i.e., the hotspot itself is spatially variable.

Hanslík et al. (1990) and Kühn (1996, 1997) reported that maximum pollution by radionuclides in Boreček in the latest 1980s and early 1990s was along the river banks and abandoned channels. That distribution is not the case in the hotspot described in this paper. Currently, 20 years after these pioneering studies, the most polluted samples are located on the floodplain. In addition, Kühn reported in 1997 that the actual levels of gamma activity in individual near-channel sites in Boreček were lower than those published by Hanslík et al. (1990). The most plausible explanation for these discrepancies is sediment reworking in the channel belt (described in Results). Indeed, the 2011-2013 the sediments taken from the channel belt (MHP3 in this study, LMP9 in Majerová et al. 2013) are less polluted than those from distal floodplains in the corresponding reach of river. It is likely that a portion of the pollutants from

these formerly maximally polluted channel sediments (deposited in the 1970s and 1980s) were transported farther downstream and partly transferred from the channel vicinity to the distal parts of the floodplain.

Kühn (1996) reported on another hotspot located a few hundred metres upstream of our study area, just a few hundred metres downstream of the confluence of the Ploučnice River and Ploužnice Creek, at the end of the engineered river reach (Figure 1). In this hotspot studied by Kühn, the typical thickness of U-polluted strata in overbank fines was only a few cm, and the maximum concentrations of U were 40-75 ppm in the <63- $\mu\text{m}$  fraction (Kühn 1996), i.e., much less than that in the active floodplain in the area shown in Figure 2. In contrast, up to 240 ppm of U was found in the <63- $\mu\text{m}$  fraction near the active and abandoned channels (Kühn 1996). The studied hotspot (Figures 2 and 3) is now most likely the most polluted part of the Ploučnice floodplain. There are no Czech or European regulations regarding U in soils, and the most frequently used guideline is the Canadian norm (CCME 2007). The highest concentrations of U in the study area (above 600 ppm) exceeds not only the CCME limits for agricultural, residential/park land and commercial lands but also the highest allowed value of 300 ppm for industrial land. The maximum content of Zn (above 1000 ppm) exceeds Czech and European guidelines for agricultural soils. In the sediments of Boreček, most of the uranium in the polluted sediments is present in the fractions of Fe and Mn oxides and organic matter, and most of the zinc is in the fractions of Fe and Mn oxides (Kühn 1996), all of which are susceptible to reductimorphic processes inherent to floodplain sediments with a variable water table. The study area therefore merits further monitoring, particularly if the floodplain should be engineered or planned for agricultural use, e.g., hay production.

#### *5.4. Origin of pollution signal in overbank fines and lag of “signal of improvement”*

The post-depositional movements of the primary pollution may make the reconstruction of the pollution history in the fluvial systems more complex than expected. The downstream transport means that the temporal evolution of the pollution will depend on the facies (and hence on the distance from channel) and distance from the pollution source; these are consequences of fluvial activity and depositional patterns of a given river system. The example from the Ploučnice River system indicates that reconstruction of the past pollution is not a trivial task: most likely only the onset of pollution may have produced an isochrone in the fluvial sediment record, the pollution maximum may be masked by secondary pollution, and a decrease in the primary pollution is not necessarily apparent in the sediment record. The primary signal is persistent in the distal floodplain but not in the channel belt, where it may be

removed by lateral erosion. Channel banks, however, may better reflect a “signal of improvement”. On the other hand, the “archival” value of the channel bank sediments is limited by their complex stratigraphy, increased probability of hiatuses and secondary chemical pollution due to physical contact with river water (Matys Grygar et al. 2013).

The fact that primary pollution historically deposited in fluvial sediments may become a source of secondary pollution is well known (Hudson-Edwards et al. 1999, Bird et al. 2008, Turner et al. 2008, Žák et al. 2009, Zachmann et al. 2013, Ciszewski et al. 2013). The secondary pollution must inevitably produce a signal temporally very different from the evolution of the primary pollution. The primary input of pollutants to most Czech rivers after 1989 has declined due to the fall in domestic industrial production and simultaneous growth of environmental concerns, yet no sedimentary “signal of improvement” in the Jizera and the Morava Rivers in the Czech Republic is clearly visible (Matys Grygar et al. 2012, 2013). Similarly, in Germany after the re-unification, the “signal of improvement” is still absent in the middle and lower parts of the Elbe River (Zachmann et al. 2013).

The secondary pollution is a function of sediment deposition/reworking patterns and hydrological conditions. Its understanding requires an analysis of floodplain architecture and channel behaviour. In addition, the results of this study indicate that the secondary pollution is element specific: the spread of Ni and Zn is more pronounced than that of U, whereas Ba seems to be least remobilised from its location in the sediment sinks. This pattern may be related to the chemical stability and insolubility of radiobarite. Secondary pollution can also be influenced by (bio)(geo)chemical processes, which were not addressed in this study.

The secondary pollution by sediment reworking is a mechanism which must be taken into account if pollution history is evaluated. A pattern of transfer of pollutants through a fluvial system with well-defined time constraints is shown in Figure 11. This pattern is derived from the results discussed in this paper. There are two mechanisms that may produce the onset of a pollution signal in response to primary pollution: downstream propagation by bedload (mode 1) or by suspended load during overbank flood (mode 2). Bedload is transported downstream rather slowly but more continuously, whereas suspended load in overbank flooding is spread much more quickly but only during the limited time of overbank discharge. These two modes are just end members of the actual situation, although one may dominate under certain circumstances.

Mode 1 would be applicable to a continuous input of pollutants to the river system irrespective of the actual hydrological situation and river discharge. The overbank flows may then dilute the primary pollution, as was observed after the millennial flood in the Vltava River in 2002 (Navrátil et al. 2008), but

it can simultaneously export the particulate pollutants from temporary sinks in the channel belt to the floodplain. The previous and current analyses of the hotspots in the Boreček area have clearly shown the transport of the near-channel sediments onto the floodplain. The “cleaning” of the channel belt by channel-belt sediment recycling and secondary pollution of the floodplain during each subsequent flood are very important components of this mode of pollutant transport. The onset of the pollution signal in the sediment record is then isochronous only in the floodplain along the maximal transport path before the first important (extreme) flood event. No pollution isochrone can exist in the channel belt deposits under the conditions of Mode 1.

Mode 2 in Figure 11 is a different situation: under normal circumstances, solid pollutants accumulate in temporary sinks in the watershed, including industrial areas disconnected from the trunk channel. Then, an extreme rainfall followed by an overbank flood spreads the pollution across the floodplain and downstream of the source in an event-like manner by opening new and activating permanent routes of sediment transport. Mode 2 is typical for the catastrophic events associated with damage to tailing ponds by extreme rainfall (Fleit and Lakatos 2003, Osán et al. 2007, Turner et al. 2008, Bird et al. 2008, Nguyen et al. 2009). A pollution isochrone can then be assigned to the first exceptional flood after the onset of the pollution. The isochrones of the onset of pollution are formed in both the channel belt and the floodplain, but the former is then continuously erased in the direction downstream of the pollution source. In the Ploučnice system, the flood of 1981 was probably the cause of the “Ba-event” layer associated with the maximum U concentrations.

A situation much more complex than that shown in Figure 11 will occur if the activation of a pollution source is causally connected with a systematic change in the river hydrology, such as when ore processing requires changes in the flow discharges up to a level of a changed fluvial style (Ciszewski et al. 2012). In that case, the onset of pollution can overlap with the facies change and changes in the preservation potential of the sedimentary record.

## 6. Conclusions

Geochemical local background functions and local enrichment factors were demonstrated to be efficient in identifying pollution-based horizons, some of which are isochronous in overbank deposits of the Ploučnice. The same method may be applicable to other river systems with aggradation (overbank deposition) during the onset of pollution and afterwards. We studied a pollution hotspot in the Ploučnice floodplain with concentrations of U and Zn exceeding limits for soils. The inherent behaviour of the

Ploučnice River is reworking a substantial portion of these overbank sediments on a timescale of decades to centuries. Our analyses and discussion of the results obtained by previous researchers after the termination of the primary pollution clearly indicate that reworking of the transient channel sediments, both as partial downstream transport of bedload and partial transfer to the floodplain as suspended load, contributed substantially to the pollution record in the overbank sediments. Although the study area was spatially limited, it provided a good example of these pollutant fates under the conditions described. The described general mechanisms should, however, be applicable to any other river system with heritage pollution.

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Table 1: Calibration functions for XRF analysis (12 samples).  $c$  is the concentration (ppm), and  $x$  is the XRF signal (c.p.s.) or signal ratio (c.p.s./c.p.s.). Small regression coefficients in the case of Pb and Rb are due to a narrower range of concentrations of these elements in the sediments analysed.

Element	Calibration function	$R^2$
Fe	$c = 5.08 \cdot x$	0.962
Ni	$c = 3.84 \cdot x - 24.09$	0.993
Pb	$c = 3.18 \cdot x$	0.713
Rb	$c = 1.375 \cdot x$	0.830
U	$c = 0.0062 \cdot x^2 + 3.092 \cdot x - 6.8$	0.994
Zn	$c = 2.39 \cdot x$	0.998
Element ratio		
Al/Si	% fraction < 4 $\mu\text{m}$ = $412 \cdot x + 8$	0.769

Table 2: Background functions of target elements.  $n$  is total number of samples. Threshold LEF is the value above which the sample can be considered as exceeding the natural variability at a given probability  $P$ .

Background function	$n$	$R^2$	Threshold LEF (P=95 %)	Threshold LEF (P=99%)
Ba (c.p.s.) = $0.199 \cdot \text{Rb (ppm)} + 1.83$	153	0.773	1.6	1.9
Fe (ppm) = $0.0607 \cdot (\text{Ti (c.p.s.)})^2 + 24 \cdot (\text{Ti (c.p.s.)})$	151	0.805	1.4	2.0
Ni (ppm) = $0.226 \cdot \text{Rb (ppm)} + 1.3$	155	0.751	1.4	1.9
Pb (ppm) = $0.0484 \cdot \text{Ti (c.p.s.)} + 9.2$	106	0.709	1.3	1.6
U (ppm) = $0.0317 \cdot \text{Rb (ppm)} + 0.8$	105	0.615	1.4	1.6
Zn (ppm) = $0.0045 \cdot (\text{Rb (ppm)})^2 + 0.3 \cdot \text{Rb (ppm)}$	155	0.878	1.6	2.3

Table 3: Enrichment factors (LEFs) and concentrations ( $c$ ) of target elements in the 2013 overbank fines the in Boreček area.

Element	LEF range	LEF median	$c$ range (ppm)	$c$ median (ppm)
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Ba	0.8-2.8	1.4	-	-
Ni	1.7-5.6	2.7	13-89	41
U	1.4-9.5	2.5	2-97	15
Zn	4.6-16.4	8.5	55-688	345

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Figure 1: The Czech Republic with grey highlighted watershed of the Ploučnice (A, detail in B); the reach of the Ploučnice with U-mining area and areas reported in this paper (C); the detailed map of the studied hotspot in Boreček (D). Areas of gamma activity pollution were taken from aerial survey (Gnojek et al. 2005).

Figure 2: Digital elevation model (DEM) of Boreček (A) and its geomorphological interpretation (B) with locations of sediment sampling sites (● sediment cores, ○ samples of spring 2013 flood deposits) and position of electrical resistivity tomography (ERT) profiles. Legend to geomorphological interpretation (B): A sandstone plateau, B valley-side, C terrace, D abandoned (high) floodplain, E active (low) floodplain, F active channel, G cut-off, H paleo-channel, I point-bar, J natural levee, K drill cores, L ERT profile. Q5, Q20 and Q100 inundation areas in panel A were taken from Povodí Ohře, state enterprise without readjustment of some minor discrepancies with DEM.

Figure 3: Aerial photograph of studied hotspot with locations of 2013 flood sediment samples. The position of the river channel in 1938 is shown using blue dashed line. The position of current river channel is shown using solid line with colours denoting the total rate of lateral channel shift between 1938 and 2011. In the inset there is a historical aerial photograph showing former land use of the abandoned floodplain.

Figure 4: ERT sections (location shown in Figure 2) with indicated areas of the lower active and the higher abandoned floodplain and the terrace

Figure 5: Background functions for Ba, Ca, Ni, Sr, U and Zn. The parameters of the regression functions are listed in Table 2.

Figure 6: Distribution functions of U concentrations (left column) and  $U/U_{\text{bgf}}$  ratios (right column) in background samples (unpolluted sediments unaffected by post-depositional migrations).

Figure 7: Depth profiles in sediment cores in active floodplain downstream from Boreček (core location in Figure 1)

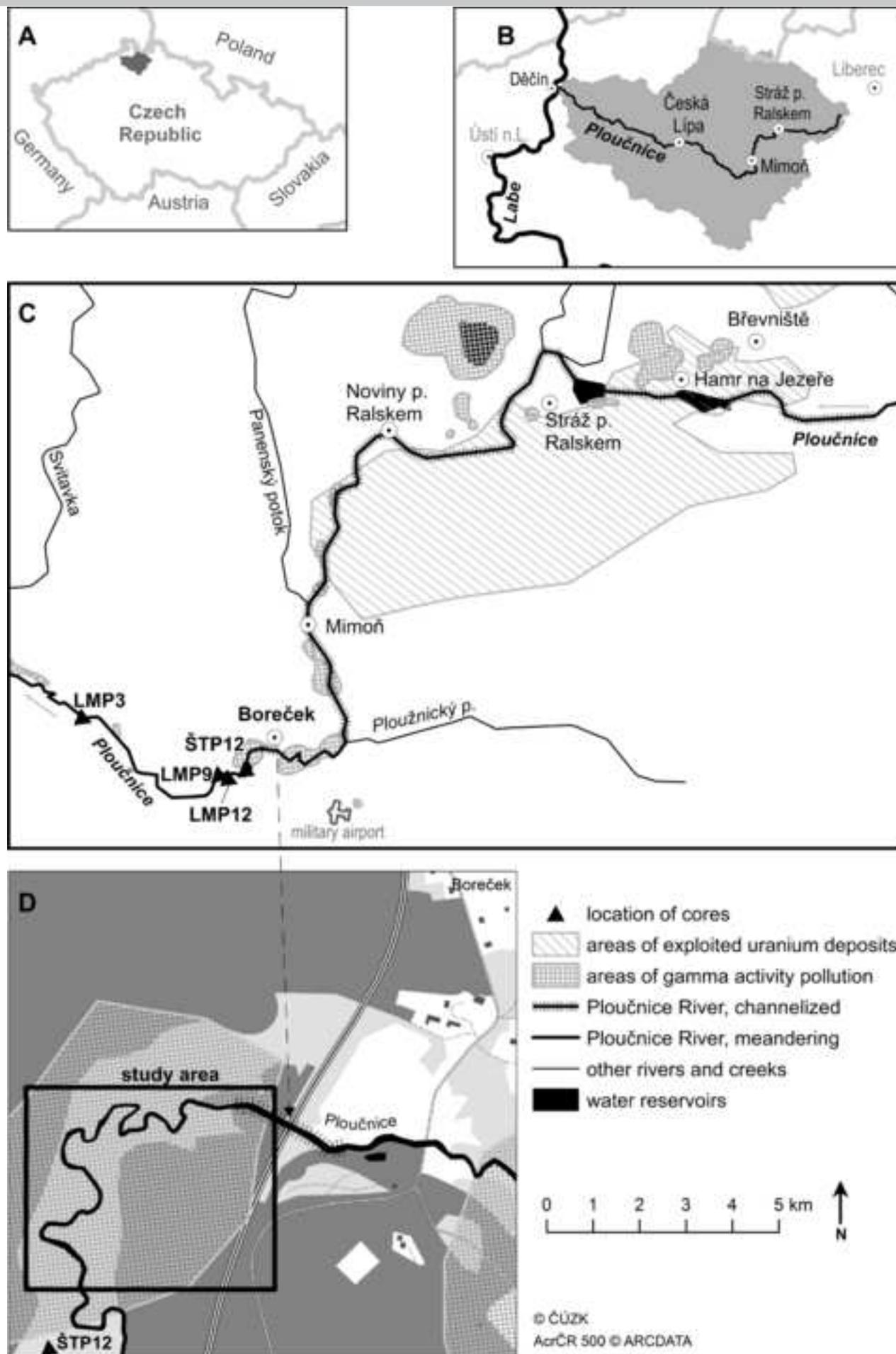
Figure 8: Detailed view of upper 40 cm of LMP12 profile with isotope analyses producing time

constraints of the pollution history

Figure 9: Depth profiles of sediment cores in Boreček (core locations in Figure 2)

Figure 10: Correlations of  $^{206}\text{Pb}/^{207}\text{Pb}$  with Sb/Pb in pre-Pb, pre-U mining and U-polluted sediments. Only sediments with predominant silt or clay size fractions are shown.

Figure 11: Two modes of the downstream propagation of pollutants in fluvial systems. The level of pollution is denoted by the intensity of the red colour.



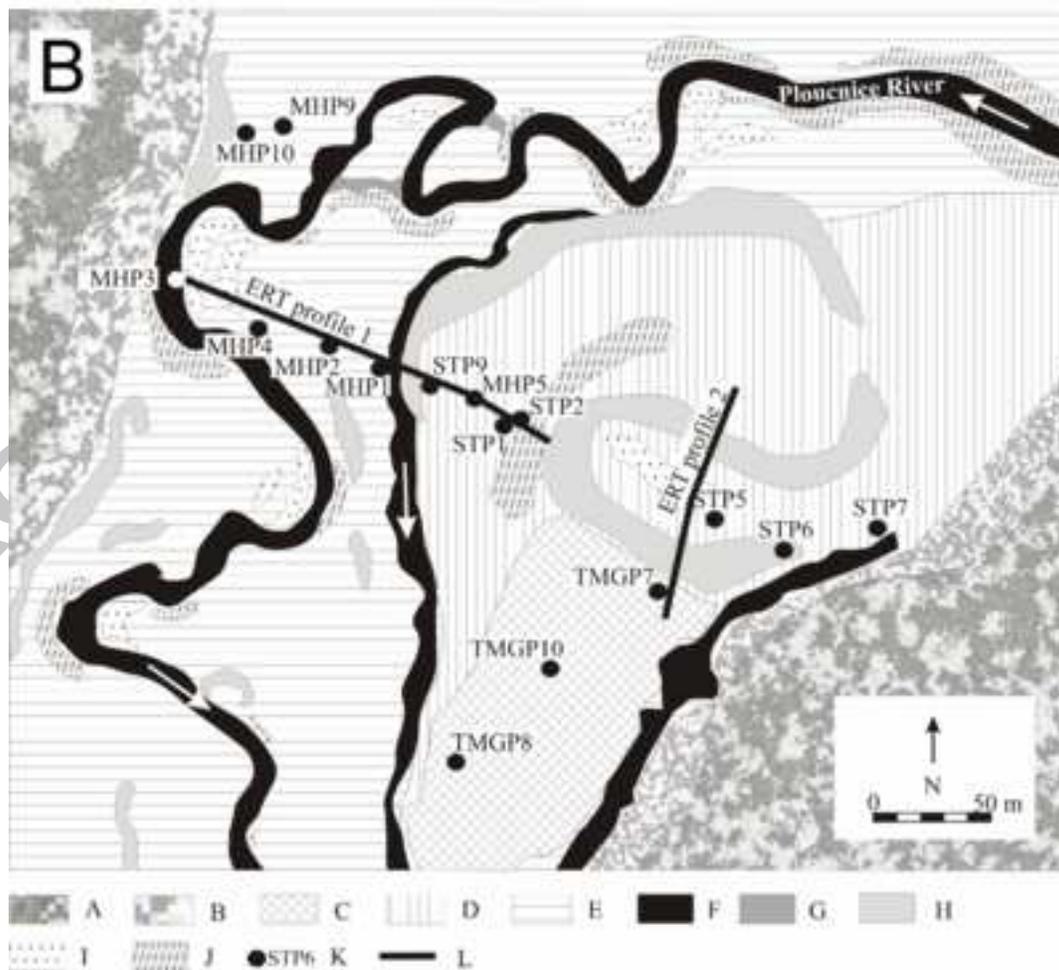
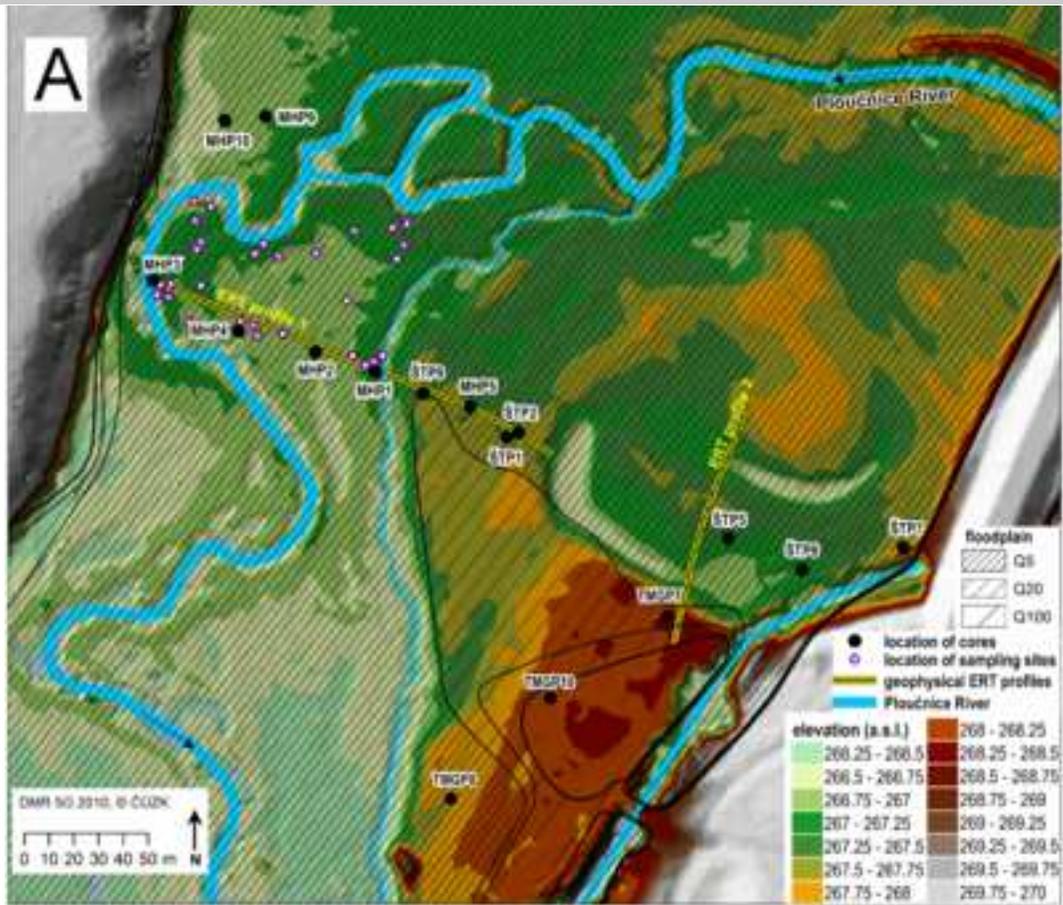
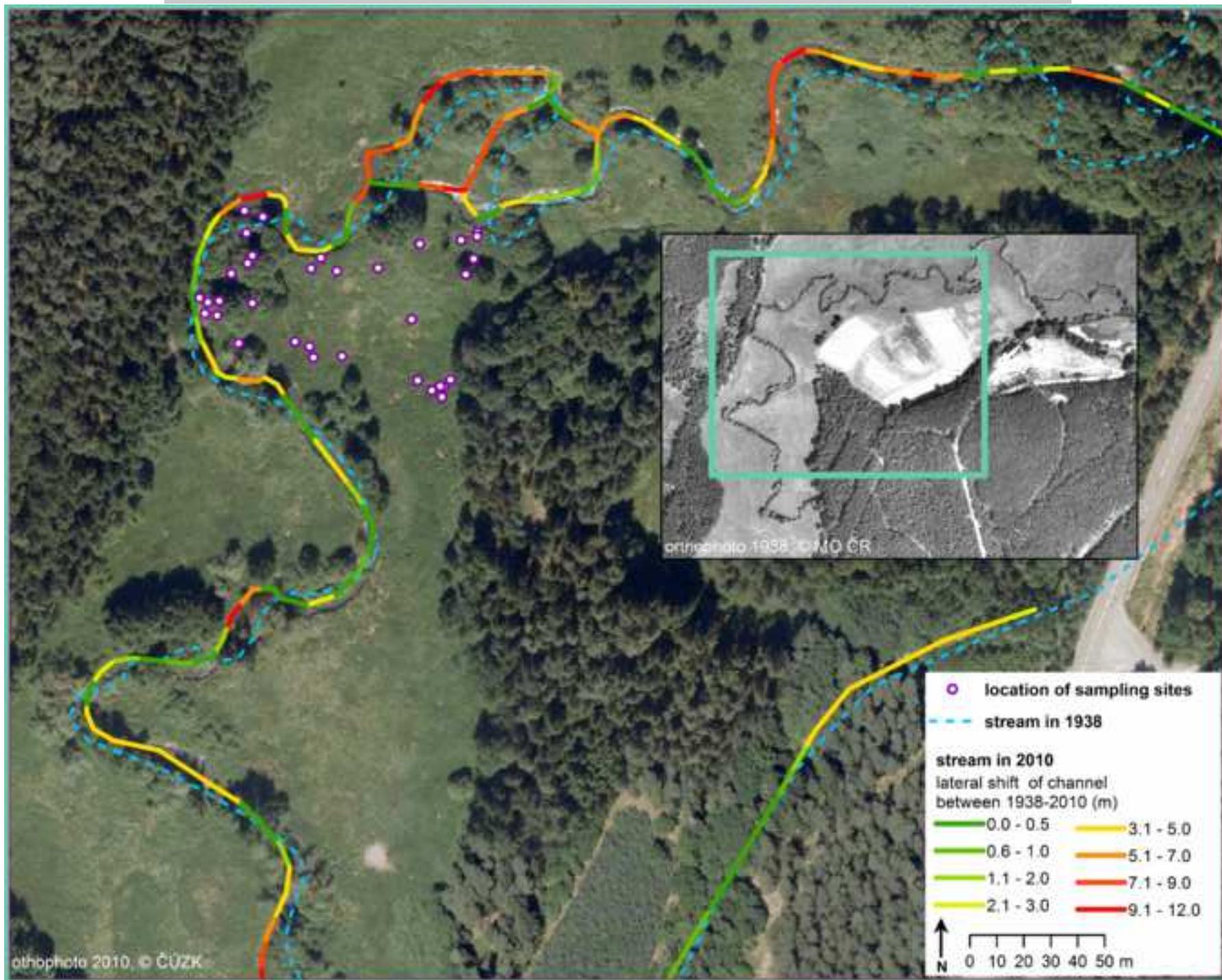
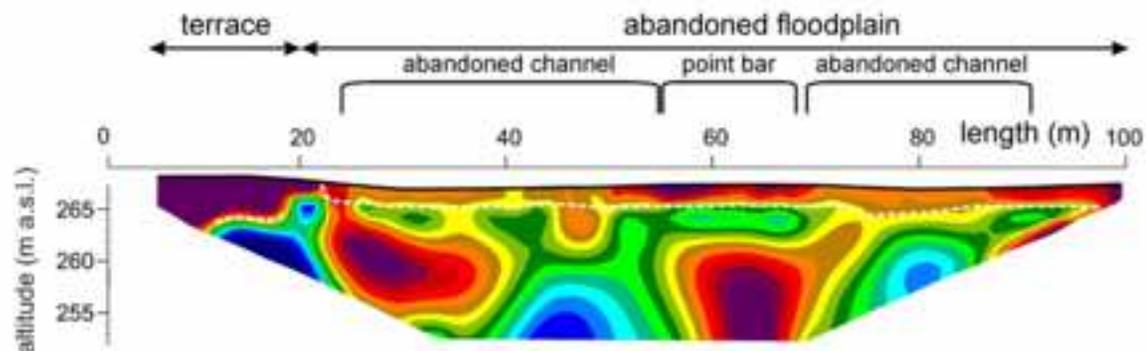


Figure 3



ERT profile 2



ERT profile 1

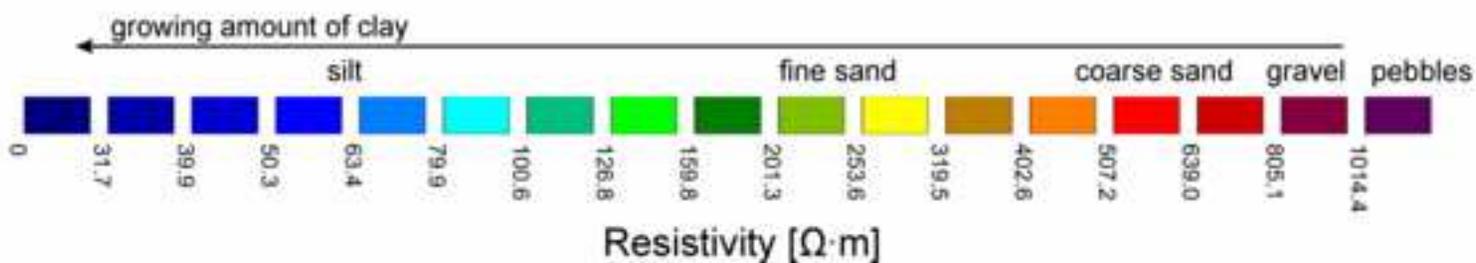
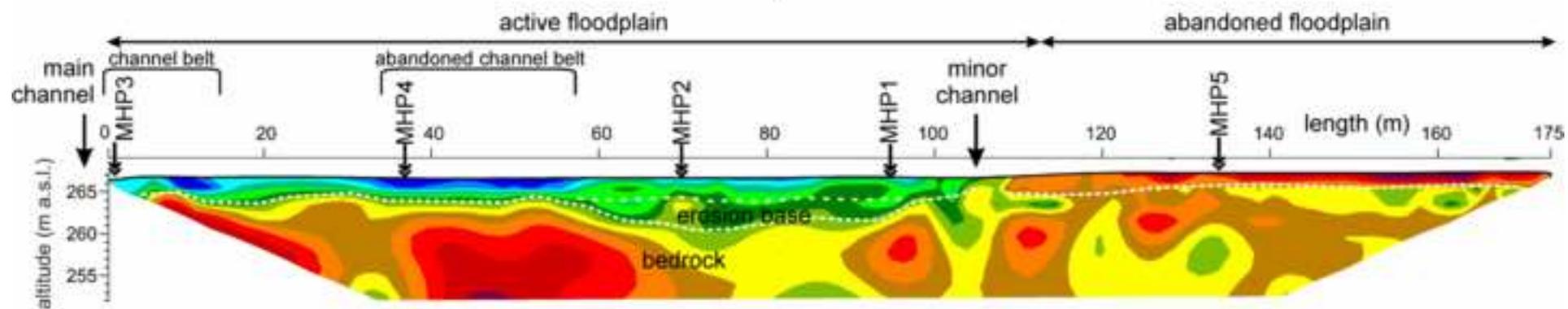


Figure 5

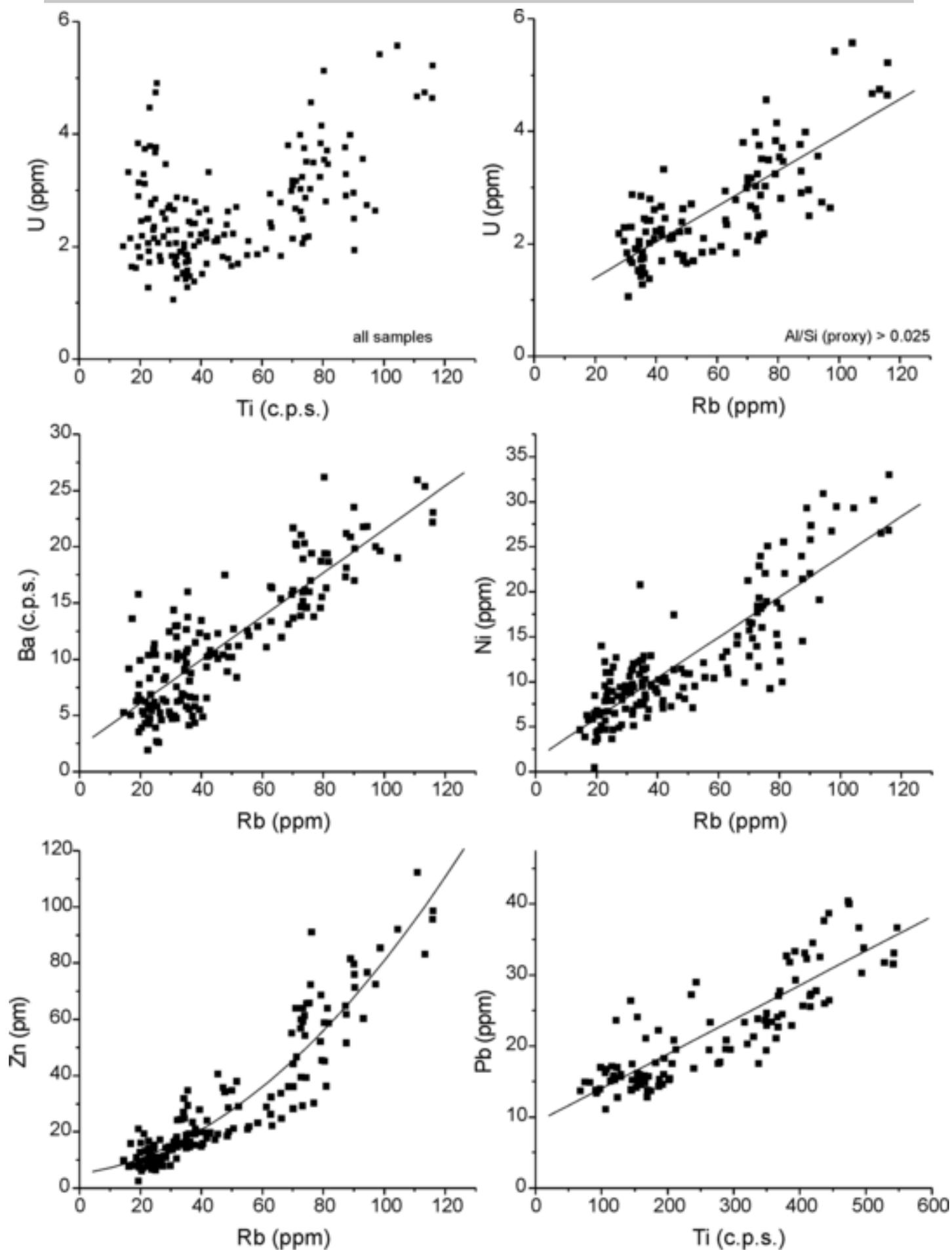
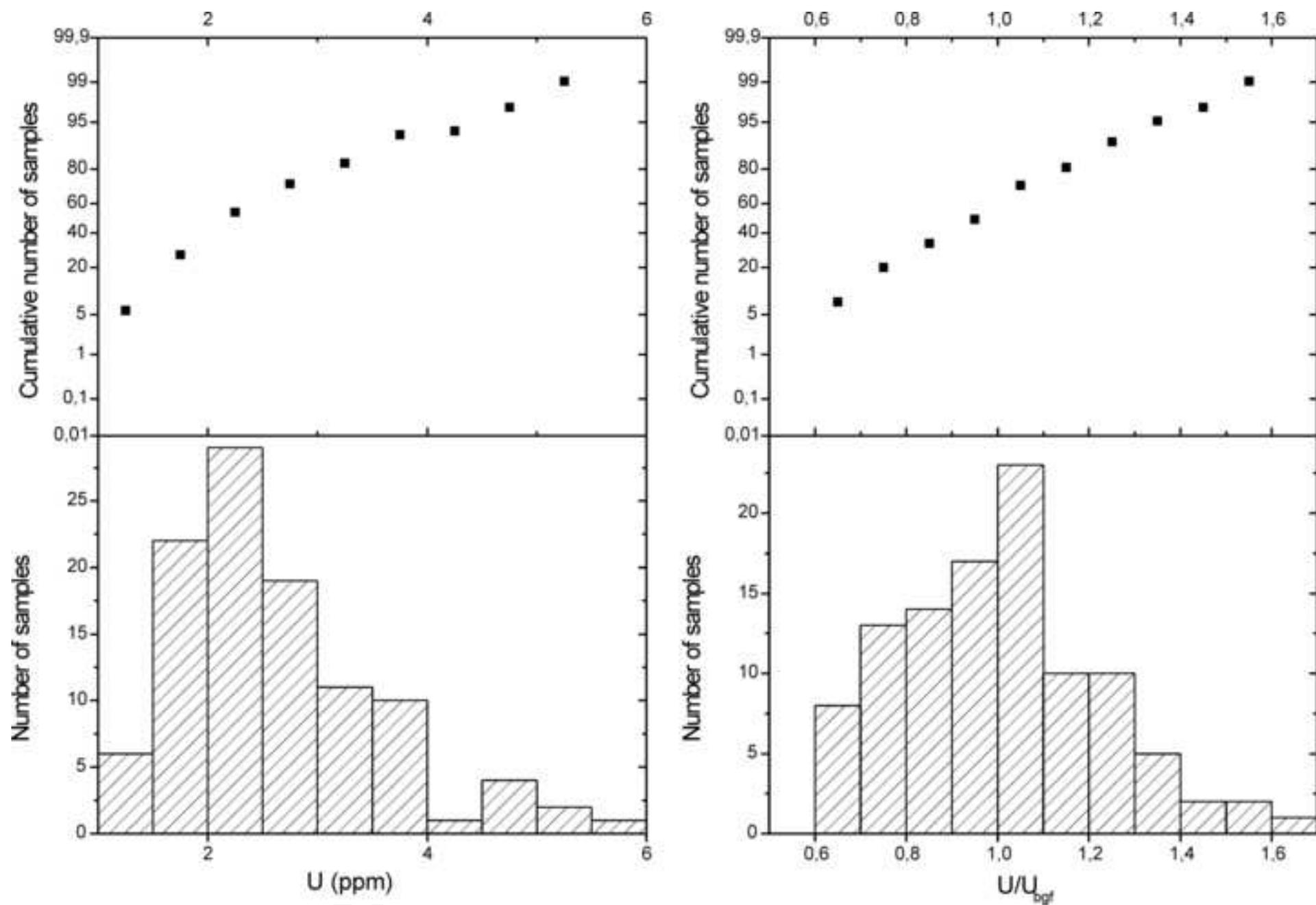
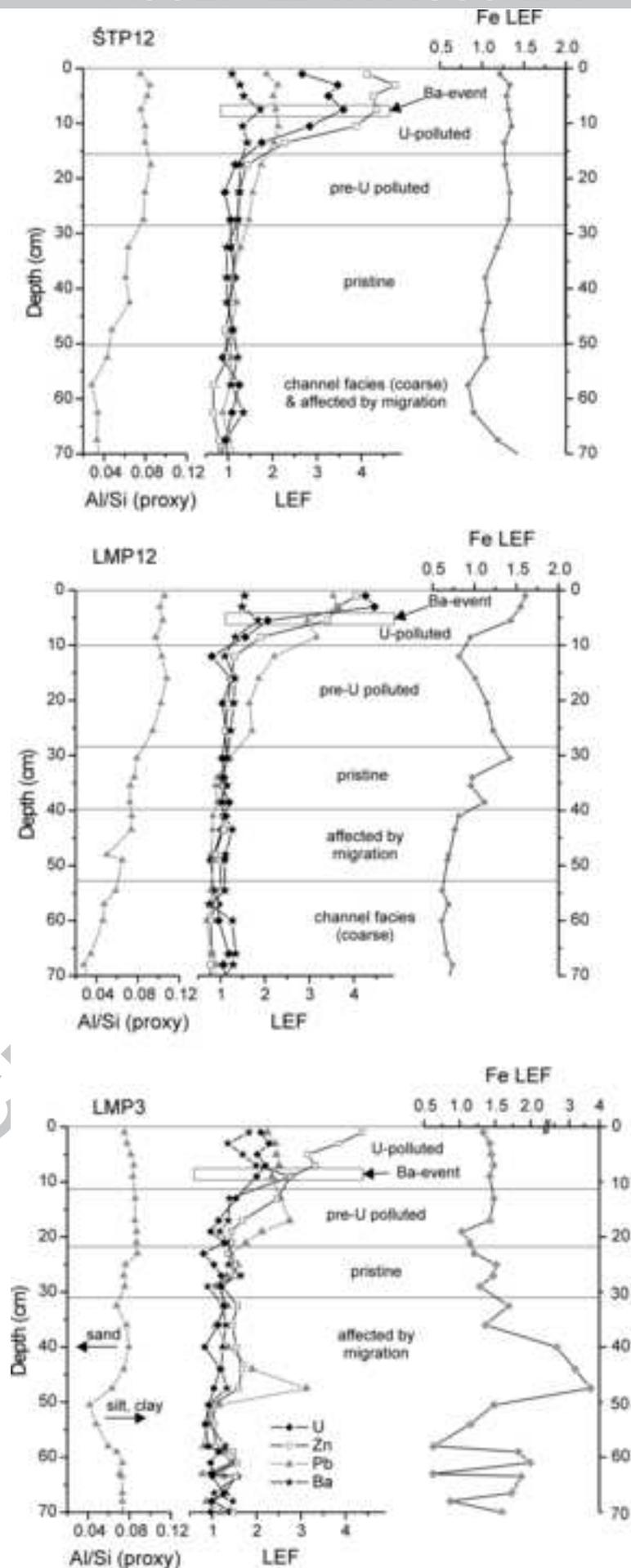


Figure 6

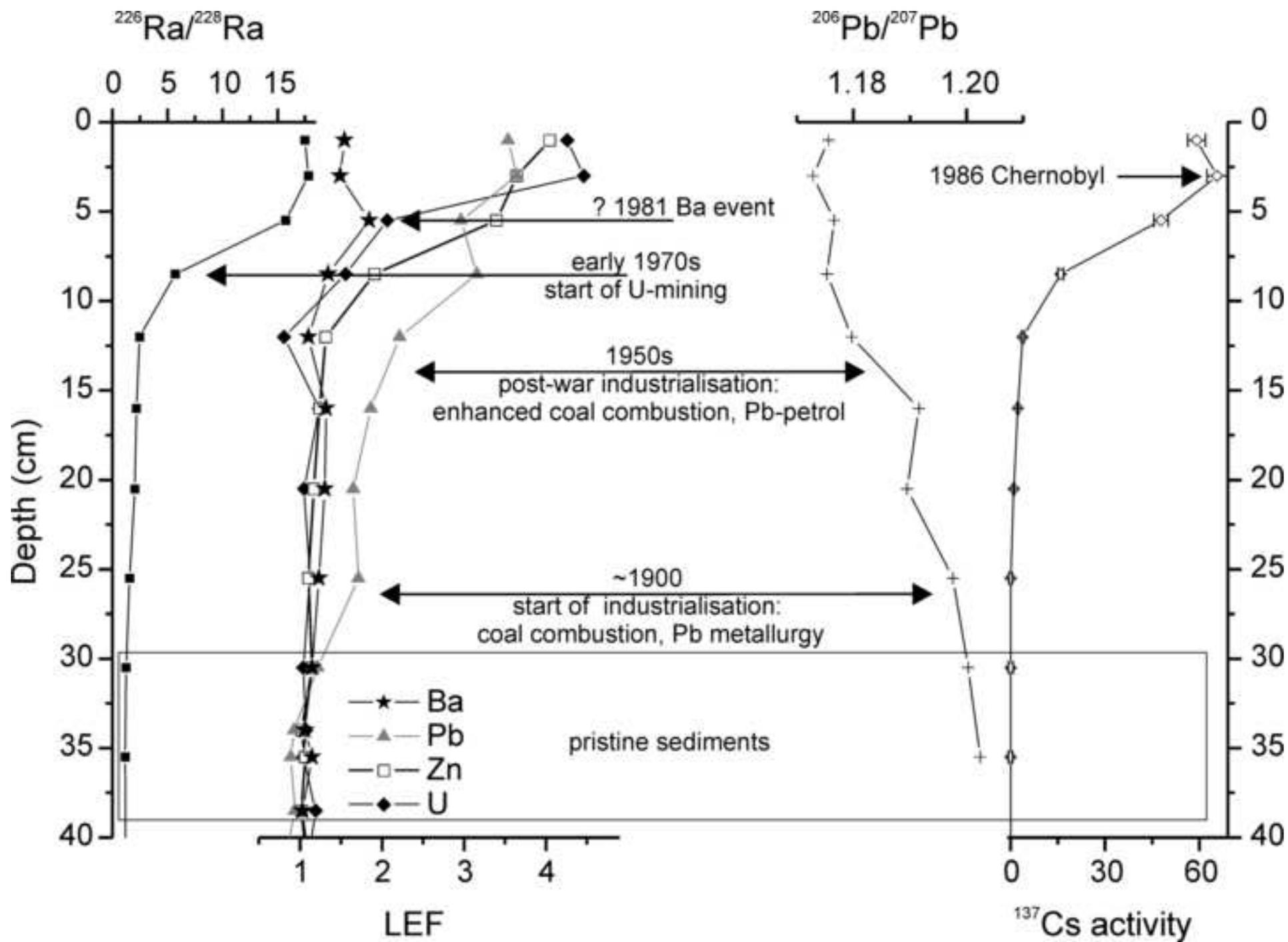




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Figure 8



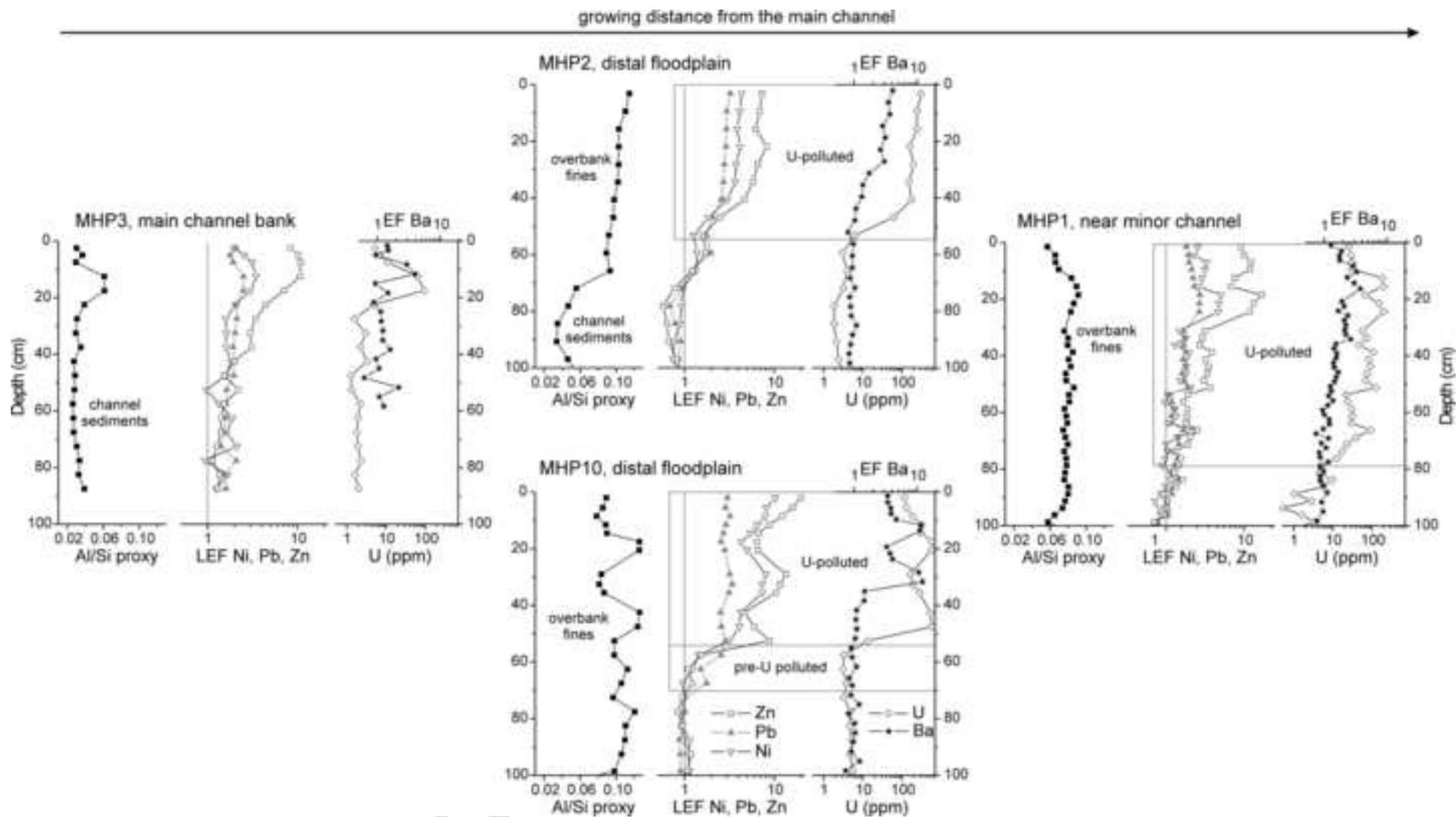


Figure 10

