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Pollution assessment using local enrichment factors: the Berounka River (Czech Republic)

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Abstract

Purpose The Berounka River is considered a relatively clean river, but recent studies have reported various levels of pollution. The purpose of this work is to identify anthropogenic pollution by metals (i.e. Pb, Zn, Cu) and magnetic particles in the sediments of that river and its tributaries.

Materials and methods Samples were obtained from hand-drilled cores taken from representative areas within the fluvial system; in distal floodplains (overbank fines) and closer to the channel (laterally deposited sediments). Samples were subjected to analysis using mass magnetic susceptibility (MS), X-ray fluorescence spectrometry (XRF) and also by inductively coupled plasma mass spectrometer (ICP MS) which allowed for a determination of ^{206}Pb/^{207}Pb isotope ratios. Macroelement ratios (K/Ti and Ti/Al) were used to distinguish variegated sediment provenance in the Berounka system. Normalization of trace elements by Ti (in the case of trace elements) and by Fe (magnetic susceptibility) allowed us to establish lithogenic background functions of trace elements and magnetic susceptibility within these two geologically different areas. A pollution assessment of the study area was performed using magnetic susceptibility and local enrichment factors (LEFs) for the risk elements. By comparing 1/(LEF Pb) and Pb isotopic composition, the origins of Pb within the catchment were determined. This unique method was able to distinguish Pb from various origins.

Results and discussion The upper parts of the floodplain cores contained higher levels of trace elements and magnetic particles (anthropogenically polluted), but samples taken from the cores in the active channel belt exhibited considerably higher concentrations of trace elements and magnetic particles than the upper parts of the floodplain cores and to much greater depths. We interpreted the deeper parts of the floodplain cores as a local lithogenic background. The upper parts of floodplain sediments hence showed moderate pollution (LEF of Pb and Zn ~2, MS ~2.5); whereas laterally deposited sediments showed significantly higher LEF values (LEF of Pb ~6, Zn ~9, MS ~8).

Conclusions The analysis of the sediments confirmed that the Berounka River system contains higher concentrations of trace elements and magnetic particles than can be accounted for by natural geological processes. Our pollution assessment of the Berounka River and its tributaries demonstrated that their sediments are moderately polluted from sources situated on its tributaries: Ag–Pb mining near the city of Stříbro in the Mže catchment; Pb–Zn mining in the Příbram ore district in the Litavka catchment and Fe ore processing and smelting in the Klabava catchment.

Keywords Berounka River · Fluvial sediments · Local enrichment factors · Normalization · Pollution assessment

1 Introduction

The assessment of the pollution of river systems has been a part of many recent studies (e.g. Gao et al. 2014; Resongles et al. 2014; Tang et al. 2014; Xu et al. 2014; Dhivert et al.

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2015; Xu et al. 2015). However, there remains an absence of a universal pollution assessment methodology. A necessary part of pollution evaluation is a basic knowledge of the depositional pattern and sampled sedimentary facies (e.g. Macklin et al. 2006; Matys Grygar et al. 2011, 2013). The comparison of results from similar sedimentary facies and the use of a normalization process to avoid differences within lithological composition of samples deposited under different hydraulic conditions are also essential (e.g. Devesa Rey et al. 2013; Beck et al. 2013; Matys Grygar et al. 2013).

An evaluation of pollution levels can be performed by calculating various factors, such as geoaccumulation index (I_{geo}), the metal index (I_m), enrichment factors (EF) (Covelli and Fontolan 1997) or the pollution index (Xu et al. 2015). These methods offer various approaches to comparing actual values of risk elements in an evaluated sample to some reference value of the environment. For reference, the average values of the Earth's crust (Taylor 1964) or shale (Turekian and Wedepohl 1961) are used but they are often too crude to quantify "weak" pollution (Covelli and Fontolan 1997; Martin 1997). To overcome that shortcoming, the use of local lithogenic background values from the given study area is recommended by many authors (e.g. Reimann and de Caritat 2005; Beck et al. 2013). as it reflects the geological character of the study area and actual transport and sorting processes to which the evaluated sediment has been subjected, and allows for proper interpretation of potential geological anomalies at the regional scale. The content of magnetic particles in soils and sediment is also often used for pollution mapping (Petrovský et al. 2001; Knab et al. 2006). However, the level or magnetic minerals in any sediment is also a function of catchment geology and sorting processes; magnetic susceptibility values can also be evaluated in terms of local enrichment with respect to the local background (e.g. Nováková et al. 2013; Faměra et al. 2013).

Surface water pollution and water quality within the Berounka River were studied by Langhammer (2001). Surface water chemistry and stream sediment pollution were also studied within the Berounka River tributaries (e.g. in the Střela River, Langhammer and Kaplická 2005), where values of Cd, Pb, Zn, Ni and Cu in stream sediments showed moderate contamination (values of Igeo >3 and higher). Concentrations of Cd in stream sediments of the Klabava River exceeded reference values by up to several hundred times, whereas the levels of other risk elements showed considerable decrease since the flood event in 2002 (Volaufová and Langhammer 2007). The Litavka River, a tributary of the Berounka in the Příbram mining region, has a long history of polymetallic ore mining and processing and is hence highly likely to be polluted. It flows into the Berounka River in the town of Beroun. The contamination of the Litavka River due to past processing and smelting of Pb-Zn-Ag-Sb ore in the Příbram metropolitan area has been well studied in previous works (e.g. Ettler et al. 2006; Mihaljevič et al. 2006; Vaněk et al. 2008; Žák et al. 2009; Nováková et al. 2013). Therefore, the Litavka could be a very important pollution source. The chemical composition of bulk samples taken from the Berounka floodplain after the massive floods in 2002 were studied by Navrátil et al. (2008). Several studies conducted within the Berounka catchment confirmed the presence of mild concentrations of mercury and methylmercury (e.g. Kružíková et al. 2008), as well as organic pollutants such as PAH and PCB (Havelkova et al. 2008) in fish meat.

The primary aim of this work was to evaluate the regional pollution of the Berounka River catchment by trace metals (e.g. Cu, Pb and Zn) and magnetic particles by calculating local enrichment factors (LEF), a task which calls for the identification of pristine sediments, the choice of the proper normalization element, and the establishment of local lithogenic background functions. The calculated LEFs and measured Pb isotopic ratios then can be used to distinguish pollution sources within the study area and to evaluate the extent of the contribution of the Berounka tributaries to the total pollution within the entire catchment.

2 Materials and methods

2.1 Study site

The origin of the Berounka River is in the west part of the city of Plzeň, Czech Republic, and is a result of the confluence of four rivers: the Mže, the Radbuza, the Úhlava and the Úslava. The average discharge of the Berounka River at the confluence with the Vltava River is approximately 36 $m^3 s^{-1}$, and the Berounka's total catchment area covers ~8861 km^2, including not only agricultural and urban areas with industrial enterprises and past and present mining areas but also two large protected landscape areas; Křivoklátsko and Český Kras. The Berounka fluvial system includes several important tributaries which can be described as meandering rivers, particularly the Třemošná, the Střela, the Klabava and the Litavka (see Fig. 1). Tributaries studied within this work are the Radbuza, the Úhlava, the Úslava, the Mže and the Klabava.

The entire study area includes several geological units (Fig. 1). The headwaters of Mže are characterized mainly by granitic and sedimentary rocks. Smaller areas containing granitic and granodioritic rocks are present in lower reaches of the Úhlava. The Radbuza, the Úhlava and the Úslava have mainly Moldanubian gneisses, shales, and marbles in their catchments. Downstream of Plzeň, the Berounka River further flows through an area with mafic volcanics. After the confluence with the Klabava River, the Berounka passes through the Lower Paleozoic sediments and then along a massive body of mafic volcanics. Such a complex catchment geology is expected to produce uneven background concentrations of risk elements and magnetic particles.

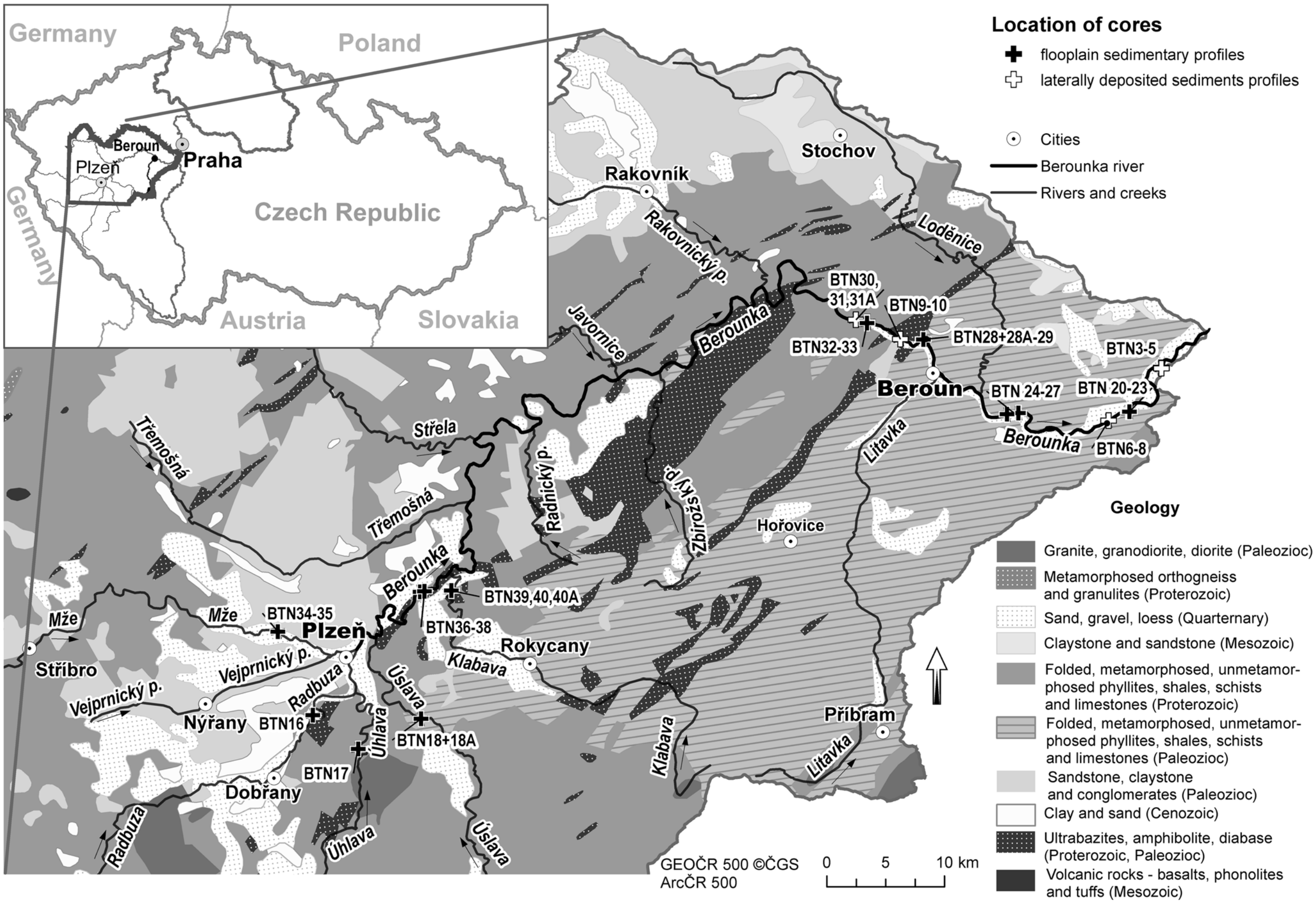


Fig. 1 Geological map with positions of all sampling sites: floodplain profiles (*black crosses*); and channel belt sediments (*white crosses*). The headwaters of the Mže, Radbuza, Úhlava and Úslava are not shown

The Berounka valley has developed by incision into the bedrock in most studied areas such that there are only steep river terraces (Tyráček et al. 2004). Accordingly, the natural floodplain in some river reaches is almost nonexistent, and as a consequence there is very limited space for sediment deposition. Regions characterized by confined valleys are followed by regions characterized by broader floodplains in an alternating fashion. This diversity produces variable sedimentation dynamics within the catchment. For example, the Berounka has a meandering pattern and broad floodplain just downstream of Plzeň where sampling points BTN36-38 are located (see also Fig. 2a), but downstream from the confluence with the Střela it has a bedrock-confined channel in a deep valley with almost no space for overbank deposition (see also Fig. 2b). Upstream from the city of Beroun the channel character changes, and except for a few occasional reaches with broader floodplains up to the confluence with the Vltava River, there are only laterally deposited sediments in the valley.

Nearly the entire flow of the Berounka has been anthropogenically influenced in the past. Outside of places where there is a natural bedrock-confined channel, many embankments and flood defences have been built up along the river course during the previous century to protect these areas from flooding. As a result, there are large segments of the river with almost no recent sediments available for sampling and almost no enhanced redeposition of sediments within the channel belts during the high discharges. In such places, intensive building and other human activities converted the floodplain to a place where sampling is complicated.

Two geomorphic/sedimentary settings were used for sampling: (i) laterally deposited sediments from the river banks (channel belt) and (ii) floodplain sediments in several (somewhat spread out) parts of the river where the undisturbed floodplain can still be found; the sampling sites are shown in Fig. 1.

2.2 Methods

All samples were air-dried and subjected to mass magnetic susceptibility using Kappa-Bridge (KLY 2, Agico, Brno, Czech Republic). Samples were then hand-grinded in an agate mortar and subjected to elementary analysis by X-ray fluorescence spectrometry (ED XRF, MiniPal4, PANalytical, The Netherlands). The measuring cells have 1¼ inch Mylar windows. The ED XRF results were calibrated by analysis of selected samples using inductively coupled plasma mass

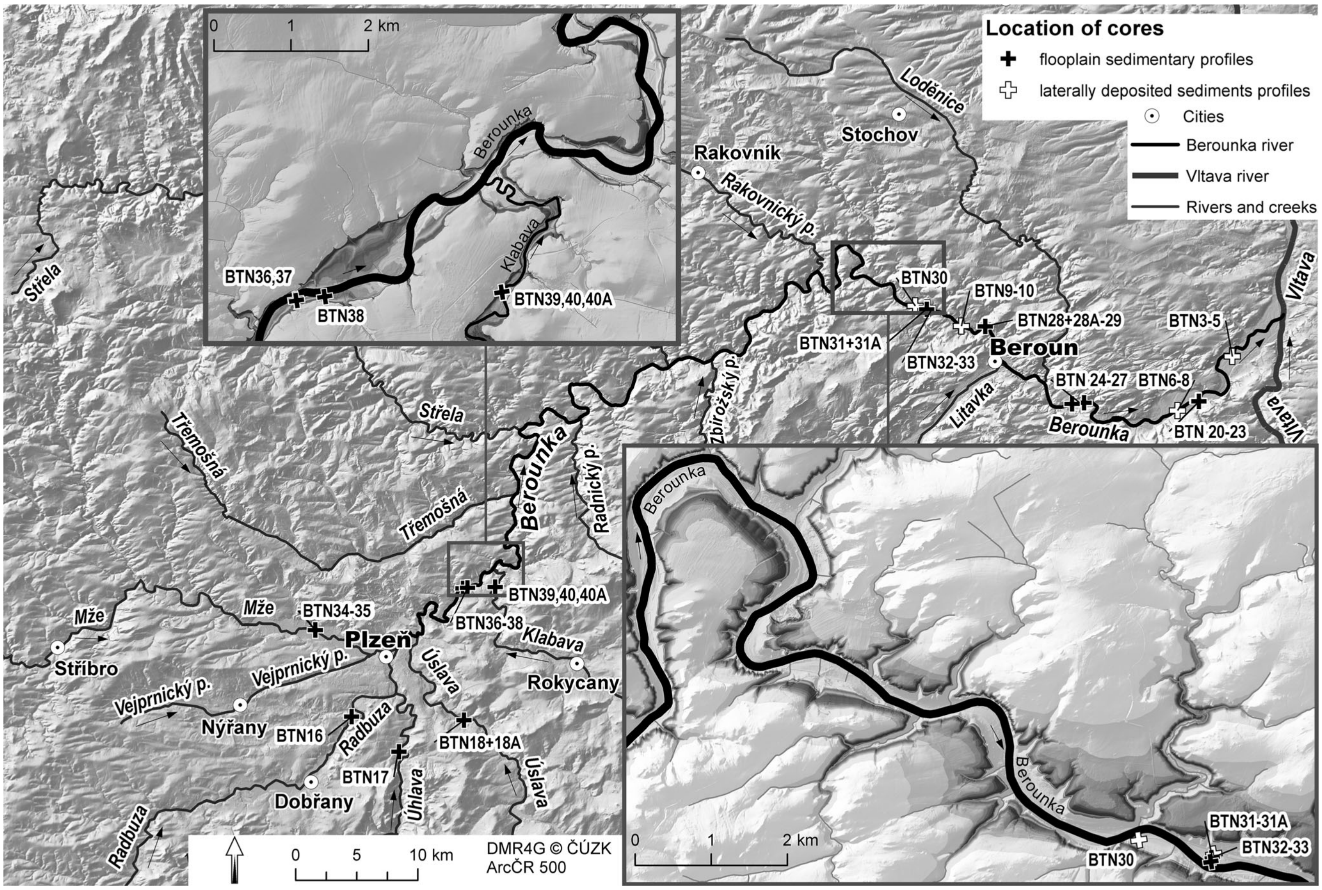


Fig. 2 Digital terrain model (DTM) of the Berounka River downstream of Plzeň, showing the meandering part of the river channel downstream of Plzeň (**a**) and also the beginning of incised part of the fluvial system, without sufficient space for sediment deposition (**b**)

spectrometer (ICP MS, X Series 2, Thermo Scientific, Germany). The ED XRF signal for K was not calibrated and is given in X-ray detector counts per second (c.p.s.) for its characteristic Kα line.

Solutions for ICP MS analyses were prepared by total dissolution in mineral acids as described elsewhere (e.g. Grygar et al. 2010). External reproducibility of the measurements was controlled using SRM 2709 (San Joaquin Soil, NIST, USA). After the dilution of ICP MS samples (to have the final content of Pb<20 μg L^{-1}), Pb isotopic composition (ratios of ^{206}Pb/^{207}Pb) was determined. Correction for the mass bias was performed using SRM 981 (Common Lead, NIST, USA). Calibration curves listed in Table 1 were used for recalculation of ED XRF results into concentrations.

3 Results

3.1 Distinguishing various sediment source areas

A geological map (Fig. 1) shows the variable geological composition of the catchment of the Berounka and its tributaries. Scatter plots of K versus Ti and Ti versus Al are shown in Fig. 3, illustrating differences between the catchments. Examination of K and Ti contents and the K/Ti ratio are very efficient methods and are generally applicable in distinguishing acidic, neutral and alkaline rocks.

Ratios of K/Ti allowed us to distinguish the sediments of the Mže and the Radbuza flowing from the southwest; these have larger K/Ti ratios (Fig. 3a) typical of granitic or other felsic rocks. In contrast, markedly lower K/Ti ratios were found in the sediments of the Úhlava, the Úslava and the Klabava, flowing from the south and the east. The Plzeň area of the Berounka River has an intermediate K/Ti ratio throughout, as it is a mixture of the previous two groups. Further downstream (the Berounka in the Beroun area), the K/Ti ratio is lower than in the "averaged" tributaries, which can be attributed to the more significant contribution of mafic rocks between Plzeň and Beroun. Those general trends are also obvious in Ti versus Al plots: Ti/Al ratios have the lowest values variable: the sediments of the Mže (Fig. 3b; black squares) and these ratios are relatively high in the Berounka in the Beroun area. From the contrasting nature of the geochemistry of the main lithogenic elements, it follows that natural risk element concentrations will probably also vary.

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

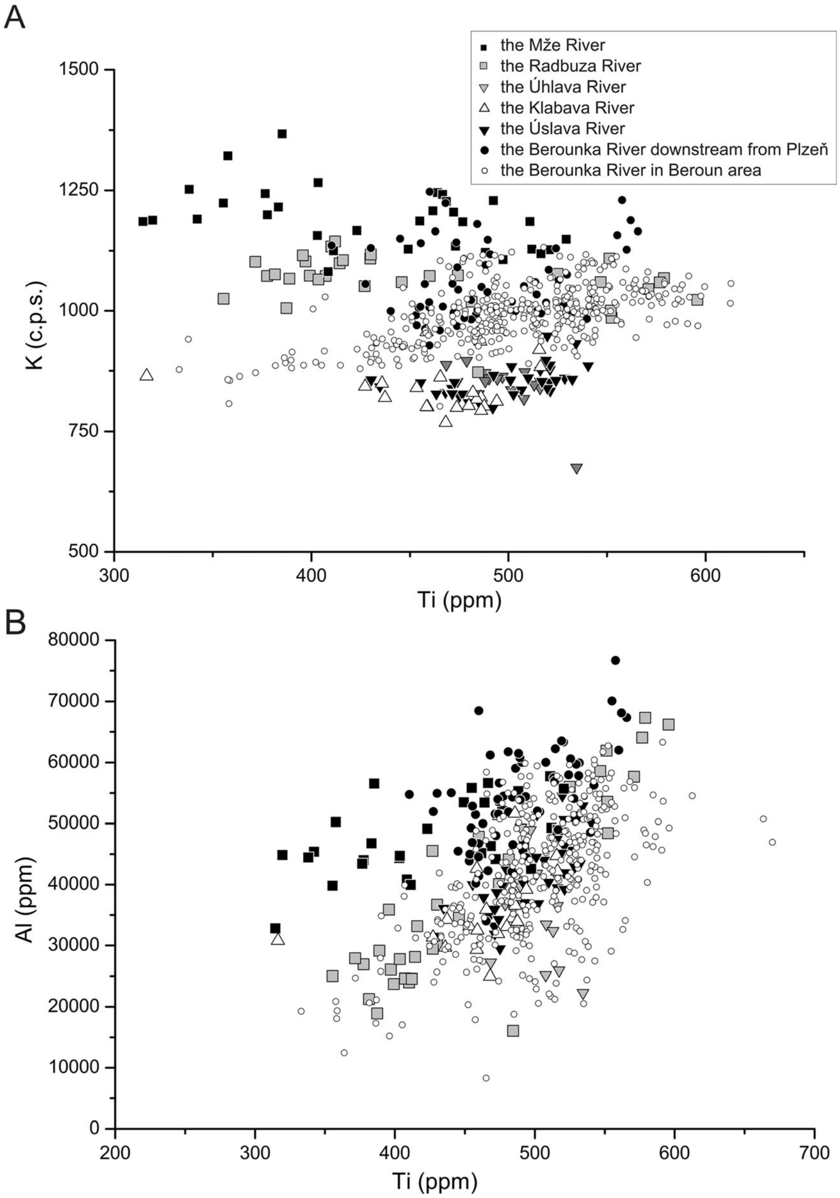
ED XRF signal	Calibration equations	Number of samples	r^2
Pb	Pb (ppm)=4.199×Pb (c.p.s.)	33	0.969
Zn	Zn (ppm)=2.272×Zn (c.p.s.)	35	0.994
Cu	Cu (ppm)=2.535×Cu (c.p.s.)	35	0.97
Cr	Cr (ppm)=4.164×Cr (c.p.s.)−32.187	35	0.854
Ni	Ni (ppm)=4.268×Ni (c.p.s.)−27.396	33	0.958
Ti	Ti (ppm)=7.4719×Ti (c.p.s.)	35	0.646
Al	Al (ppm)=5144.8×Al (c.p.s.)−65787	26	0.778
Fe	Fe (ppm)=4.069×Fe (c.p.s.)	26	0.916

3.2 Local enrichment factors

3.2.1 Normalization

Normalization curves of Pb and Zn with Ti as a predictor for sediments from the Plzeň and from the Beroun areas are shown in Fig. 4a and b. Just as the geochemistry of these two river reaches differs, the background Zn and Pb concentrations also differ; therefore, two regional normalization curves were established. Normalization of Pb and Zn using Ti (Fig. 4a, b) was statistically more significant than normalization using Al (Fig. 4d). To demonstrate how important the sediment provenance is for the background concentrations of Pb and Zn, we also plot a series of pristine sediments from the Morava River, a river in the eastern part of the Czech Republic with a catchment that is

Fig. 3 *Scatter plots* of K versus Ti (**a**) and Ti versus Al (**b**) used for distinguishing source areas of sediments



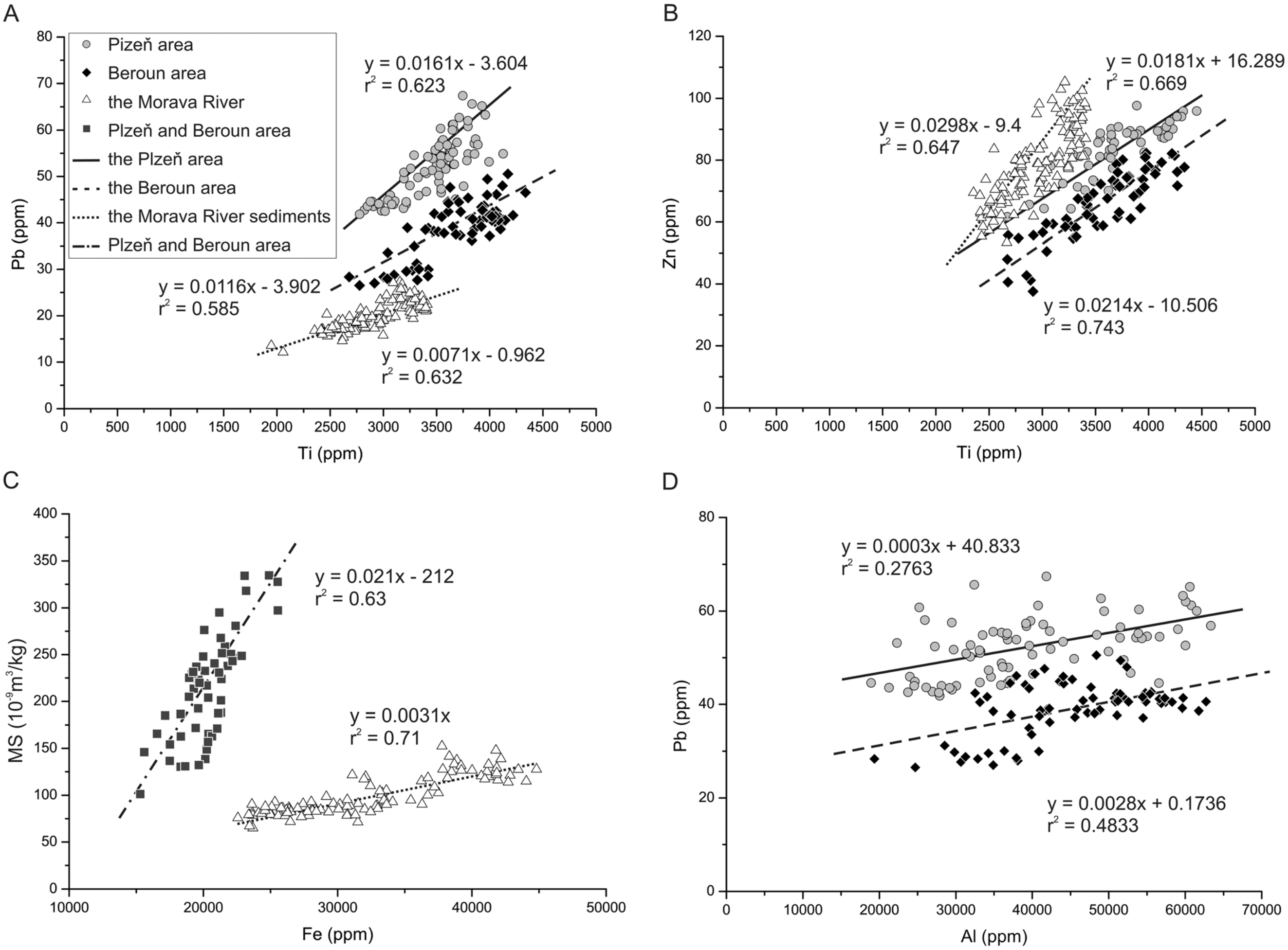


Fig. 4 Normalization equations (lithogenic background functions) for Pb (**a**) and Zn (**b**) with Ti as normalizer and MS (**c**) with Fe as normalizer, for comparison background functions for the Morava River are shown (data were taken from Nováková et al. 2013). In **d**, there are background functions for Pb with Al as normalizer

derived from Mesozoic marine sediments and rocks formed by their metamorphosis. The Morava River data were taken from Nováková et al. (2013). The differences between the two parts of the Berounka catchments are indeed comparable to the differences between the Berounka and the Morava catchments.

Normalization curves for Cu, Cr and Ni were, however, not sensitive to natural difference and were uniform for the Berounka sediments throughout the entire area of the study (Table 2). Magnetic susceptibility values were normalized by Fe content, and, together with the Pb/Ti and Zn/Ti normalization shown in Fig. 4a and b, were compared with the corresponding plot for the Morava River sediments (the data were also taken from Nováková et al. 2013). The normalization equations that were used for the calculation of the supposed pre-industrial lithogenic background values of all the samples are also listed in Table 2.

Normalization equations for risk elements and magnetic susceptibility were further used to calculate the predicted pre-industrial values of all the samples. The LEFs were then calculated as a ratio of the actual concentrations of risk element in the sample and the calculated predicted lithogenic background value in the sample (Matys Grygar et al. 2014):

$$\mathrm{LEF} = (\text{actual conc. of element}) \\ /(\text{conc. of element predicted by background functions}) \quad (1)$$

The calculated LEF accounts for both the influences of local geochemistry and the sorting processes occurring in a given river reach, which distinguishes the LEF from conventionally defined enrichment factors (EF) (Matys Grygar et al. 2014).

3.2.2 Depth profiles of local enrichment factors (LEF)

The effect of sampling site heterogeneity is demonstrated in Fig. 5, where typical depth profiles of LEFs are shown for Pb, Zn and MS in the laterally deposited sediments of the channel belt (BTN6 profile, Fig. 5a) and overbank fines sampled in the distal floodplain (profile BTN23, Fig. 5b). The profile in the channel belt showed increased LEF values of Pb, Zn and MS

Table 2 Lithogenic background functions for risk elements normalized by Ti and magnetic susceptibility (MS) normalized by Fe

ED XRF signal	Normalization equations	Number of samples	r^2
Pb/Ti[a]	Pb (ppm)=0.0161×Ti (ppm)−3.6044	79	0.623
Pb/Ti[b]	Pb (ppm)=0.0116×Ti (ppm)−3.902	90	0.58
Zn/Ti[a]	Zn (ppm)=0.0186×Ti (ppm)+16.290	53	0.669
Zn/Ti[b]	Zn (ppm)=0.0214×Ti (ppm)−10.506	87	0.743
Cu/Ti	Cu (ppm)=0.0066×Ti (ppm)+3.102	139	0.636
Cr/Ti	Cr (ppm)=0.0246×Ti (ppm)−30.695	393	0.456
Ni/Ti	Ni (ppm)=0.00601×Ti (ppm)+5.673	183	0.50
MS/Fe	MS (10^{-9}m^3/kg)=0.0182×Fe (ppm)−156.08	56	0.648

[a] Data from the Plzeň area

[b] Data from the Beroun area

towards the bottom of the profile (LEF 3–4 for Pb, 6.5–7.5 for Zn, 3–6 for MS); i.e. pollution in the entire core and downward increasing trend. Contrarily, the values of LEFs in the floodplain profile were very low in the bottom parts of profiles (unpolluted sediments with LEF 0.8–1 for Pb, probably unpolluted 1–1.5 for Zn, unpolluted 0.7–1 for MS) with LEFs indicating pollution in the upper parts of profiles (LEF up to ~1.8 for Pb, ~2 for Zn, ~2.5 for MS), but to a lesser extent than in the channel belt deposits.

The differences between sediments proximal to the channel and sediments at a distance from the channel suggest that one should be cautious when making a comparison of sediments from the top and bottom parts of sediment profiles. Concentrations of risk elements (Pb, Zn, Cu, Ni, Co, Sb and Cd; in ppm units) from upper and lower parts of profiles from different sedimentary environments within the Berounka catchment are shown in Table 3. Isotopic ratios of ^{206}Pb/^{207}Pb were also used to unequivocally distinguish anthropogenically influenced sediments from pre-industrial sediments with local geogenic background (see Fig. 5b). The results showed the presence of Pb with typical recent local "anthropogenic" values of ^{206}Pb/^{207}Pb ~1.17 (Sucharová et al. 2014) within the entire profile from the channel belt sediments (see also Fig. 4a). Anthropogenic values of ^{206}Pb/^{207}Pb (~1.18) were present only in the upper part of the BTN23 floodplain profile, whereas the lower part of profile indicated a lithogenic origin of Pb (^{206}Pb/^{207}Pb ~1.20) (Novák et al. 2003; Komárek et al. 2008; Matys Grygar et al. 2011; Nováková et al. 2013).

3.2.3 Downstream change of local enrichment factors (LEFs)

Calculation of LEFs for all samples enabled us to describe downstream changes of pollution by Pb (A), Cu (B), Zn (C) and MS (D) within the Plzeň and Beroun study areas (separated by a grey vertical line in Fig. 6, the locations of the Plzeň and Beroun metropolitan areas are marked by dashed vertical lines). The LEF values of Pb, Zn and MS in lower parts of floodplain profiles were up to 1–1.5 (mostly no enrichment), whereas values of Pb LEFs in upper parts of all floodplain profiles were generally slightly elevated (LEF of Pb ~2; Cu ~2; Zn ~2.5; MS ~2.5). The results of ICP MS analyses of selected sediment samples are also shown in Table 3.

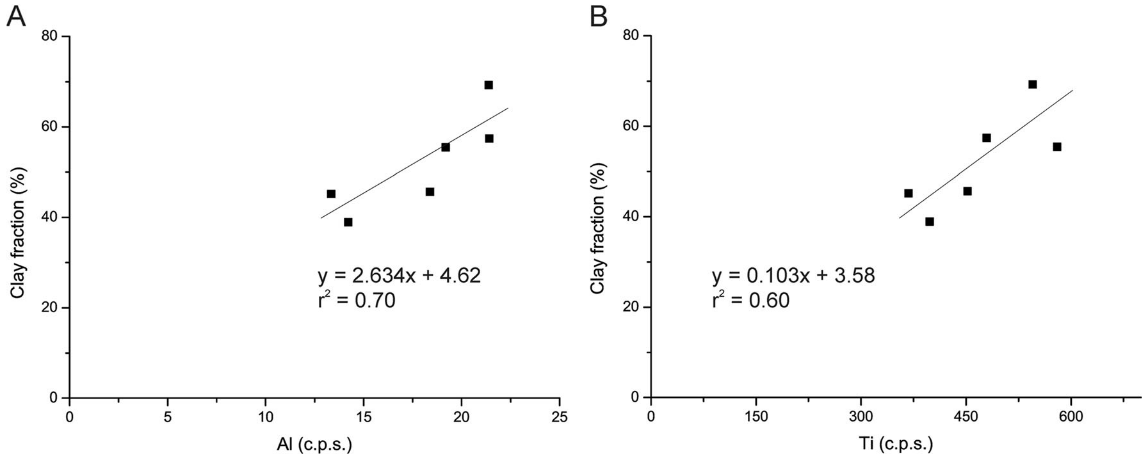


Fig. 5 Typical depth profiles of local enrichment factors (LEF) of Pb, Zn and MS obtained from two types of sampling sites—channel belt and floodplain. **a** Depth profile BTN6 was taken from sediments next to the river channel. **b** Depth profile BTN23 was obtained from the floodplain. Isotopic ratios of ^{206}Pb/^{207}Pb were used for distinguishing anthropogenically contaminated part of profile (*grey rectangle*), while from lower part of profile lithogenic background values of risk elements (*white rectangle*) were inferred

Table 3 Selected ICP MS analysis results for Pb, Zn, Cu, Ni, Co, Sb and Cd within the floodplain profiles and laterally deposited riverbanks in the Plzeň area (BTN36) and the Beroun area (BTN23, BTN9, and BTN 4)

Profile, depth (cm)	Pollution status	Position	ICP MS results (ppm)						
			Pb	Zn	Cu	Ni	Co	Sb	Cd
BTN34 20–25	Polluted from Stříbro (the Mže)	Floodplain profile	177	157	35	29	14	3	1.7
BTN34 55–60	Pristine	Floodplain profile	138	110	28	30	15	2	0.3
BTN36 10–15	Polluted from Plzeň and Stříbro	Floodplain profile	110	90	23	28	13	2.4	0.5
BTN36 65–70	Pristine	Floodplain profile	82	90	23	28	13	2	0.5
BTN39 10–15	Pristine (the Klabava R.)	Floodplain profile	40	97	34	36	14	3	0.5
BTN9 75–80	Polluted (from Plzeň area)	Laterally deposited sediment	139	316	75	40	21	5	1.5
BTN29 10–15	Pristine (before Beroun)	Floodplain profile	39	104	36	35	16	4.5	0.5
BTN6 35–40	Polluted with contribution from the Litavka R	Laterally deposited sediment	159	540	64	58	26	7	5.3
BTN23 100–115	Pristine	Floodplain profile	21	135	41	62	24	2.8	0.8
BTN4 65–70	Polluted from upstream sites	Laterally deposited sediments	143	523	51	56	24	6	5

The LEFs of Pb in all analyzed sediments are shown in Fig. 6a. In the case of the Mže River (with historical Pb mining in the Stříbro area), LEF of Pb were increased up to ~4, as well as in profiles from channel belt sediments in the lower course of the river (LEF of Pb up to ~4.5 at location BTN30) and in the area after the confluence of the Berounka with the Litavka (in profiles BTN24 and BTN25; LEF of Pb ~4.5); and also in further downstream riverbank sediments (profiles BTN4-6; LEF of Pb of up to 4–6). The LEFs of Cu (Fig. 6b) in the Klabava River showed values elevated up to ~4 and slightly elevated values were found also in all channel belt (riverbank) sediments (LEF of Cu 3–4).

Slightly elevated LEF values of Zn were confirmed in the upper parts of floodplain profiles deposited downstream of the confluence with the Litavka River (3–6 in profile BTN24-26). Channel belt sediments showed also much higher LEF values of Zn (~7.5 in BTN9 and BTN6). Increased LEF of Zn was found also in the floodplain profiles BTN20-22 (~5.5), and finally, the highest values (~10) were found in the river bank profiles BTN4-5 in the lowermost studied site.

Magnetic susceptibility showed increased values in sediments from the Radbuza and the Mže Rivers (LEF of MS ~7.5) and the highest values were found in the Klabava River sediments (up to ~18). After the confluence with the Klabava River, values of MS were elevated (up to ~5) within entire downstream profiles, except for floodplain profile BTN23, which showed very low values (~0.5).

3.2.4 The origin of Pb in the sediments

Isotopic composition of $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ was also used to discern the different origins of Pb within the study area by comparing the observed values of $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ with values reflecting natural Pb content. For that, we use plots of $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ against 1/LEF, the reciprocal of the local enrichment factor of Pb (Fig. 7) as proposed by Ayrault et al. (2014). The $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ plot against 1/LEF has the following characteristic nodes: for 1/LEF = 1 we obtain $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ of pristine end member, for 1/LEF limiting to zero the $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ of the pollution end member. The plot (Fig. 7) allowed us to distinguish the Plzeň area sediments from the Beroun area sediments because they have different pristine end member $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ ratios. The pollution end member has the same $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ ratio (within the error of analysis).

4 Discussion

4.1 Element ratios as an efficient tool to handle natural variability

Establishment of local lithogenic background values is a crucial part of pollution assessment on a regional scale (e.g. Reimann and de Caritat 2005; Beck et al. 2013). In fluvial pollution studies, this task can be formulated as a question: “how to recognize polluted sediments if they have variable provenance and lithology (grain size)?” (Bábek et al. 2015). These influences are interrelated and should be treated simultaneously. In both cases, element ratios can help. In the case of the Berounka, the variegated provenance is clear from both geological map (Fig. 1a) and scatter plots of selected lithogenic elements (Fig. 3); the variations reflect the variable proportions of mafic and felsic rocks in individual subcatchments of the Berounka.

Variegated sediment provenance can probably explain why Pb and Zn concentrations in pristine sediment samples, when plotted against Al or Ti (two possible normalizers to correct for the grain size effects), are inconsistent along the Berounka catchment. Background concentrations of Pb and Zn are larger in the Plzeň area than in the Beroun area. The sediment provenance, however, is not relevant for Cu, Cr, Ni and MS, for

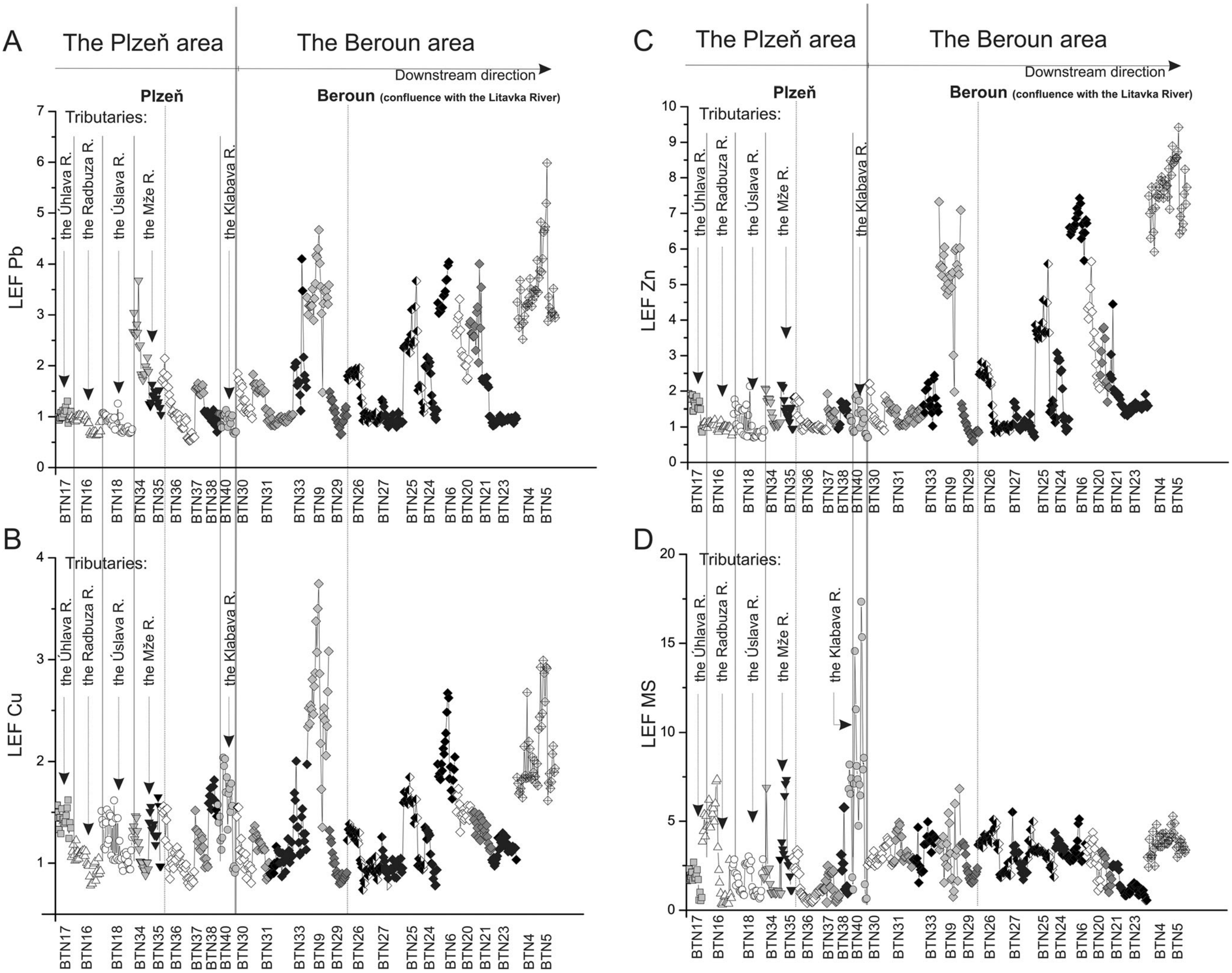
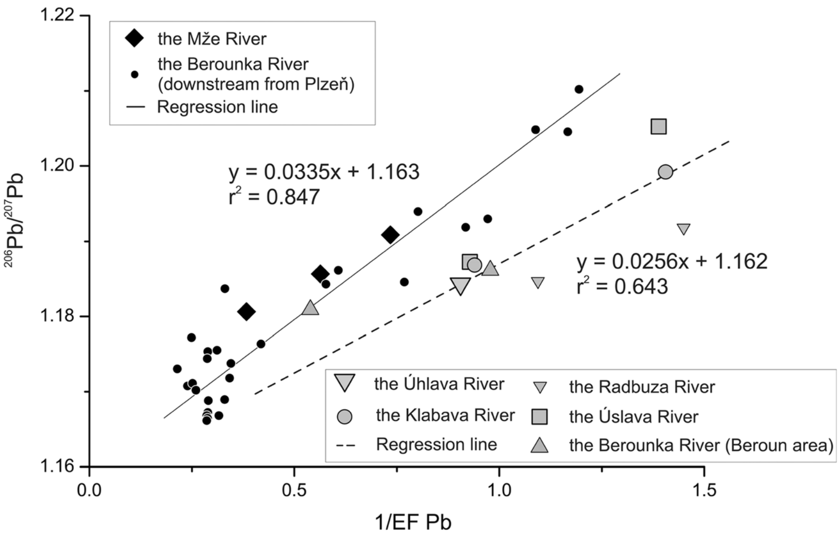


Fig. 6 Downstream change of local enrichment factors (LEF) of Pb (**a**), Cu (**b**), Zn (**c**), and MS (**d**) within the samples from the Berounka catchment, with distinguished tributaries in the Plzeň area (marked by *solid vertical lines*). Locations of Plzeň and Beroun are indicated by *longer dashed grey vertical lines*

Fig. 7 Isotopic ratio of ^{206}Pb/^{207}Pb versus 1/LEF Pb for evaluation of origins of Pb in sediments within the Berounka River catchment



which unique normalizing functions were found (Table 2, Fig. 4). Normalization curves for Pb, Zn and MS were also compared with results from the Morava River floodplain sediments (SE part of Czech Republic, data from work of Nováková et al. (2013) were added to Fig. 4) to evaluate the importance of sediment provenance. The provenance is important and highlights the relevance of using LEFs based on local lithogenic background functions rather than global reference values or element ratios. We compared the use of two normalizing elements: Al, conventionally used in fluvial sediments; and Ti, the use of which has already been proven in studies on sediments of the Jizera (Matys Grygar et al. 2013). the Ploučnice (Matys Grygar et al. 2014) and the Morava rivers in Czech Republic (Bábek et al. 2015). Titanium normalization produced background functions with larger regression coefficients and lower thresholds for LEF values, showing enrichment above the natural variability (Table 4). Local enrichment factors with a suitable (empirically selected) normalizing element can hence be used for identification of even very small pollution levels, which could otherwise easily be masked by variable provenance geochemistry (Fig. 4 is very instructive in this sense).

While normalization of heavy metal concentrations to correct for lithological variability has become conventional, normalization of MS values using Fe concentrations is a new approach for handling natural lithogenic variability of sediments and the possible influence of reductimorphic and other pedogenetic processes (Nováková et al. 2013; Faměra et al. 2013). The comparison of lithogenic background functions for MS in the Berounka and the Morava rivers (Fig. 4) also demonstrates the necessity of using local background functions for magnetic parameters.

4.2 Importance of depositional pattern for pollution assessment

The depositional pattern of the Berounka and its tributaries considerably influences the results of pollution tracing. General differences between two different types of sampling sites—the floodplain sediments and laterally deposited sediments—are shown in Fig. 5. The necessity of sampling two different sedimentary facies is dictated by floodplain morphology; the laterally deposited sediments are prevailing in the parts of the river course that are confined by bedrock. In fact, the sediments deposited along the current river banks (e.g. profile BTN6; Fig. 5a) were considerably more polluted than floodplain deposits. Due to a low preservation potential of the near channel sediments and more relevant reductimorphic processes at larger depths closer to the river channel, they have a complex stratigraphy and cannot be as easily used for tracing pollution history as distal floodplain sediments can be (if the latter are represented in a studied fluvial system). The sediments near the Berounka channel are usually polluted in their entire depth to a larger degree than floodplain deposits; similar results were obtained in the study of the Jizera sediments (Matys Grygar et al. 2013).

Table 4 Threshold values of Pb and Zn LEF above which sediment samples can be considered enriched with respect to the local geogenic background functions at probability 99.7 % (Gaussian $3 \cdot \sigma$)

Target element	Normalization elements	Threshold LEF	
		Plzeň area	Beroun area
Pb	Ti	1.22	1.27
Pb	Al	1.31	1.35
Zn	Ti	1.22	1.43
Zn	Al	1.27	2.49

Pollution depth profiles taken in the floodplain (see also Fig. 5b, profile BTN23) had a different appearance; they have an anthropogenically contaminated layer (although with only slightly increased values of LEFs) on sediments with natural lithogenic background values. Floodplain sediments can have a more reliable stratigraphy suitable for averaged regional pollution assessment. On the other hand, floodplain profiles, which are deposited slower and have a thinner polluted layer, are more exposed to natural processes of bioturbation, soil formation (Reimann and Garrett 2005) and anthropogenic influences (e.g. land use changes), which can blur the risk element depth profiles. It is important to consider in any pollution study that risk element concentrations in lateral (channel) deposits cannot be directly compared with those in floodplain sediments (Matys Grygar et al. 2013; this paper). The reason why pollution in the channel sediments is larger than that in floodplains is that the latter are being deposited during extreme floods when “younger” particulates including pollutants are more diluted by older sediments mobilized by bank erosion (Navrátil et al. 2008).

4.3 Identification of pollution sources

Downstream changes of LEFs (Fig. 6) reveal potential sources of pollution within the Berounka catchment, however, with a limited degree of certainty discussed in this paper. Polluted floodplain sediments (prevailing in the Plzeň area) cannot be directly compared with the channel belt deposits (prevailing in the Beroun area).

Evidently, the pollution of the Berounka tributaries mirrors the past mining and industrial activities within their catchment. Because these sources of pollution were not present in the Úhlava, the Úslava and the Radbuza catchments, the LEF values of Pb, Zn and MS in their sediments show weak or no pollution (Fig. 6). However, as a result of the past Ag–Pb mining activities and Pb–Zn polymetallic ore processing in the town of Stříbro, the Mže floodplain shows local enrichment by Pb, Zn and also MS. At the confluence of all four rivers, in the city of Plzeň, where the Škoda industry and paper production factory are located, however, these potential point pollution sources cannot be distinguished from the influence of the Mže catchment.

The Klabava floodplain sediments are considerably enriched by magnetic particles and Cu (Fig. 6). The former can be attributed to Fe ore mining and processing and machinery in that catchment (Ejpovice, Rokycany, Kamenný Újezd and Hrádek u Rokycan). Volaufová and Langhammer (2007) also reported that the industrial area between the cities of Hrádek and Rokycany has caused the Klabava River to be polluted by Cd.

The contamination found in the deposits in the Berounka channel belt BTN9 (just upstream from Beroun) could only originate from the Plzeň area because there is no large pollution source between the confluence of the Berounka and the Klabava and Beroun. It is worth mentioning that channel belt deposits BTN30 not far upstream from BTN9 (core position is Figs. 1 and 2) are much less polluted. This demonstrates that channel belt deposits alone cannot be used for pollution tracing, probably due to their complex stratigraphy—not all sediments in the channel belt are so recently polluted.

The sediment profiles most polluted by Cd, Pb, Sb and Zn (Fig. 6, Table 3) were found downstream of Beroun. The Beroun and the nearby Králův Dvůr have some industrial production and metalworks, but what is probably more important is that the Litavka River brings pollution as a result of mining and processing of Ag-Pb–Sb–Zn ores in the Příbram region (e.g. Ettler et al. 2006; Vaněk et al. 2008; Žák et al. 2009; Nováková et al. 2013). While some Pb and Zn pollution has obviously originated also from the Plzeň area (as proven by pollution in BTN9), Cd and Sb concentrations in the BTN6 and BTN4 profiles are the largest from all studied sediments. The contribution of the Litavka River to the contamination of the Berounka River after the extreme flood event in 2002 was reported by Navrátil et al. (2008).

Isotopic ratios of Pb are often used to evaluate Pb origin (Novák et al. 2003; Komárek et al. 2008). We used the linear relation between Pb isotopic composition and values of 1/LEF Pb proposed by Ayrault et al. (2014) for distinguishing the natural and anthropogenic end members of Pb (Fig. 7). Unfortunately, according to the work of Novák et al. (2003). both the Příbram and Stříbro ore districts have very similar ^{206}Pb/^{207}Pb isotopic ratios (~1.16). Such values of ^{206}Pb/^{207}Pb isotopic ratios were also reported in the Litavka floodplain (Žák et al. 2009; Kotková 2014; Nováková et al. 2013) and stream sediments (Ettler et al. 2006). The value ~1.16 is, however, also typical for the “central European” mixture of Pb consisting mainly of anthropogenic Pb of undifferentiated sources. Mean surface ^{206}Pb/^{207}Pb isotopic ratios obtained from the living moss in the Czech Republic are in range of 1.160–1.163 in the Berounka catchment (Sucharová et al. 2014). Consistent with those quite similar values, the plots of isotopic ratios versus pollution extent (Fig. 7) found unique ^{206}Pb/^{207}Pb ratios for pollution end members (1.162 and 1.163). Those plots, however, have yielded one unexpected and valuable discovery: the natural end members of Pb in Plzeň and Beroun areas have different ^{206}Pb/^{207}Pb ratios, 1.188 and 1.197, respectively. This difference confirms that there is a difference in the natural geochemistry of the two areas identified in the search for the lithogenic background functions (Fig. 4).

5 Conclusions

Identification of the natural geochemical variability and the sources of pollution of the Berounka River and its tributaries were based on the examination of simple element ratios. Macroelement ratios (K versus Ti and Ti versus Al) were effective in distinguishing different geological provenances within the study area. We determined that risk elements can be effectively normalized by Ti (using two normalization functions for two well-defined geochemical river reaches for Pb and Zn and single functions for Cr, Ni and Cu). For the first time, we used Fe for normalization of magnetic susceptibility, which allowed us to establish local lithogenic background functions for the study area. Assessment of pollution levels was performed by calculating the LEFs of risk elements and with MS. To evaluate ^{206}Pb/^{207}Pb isotopic composition of natural and pollution end members, we successfully used a linear dependence of ^{206}Pb/^{207}Pb against 1/LEF. The main sources of pollution that were identified were historically industrial areas known for Pb and Fe mining and metallurgy in three subcatchments of the tributaries of the Berounka.

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References

Ayrault S, Le Pape P, Evrard O, Priadi CR, Quantin C, Bonté P, Roy-Barman M (2014) Remanence of lead pollution in an urban river system: a multi-scale temporal and spatial study in the Seine River basin, France. Environ Sci Pollut Res 21:4134–4148

Bábek O, Matys Grygar T, Faměra M, Hron K, Nováková T, Sedláček J, (2015) Geochemical background in polluted river sediments: how to separate the effects of sediment provenance and grain size with statistical rigour? Catena 135:240–253

Beck M, Böning P, Schückel U, Stiehl T, Schnetger B, Rullkötter J, Brumsack H (2013) Consistent assessment of trace metal contamination in surface sediments and suspended particulate matter: a case study from the Jade Bay in NW Germany. Mar Pollut Bull 70:100–111

Covelli S, Fontolan G (1997) Application of a normalization procedure in determining regional geochemical baselines. Environ Geol 30:34–45

Devesa Rey R, Iglesias ML, Perez-Moreira R, Diaz-Fierros F, Barral MT (2013) Application of the Weng's ratio for the identification of Zn, Cu, and Pb contamination in soils and sediments. J Soils Sediments 13:932–942

Dhivert E, Grosbois C, Rodrigues S, Desmet M (2015) Influence of fluvial environments on sediment archiving processes and temporal pollutant dynamics (Upper Loire River, France). Sci Total Environ 505:121–136

Ettler V, Mihaljevič M, Šebek O, Molek M, Grygar T, Zeman J (2006) Geochemical and Pb isotopic evidence for sources and dispersal of metal contamination in stream sediments from the mining and smelting district of Příbram, Czech Republic. Environ Pollut 142:409–417

Faměra M, Bábek O, Matys Grygar T, Nováková T (2013) Distribution of heavy-metal contamination in regulated river-channel deposits: a magnetic susceptibility and grain-size approach; River Morava, Czech Republic. Water Air Soil Pollut 224:1525

Gao C, Lin Q, Bao K, Zhao H, Zhang Z, Xing W, Lu X, Wang G (2014) Historical variation and recent ecological risk of heavy metals in wetland sediments along Wusuli River, Northeast China. Environ Earth Sci 72:4345–4355

Grygar T, Světlík I, Lisá L, Koptíková L, Bajer A, Wray DS, Ettler V, Mihaljevič M, Nováková T, Koubová M, Novák J, Máčka Z, Smetana M (2010) Geochemical tools for stratigraphic correlation of floodplain deposits of the Morava River in Strážnické Pomoraví, Czech Republic from the last millennium. Catena 80:106–121

Havelkova M, Blahova J, Kroupova H, Randak T, Slatinska I, Leontovycova D, Grabic R, Pospisil R, Svobodova Z (2008) Biomarkers of contaminant exposure in chub (Leuciscus cephalus L.)—biomonitoring of major rivers in the Czech Republic. Sensors 8:2589–2603

Knab M, Hoffmann V, Petrovsky E, Kapicka A, Jordanova N, Appel E (2006) Surveying the anthropogenic impact of the Moldau river sediments and nearby soils using magnetic susceptibility. Environ Geol 49:527–535

Komárek M, Ettler V, Chrastný V, Mihaljevič M (2008) Lead isotopes in environmental sciences: a review. Environ Int 34:562–577

Kotková K (2014) Prostorové rozložení těžkých kovů v nivních sedimentech Litavky a rekonstrukce historie její kontaminace (Spatial distribution of heavy metals in aluvial sediments of Litavka river and reconstruction of contamination history). Diploma Thesis, Charles Universtiy in Prague, Czech Republic

Kružíková K, Randák T, Kenšová R, Kroupová H, Leontovyčová D, Svobodová Z (2008) Mercury and methylmercury concentrations in muscle tissue of fish caught in major rivers of the Czech Republic. Acta Vet Brno 77:637–643

Langhammer J (2001) Water quality in the Berounka River basin. Acta Universitatis Carolinae 2:111–131

Langhammer J, Kaplická M (2005) Surface water and sediment contamination by heavy metals in the Střela River Basin. Acta Univ Carol Geogr 1–2:139–152

Macklin MG, Benito G, Gregory KJ, Johnstone E, Lewin J, Michczyńska DJ, Soja R, Starkel L, Thorndycraft VR (2006) Past hydrological events reflected in the Holocene fluvial record of Europe. Catena 66: 145–154

Martin CW (1997) Heavy metal concentrations in floodplain surface soils, Lahn River, Germany. Environ Geol 30:119–125

Matys Grygar T, Sedláček J, Bábek O, Nováková T, Strnad L, Mihaljevič M (2011) Regional contamination of Moravia (southeastern Czech Republic): temporal shift of Pb and Zn loading in fluvial sediments. Water Air Soil Pollut 223:739–753

Matys Grygar T, Nováková T, Bábek O, Elznicová J, Vadinová N (2013) Robust assessment of moderate heavy metal contamination levels in floodplain sediments: a case study on the Jizera River, Czech Republic. Sci Total Environ 452–453:233–245

Matys Grygar T, Elznicová J, Bábek O, Hošek M, Engel Z, Kiss T (2014) Obtaining isochrones from pollution signals in a fluvial sediment record: a case study in a uranium polluted floodplain of the Ploučnice River, Czech Republic. Appl Geochem 48:1–15

Mihaljevič M, Zuna M, Ettler V, Šebek O, Strnad L, Goliáš V (2006) Lead fluxes, isotopic and concentration profiles in a peat deposit near a lead smelter (Příbram, Czech Republic). Sci Total Environ 372:334–344

Navrátil T, Rohovec J, Žák K (2008) Floodplain sediments of the 2002 catastrophic flood at the Vltava (Moldau) River and its tributaries: mineralogy, chemical composition, and post-sedimentary evolution. Environ Geol 56:399–412

Novák M, Emmanuel S, Vile MA, Erel Y, Veron A, Pačes T, Wieder RK, Vaněček M, Štěpánová M, Břízová E, Hovorka J (2003) Origin of lead in eight central European peat bogs determined from isotope ratios, strengths, and operation times of regional pollution sources. Environ Sci Technol 37:437–445

Nováková T, Matys Grygar T, Bábek O, Faměra M, Mihaljevič M, Strnad L (2013) Distinguishing regional and local sources of pollution by trace metals and magnetic particles in fluvial sediments of the Morava River, Czech Republic. J Soils Sediments 13:460–473

Petrovský E, Kapička A, Jordánová N, Borůvka L (2001) Magnetic properties of alluvial soils contaminated with lead, zinc and cadmium. J Appl Geophys 48:127–136

Reimann C, de Caritat P (2005) Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Sci Total Environ 337: 91–107

Reimann C, Garrett RG (2005) Geochemical background—concept and reality. Sci Total Environ 350:12–27

Resongles E, Casiot C, Freydier R, Dezileau L, Viers J, Elbaz-Poulichet F (2014) Persisting impact of historical mining activity to metal (Pb, Zn, Cd, Tl, Hg) and metalloid (As, Sb) enrichment in sediments of the Gardon River, southern France. Sci Total Environ 481:509–521

Sucharová J, Suchara I, Holá M, Reimann C (2014) Contemporary lead concentration and stable lead isotope ratio distribution in forest moss across the Czech Republic. Appl Geochem 40:51–60

Tang W, Shan B, Zhang W, Zhang H, Wang L, Ding Y (2014) Heavy metal pollution characteristics of surface sediments in different aquatic ecosystems in eastern China: a comprehensive understanding. PLoS One 9(9), e108996. doi:10.1371/journal.pone.0108996

Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. Geochim Cosmochim Ac 28:1273–1285

Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the Earth's crust. Geol Soc Am Bull 72:175–191

Tyráček J, Westaway R, Bridgland D (2004) River terraces of the Vltava and Labe (Elbe) system, Czech Republic, and their implications for the uplift history of the Bohemian Massif. P Geologist Assoc 115: 101–124

Vaněk A, Ettler V, Grygar T, Borůvka L, Šebek O, Drábek O (2008) Combined chemical and mineralogical evidence for heavy metal binding in mining- and smelting-affected alluvial soils. Pedosphere 18:464–478

Volaufová L, Langhammer J (2007) Specific pollution of surface water and sediments in the Klabava river basin. J Hydrol Hydromech 55: 122–134

Xu Y, Sunb Q, Yi L, Yin X, Wang A, Li Y, Chen J (2014) The source of natural and anthropogenic heavy metals in the sediments of the Minjiang River Estuary (SE China): implications for historical pollution. Sci Total Environ 493:729–736

Xu Y, Ho HC, Xiong W (2015) Mapping a pollution index for the transboundary Red River Valley, Asia, 2009–2011. J Maps 11:396–404

Žák K, Rohovec J, Navrátil T (2009) Fluxes of heavy metals from a highly polluted watershed during flood events: a case study of the Litavka River, Czech Republic. Water Air Soil Pollut 203:343–358