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Distinguishing regional and local sources of pollution by trace metals and magnetic particles in fluvial sediments of the Morava River, Czech Republic

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Abstract

Purpose Regional contamination of southern Moravia (SE part of the Czech Republic) by trace metals and magnetic particles during the twentieth century was quantified in fluvial sediments of the Morava River. The influence of local pollution sources on regional contamination of the river sediments and the effect of sampling site heterogeneity were studied in sediment profiles with different lithologies.

Materials and methods Hundreds of sediment samples were obtained from regulated channel banks and naturally inundated floodplains and proxy elemental analyses were carried out by energy dispersive X-ray fluorescence spectroscopy (ED XRF) and further calibrated by inductively coupled plasma mass spectrometry (ICP MS). Magnetic susceptibility was determined as a proxy for industrial contamination. The age model for the floodplain sediments was established from ^{137}Cs and ^{210}Pb dating. Trace metal contamination was assessed by establishing the lithological background values from floodplain profiles and calculating enrichment factors (EF) of trace metals (i.e. Pb, Zn, Cu) and magnetic susceptibility for the entire study area.

Results and discussion Channel sediments are unsuitable for the reconstruction of historical regional contamination due to their lithological heterogeneity and the "chaotic" influence of local sources of contamination, as well as the possibility of geochemical mobility of pollutants. On the other hand, sediments from regulated river banks qualitatively reflected the actual, local contamination of the river system.

Conclusions This approach allowed us to distinguish the influence of local sources of contamination by comparison with more spatially averaged contamination signals from distal floodplain profiles. The studied area is weakly contaminated (EF ~1–2), while individual sediment strata from regulated channel banks reflect local sources of contamination and contain up to several times higher concentrations of trace metals.

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1 Introduction

Pollution of the environment by potentially toxic elements is a worldwide problem for human health. European floodplains are polluted, not only in "hot spots" such as industrial areas with important point sources of pollution, but also in more remote regions without recent or current mining activity or metallurgy in the watershed (e.g. Murad and Fischer 1978; Martin 1997). Coal combustion, the use of agrochemicals and fertilizers, cement production, chemical industries, energy production and recycling of wastes from

local mining are amongst the numerous diffuse pollution sources in most developed countries.

The aim of this work is to evaluate whether broad-scale (regional) contamination by trace metals could be used as a tracer of the onset of the collective human impact in the fluvial environment, and thus, contribute to the discussion of the "Anthropocene" (Zalasiewicz et al. 2011). The "Anthropocene" should begin at the point in which diffuse point sources create a regionally recognized signal that is not specific for a particular river, river reach or the vicinity of a particular pollution source. The onset of significant industrial contamination (identified from depth profiles of trace metal concentrations, magnetic susceptibility and Pb stable isotope ratios) in the top part of floodplain sedimentary profiles has already been used as a local chronostratigraphic marker for individual rivers, e.g. for the Geul River (Stamm 1999) and the lower Rhine River (Middelkoop 2000, 2002) in the Netherlands, rivers in the UK (Rumsby 2000), the Odra River (Ciszewski 2003) and the Warta River (Lokas et al. 2010) in Poland and the Morava River in the Czech Republic (Grygar et al. 2010; Matys Grygar et al. 2011, 2012).

Fluvial systems are inevitably impacted in various ways by the industrialization of society because most large cities are situated along major rivers, the fluvial transport of dissolved and dispersed pollutants is more efficient than atmospheric transport of aerosols with trace metals and trunk rivers collect local runoff of dust including soot, fly ash and waste waters from industrial enterprises and communal sources. Hence, aggrading rivers should be a valuable archive of historical pollutant loads. Fluvial systems have dynamic sedimentary microenvironments (Miall 1996); hence, an individual examination of each river floodplain is necessary and must respect the spatial and temporal complexity of floodplains (e.g. Erkens et al. 2009; Hoffmann et al. 2009; Matys Grygar et al. 2011). Use of floodplains as sediment archives for the reconstruction of past anthropogenic impacts requires very specific approaches, such as obtaining basic knowledge on floodplain architecture, analysis of a large set of samples, efficient laboratory methods and simple sedimentological tools for classification of floodplain sedimentary sequences. The establishment of an effective sampling strategy is a non-trivial task. In practical studies, samples are often obtained from different parts of the river valley which were deposited under variable conditions, e.g. from channel bed sediments (e.g. Ridgway et al. 1995; Sutherland 2000; Devesa-Rey et al. 2009, 2010), and sampling from currently regulated rivers in many parts of Europe is often difficult (Macklin et al. 1994). Overbank sediments are the most reliable sampling medium for regional geochemical mapping (e.g. Ridgway et al. 1995; Swennen and Van der Sluys 1998; Swennen and Van Der Sluys 2002). It has been shown that the interpretation of overbank sequences must be performed carefully because of complex processes during floodplain development (Macklin and Lewin 2008). Another hindrance to the use of fluvial sediment archives lies in the lack of broadly accepted methodologies for the quantitative evaluation of contamination of fluvial sediments in practical regional studies (Rubio et al. 2000) and the lack of legislative tools for the assessment of sediment contamination respecting the variability of the local geochemistry (Newman and Watling 2007; Medek 2011). Uncertainties arise particularly when the pollution level is close to the natural concentrations of trace metals, which is to be expected in most European floodplains which are weakly but definitely polluted by diffuse pollution sources.

The geoaccumulation index (I_{geo}) developed by Muller (1969), the metal index (I_m), proposed by Allen and Rae (1987), and the enrichment factor (EF) are used for the assessment of the level of contamination. However, comparison of actual trace metal contents with the average values for the Earth's crust (Taylor 1964) or shale (Turekian and Wedepohl 1961), which are often used, are too crude (Covelli and Fontolan 1997; Martin 1997) to reliably quantify "weak" contamination with values of EF from 1 to 2. Many recent authors strongly recommend using regional baselines based on local data for the study area (e.g. Covelli and Fontolan 1997; Martin 1997; Rubio et al. 2000; Vijver et al. 2008). However, this must be performed with consideration of the local geochemical variability (Reimann and Garrett 2005; Wang et al. 2011). The local background must always be obtained from the same kind of material (sediment) as the polluted strata to avoid substantial systematic errors (Reimann and de Caritat 2005; Sucharova et al. 2012). Particular geochemical phenomena which can blur the historically formed depth profiles of trace metal pollution in floodplain sediments, include soil formation processes (Reimann and Garrett 2005), particularly reductimorphic processes in fluvisols (Swennen and Van Der Sluys 2002; Cappuyns and Swennen 2004; Ciszewski and Malik 2004; Du Laing et al. 2009).

This work is focused on the evaluation of industrial contamination by the calculation of EFs in the floodplain sedimentary profiles along the middle and lower courses of the Morava River in the south-east part of the Czech Republic. In our previous research, we used geochemical analytical proxy methods as a very efficient tool for chemostratigraphic correlation of the normalised depth profiles of trace metals, particularly Pb and Zn (Kadlec et al. 2009; Nováková 2009; Grygar et al. 2010; Matys Grygar et al. 2012). This work is intended to extend our previous study and answer the following questions. Which sampling sites, profiles and methodologies should be used for the assessment of trace metal contamination in a rather weakly contaminated area? What is the influence of local (point) sources (in the Morava River, corresponding to the industrial area near the city of Zlín) with respect to more diffuse regional contamination? Is it possible

to extract a regional contamination signal as a chronostratigraphic marker of broad-scale industrialization and chemization (overuse of fertilizers and pesticides) of a typical central European country?

2 Materials and methods

2.1 Studied sites and sampling

The Morava River is the largest river of the eastern part of the Czech Republic with a length of 269.6 km and catchment area of 20,692 km^2 (in the Czech Republic). Originally, the Morava River in its middle and lower course had an anabranching pattern (Grygar et al. 2010; Brazdil et al. 2011) but currently there is a single regulated channel with parallel artificial channels and drainage ditches, which were built mainly during the twentieth century. Almost the entire Morava River has been regulated (straightened, embanked) during the last century, except two natural protected areas, Litovelské and Strážnické Pomoraví, which are still naturally inundated (Fig. 1). However, neither of these areas is completely unaffected by human activities. Flood defences are located along the river in these protected areas, which were built in the 1930s and have reduced the width of the inundated floodplain to about one quarter of its original size. The floodplain of the Morava River in Strážnické Pomoraví area has already been subjected to detailed study of floodplain sedimentology and stratigraphic correlation (e.g. Kadlec et al. 2009; Novakova 2009; Grygar et al. 2010; Matys Grygar et al. 2011).

The study area (see Fig. 1), the Morava floodplain and adjacent parts of the Morava watershed, is mainly agricultural with well-known sources of local contamination concentrated in the largest cities, namely in Olomouc, Přerov (upstream from the confluence of the Bečva and the Morava), Otrokovice and especially Zlín at the confluence of the Dřevnice River and the Morava River, where the internationally renowned Baťa shoe factories were established and then extended during the twentieth century. These point pollution sources are all located either on, or very close to, the main course of the Morava between the two study areas, Litovelské Pomoraví and Strážnické Pomoraví.

For the purpose of this study, samples were taken from sediment core profiles in inundated floodplains and regulated river channel banks along the main course of the Morava River and its tributaries. The positions of the sampling sites are depicted in Fig. 1. The top 0.5 m was sampled from excavated pits to minimize the risk of contamination of deeper strata by coring, and the deeper sediments were obtained by 2–4-m-long soil augers with diameters of 2 or 3 cm (Eijkelkamp, the Netherlands). Special samples (0.5 kg) for ^{137}Cs and ^{210}Pb activity measurement were also sampled from pits. All the sediment profiles were sampled continuously with a sampling density of 2–5 cm. The channel bank sediment profiles of the regulated river were sampled using automatic drilling equipment (Eijkelkamp, the Netherlands) with a diameter of 5 cm and sampling density of 2 cm.

2.2 Analyses

The measurement of magnetic susceptibility (MS) was performed directly on the air-dried samples. Subsequently, about 10 g of dry sample was ground in an agate mortar and then subjected to chemical analysis. Element analyses were performed directly with air-dried fine powdered samples without any further pre-treatment. Powders were poured into polyamide measuring cells with a Mylar foil bottom and subjected to energy dispersive X-ray fluorescence spectrometry (ED XRF) using a MiniPal 4.0 (PANalytical, the Netherlands) with a Peltier-cooled silicon drift energy dispersive detector. XRF analysis of powders is only a proxy method which needs calibration, and thus, inductively coupled plasma mass spectrometry (ICP-MS) analysis was used for calibration, similar to our previous studies (Matys Grygar et al. 2011). The calibration equations are summarised in Table 1 in Electronic Supplementary Material.

ICP-MS was performed as described previously (Grygar et al. 2010). The air-dried and fine powdered samples (0.2 g) were dry-ashed (mineralized) in a programmable furnace (Linn, Germany) with a final temperature of 450 °C. The residues were then dampened with deionised water and subsequently dissolved in a mixture of HF and HClO$_4$, evaporated twice, the residue was further dissolved in dilute HNO$_3$ and the final solutions were transferred into 100 ml volumetric flasks.

Multi-element analyses and analyses of the ratios of stable isotopes of Pb were undertaken using ICP MS (X Series 2, ThermoScientific). The quality of analytical data was checked by measuring the standard reference material (SRM) 2709a (San Joaquin Soil, NIST, USA). The Pb isotopic composition (^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios) was measured by diluting the solutions to a concentration of <20 µg l^{-1} of Pb and the correction for mass bias was performed using SRM 981 (Common Lead, NIST, USA). The detailed instrumental parameters are given elsewhere (Ettler et al. 2004).

The cation exchange capacity (ΔCu) using [Cu(trien)]$^{2+}$ was determined as a proxy analysis of the content of expandable clay minerals. The method was originally proposed for analysis of pure clay mineral specimens by Meier and Kahr (1999), further verified for clay mineral mixtures by Czimerova et al. (2006) and later optimised for sediments and soils by Grygar et al. (2010). Air-dried

Fig. 1 The location of study area in the Czech Republic and Central Europe (**a**), and the location of the lower course of the Morava River within the two study sites, Litovelské and Strážnické Pomoraví, with positions of cores (**b**)
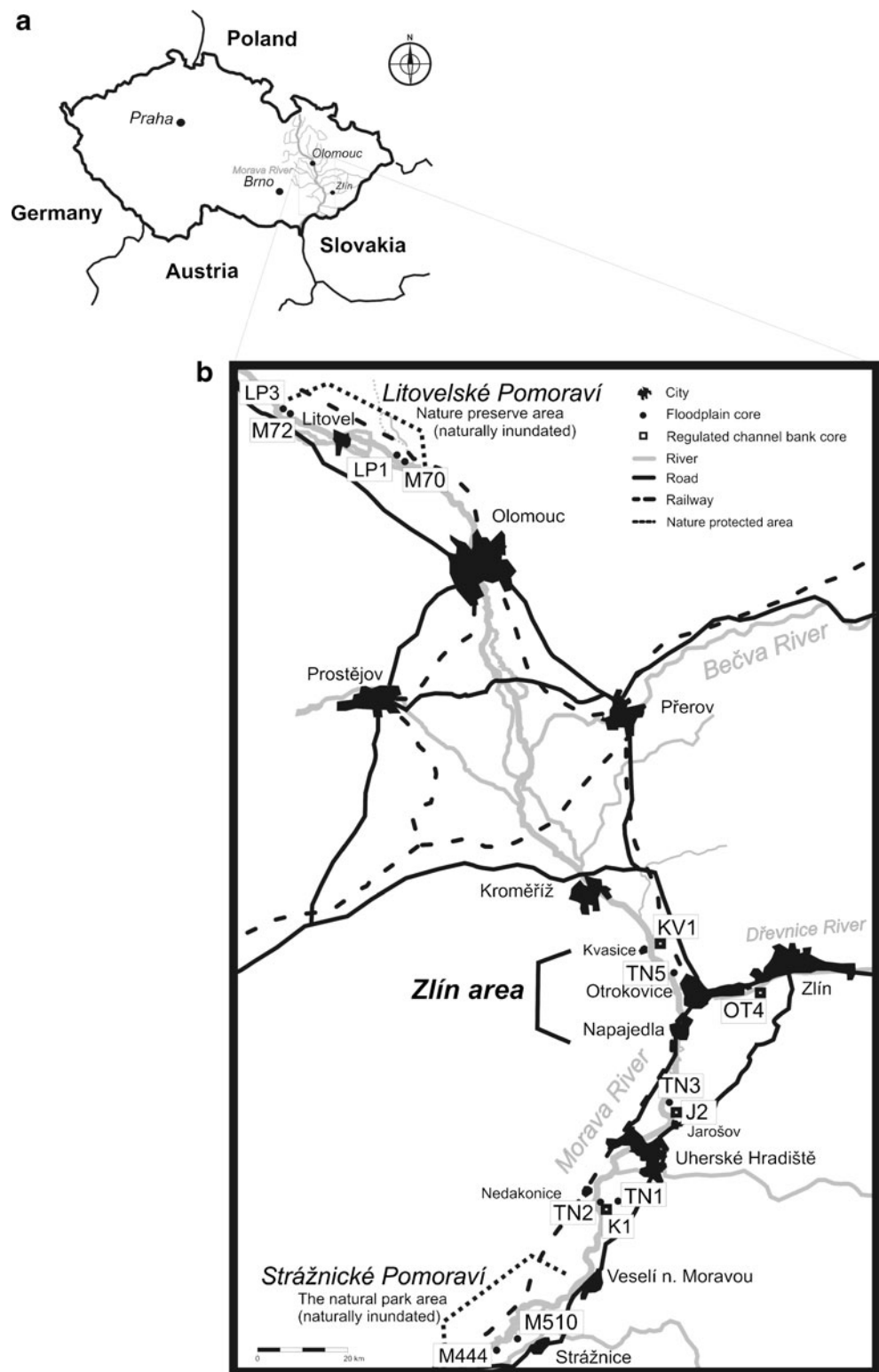
samples, ground to analytical fineness, were accurately weighed (100–500 mg) into glass beakers, wetted by 5 ml of water and then stirred using a magnetic stirrer for 5 min with 5 ml 0.01 M [Cu (trien)]SO$_4$ solution, where trien is triethylene tetramine (1,4,7,10-tetraazadekane). The suspensions were filtered into 50 ml volumetric flasks, the solid residue was washed with distilled water and the concentrations of Cu, Ca and Mg were measured by atomic emission (Ca) or absorption (Cu, Mg) spectrometry (AAS3, Zeiss, Jena, Germany). The Cu consumed was then expressed in millimoles

Table 1 Recalculated mean values of lithogenic background for each locality within the study area

	Pb/Rb	Zn/Rb	Cu/Rb	Cr/Rb	Ni/Rb	MS/Fe
Litovelské Pomoraví area						
Mean values	0.185	0.668	0.163		0.269	0.0032
SD	0.018	0.036	0.020		0.031	0.0002
Zlín area						
Mean values			0.189		0.342	
SD			0.025		0.045	
Strážnické Pomoraví area						
Mean values			0.216		0.403	
SD			0.028		0.065	
Strážnické Pomoraví and Zlín areas						
Mean values	0.162	0.643				0.003
SD	0.015	0.045				0.0003
All study areas						
Mean values				0.661		
SD				0.062		

Values of Rb-normalised Pb, Zn, Cu, Cr and Ni were obtained according to equations in Table (1) of the Electronic Supplementary Material

[Cu (trien)]$^{2+}$ per gram of sample and denoted as ΔCu. ΔCu in the studied sediments could be further used as a lithological proxy because it is directly proportional to the clay fraction content (Grygar et al. 2010).

The magnetic susceptibility of the samples was determined by using a Kappabridge Kly-2 (Agico, Brno, Czech Republic) with a magnetic field intensity of 300 Am^{-1} and a frequency of 920 Hz. The samples were then weighed and the results were recalculated to the mass-specific susceptibility expressed in m^{3}kg^{-1}. Selected samples were then subjected to magnetic separation and photographs of obtained spherules were taken by scanning electron microscope (SEM; JSM-6490LA, Jeol, Japan).

The ^{137}Cs and ^{210}Pb activities of the Morava River sediment profile LP1 (see Fig. 1) were measured after grinding about 500 g of dry sediment to fine powder. The samples were placed in plastic vessels with a volume of 500 ml. ^{222}Ra and ^{226}Rn in the samples were equilibrated for 21 days. The activities were then measured by a gamma-spectrometry using a HPGe detector (Ortec, Germany) with 35 % efficiency and an InSpector multichannel analyzer (Canberra, Canada). The summary activity of supported and unsupported ^{210}Pb was obtained by direct measurement of ^{210}Pb (46.5 keV) and the means of measured activities of ^{214}Bi (609 keV) and ^{214}Pb (352 keV) were used to determine the supported ^{210}Pb component. The activities of ^{137}Cs were used to confirm the ^{210}Pb results and maximum ^{137}Cs values (from the Chernobyl accident in 1986) were at depths corresponding to the age model based on ^{210}Pb.

About 10 g of dry sediment samples of the Morava River TN1 sediment profile was ground to a fine powder and placed in plastic vessels with a volume of 8 ml. The activities of ^{137}Cs and ^{210}Pb were then measured directly by gamma-spectrometric measurement using a low-background and SILAR high-sensitivity gamma spectrometry device, equipped with a Leadmeter Na(Tl) detector with a total efficiency of 46.2 % and a Canberra DSA 2000 multichannel analyzer controlled by GENIE 2000. Matrix effects were suppressed by a special secondary standard prepared by absorption of the primary standard ^{210}Pb and ^{137}Cs solutions ER 2X (Czech Metrological Institute) in wood sawdust. Summary activities of supported and unsupported ^{210}Pb were obtained by direct measurement of ^{210}Pb (46.5 keV). The age model was further calculated using linear approximation of the initial activity of supported ^{210}Pb.

3 Results

3.1 Lithogenic (background) contents of trace metals

Lithological and sedimentological biases were minimized by normalisation of the trace metal concentrations to conservative, immobile elements with the same facies affinity. Although there is no universal normalisation protocol (Liu et al. 2003), Al, Rb and Fe were used here based on their application in previous studies (e.g. Rubio et al. 2000; Liu et al. 2003; Orescanin et al. 2004). In the case of the floodplain sediments from the Morava River watershed, normalisation to Rb was demonstrated in our previous work (e.g. Matys Grygar et al. 2011, 2012) and the magnetic susceptibility values were normalised to Fe concentrations.

Establishing natural lithogenic background values in an area and their use for the calculation of EFs is recommended by many authors (e.g. Covelli and Fontolan 1997; Martin 1997; Rubio et al. 2000; Vijver et al. 2008). Calculation of the lithogenic background values was undertaken using the linear regressions between trace metals and normalisation element Rb; magnetic susceptibility (MS) and Fe were also used to determine the geochemical baselines and for the calculation of EFs (Vijver et al. 2008). The equations for the calculation of lithogenic background values are summarised in Table 2 in Electronic Supplementary Material. The mean values of the lithogenic (background) concentrations for each area are summarised in Table 1; the differences between pairs for adjacent study areas were evaluated using the Student's t test. Three statistically different areas were established for the Pb/Rb and Zn/Rb lithogenic values: Litovelské Pomoraví, Strážnické Pomoraví and Zlín. Ratios of Ni/Rb and Cu/Rb were different in all three locations and the Cr/Rb values were statistically consistent in all three areas.

The normalisation of Cu by Rb and MS by Fe are shown in Fig. 2a, b, respectively, which confirm the efficiency of the selected normalisation elements. In both cases, the first group of points—unpolluted floodplain sediments (full
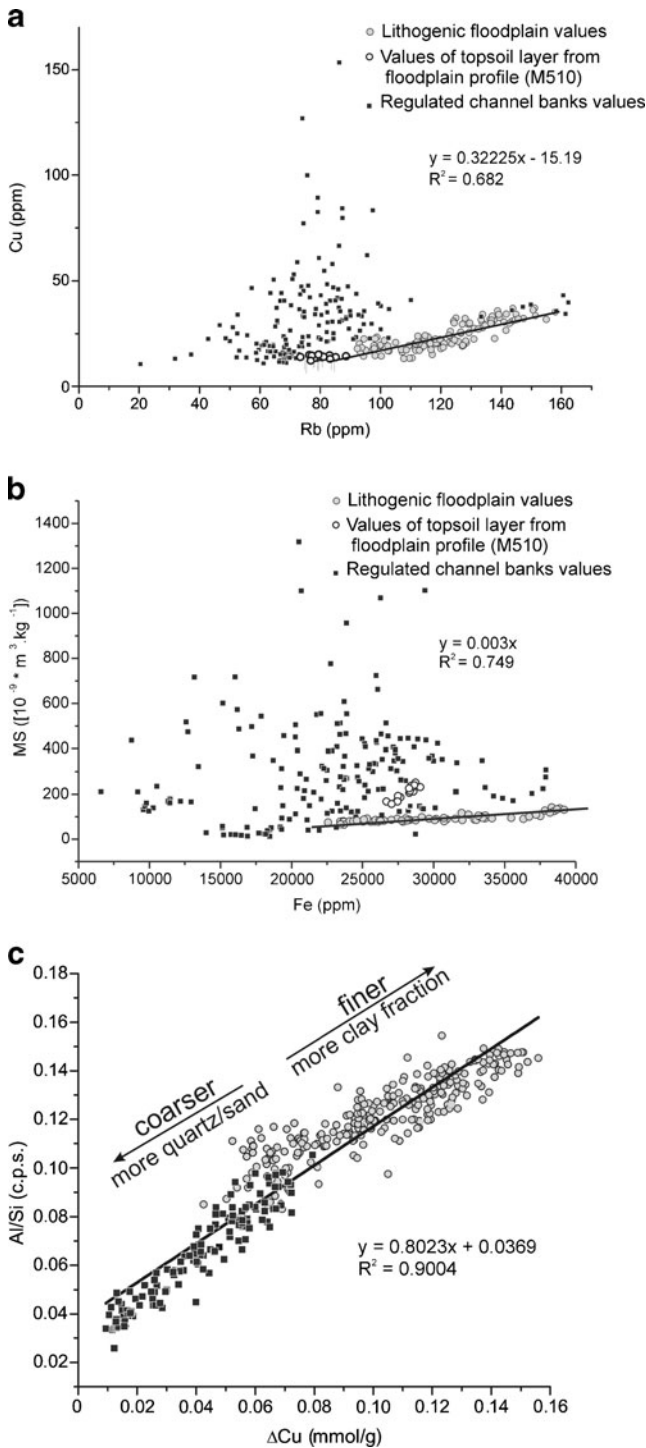

Fig. 2 Plots of **a** Cu and Rb (ppm) in the Morava River sediments. The *regression line* is for the lithogenic values. **b** Fe content (ppm) and values of MS for in the Morava River sediments. The *regression line* is for the lithogenic values. **c** Al/Si and CEC plots for the Morava River sediments. The *regression line* is for all points

circles)—have linearly correlated Rb and Cu contents (see Fig. 2a) and also Fe content and MS (see Fig. 2b); these lines represent the lithogenic content of Cu and MS. The second group of points includes topmost sediments from floodplain profile M510 (open circles). The third group of points includes sediments from regulated channel banks (full squares); generally, the Cu and MS values are greater than the lithogenic values in unpolluted floodplain sediments. It is difficult to obtain the pre-industrial concentrations of trace metals in regulated channel banks, or in the very narrow "artificial floodplain" between flood prevention defences, where the channel shape and course have been substantially altered and the stratigraphic order of the sedimentary strata is difficult to estimate. The corresponding problem of missing lithogenic concentrations relevant for the evaluation of EFs in regulated channel banks was solved by using the background values from naturally inundated floodplain profiles with similar lithology (see Fig. 2c) and known age constraints (Matys Grygar et al. 2011, 2012), and LP1 and TN1 profiles. Figure 2c gives two proxy characteristics of the Morava River sediments, related to sediment grain size (Al/Si) and the content of expandable clay minerals (ΔCu) which was proven in Grygar et al. (2010) and Matys Grygar et al. (2011). Both these parameters decrease with increasing sediment grain size. A linear dependence of both proxy parameters shows that the alumosilicate matrix of overbank fines from the inundated floodplain (full circles) and near-channel sediments from regulated river sections (full squares) have similar element/mineral composition irrespective of their generally different grain size.

3.2 Assessment of contamination using enrichment factors

Enrichment factors (EFs) are calculated as the ratio of the actual concentration of a given element from the recent part of a sediment profile to the equivalent lithogenic background value. Only "safe" sections of sediment profiles can be used to infer historic contamination, i.e. sections without signs of reductimorphic processes, namely translocations/alterations of the content of Fe and Mn oxides (MnO_x concretions and FeO_x concretions and stains) which could influence the trace metal contents (Cappuyns and Swennen 2004; Du Laing et al. 2009; Matys Grygar et al. 2011). In addition, the content of ferrimagnetic minerals could be influenced by their dissolution in anoxic conditions (Foster et al. 1998). Predicted lithogenic background values of trace metals for recent, industrially polluted strata were obtained from the linear regression equation between the given element and the normalisation element (see Table 2 in the Electronic Supplementary Material). Values of EF were then calculated using:

$$EF = M_R / M_{LBG}$$

where M_R is the actual trace metal concentration and M_{LBG} is the lithogenic background concentration. Typical EFs, lithogenic background values and concentrations of trace metals in floodplain profile TN1 are depicted in Fig. 3a. Maximum Pb EFs, with values of ~1.8, occurred in the topmost strata of the profile, the onset of enrichment being at a depth of 0.6 m.

The EF of MS (EF$_{MS}$) in the floodplain sedimentary profiles was calculated using the measured MS value of each sample and the calculated lithogenic background value of MS (which was obtained from the regression of MS and total Fe content according to the corresponding equation in Table 2 in the Electronic Supplementary Material):
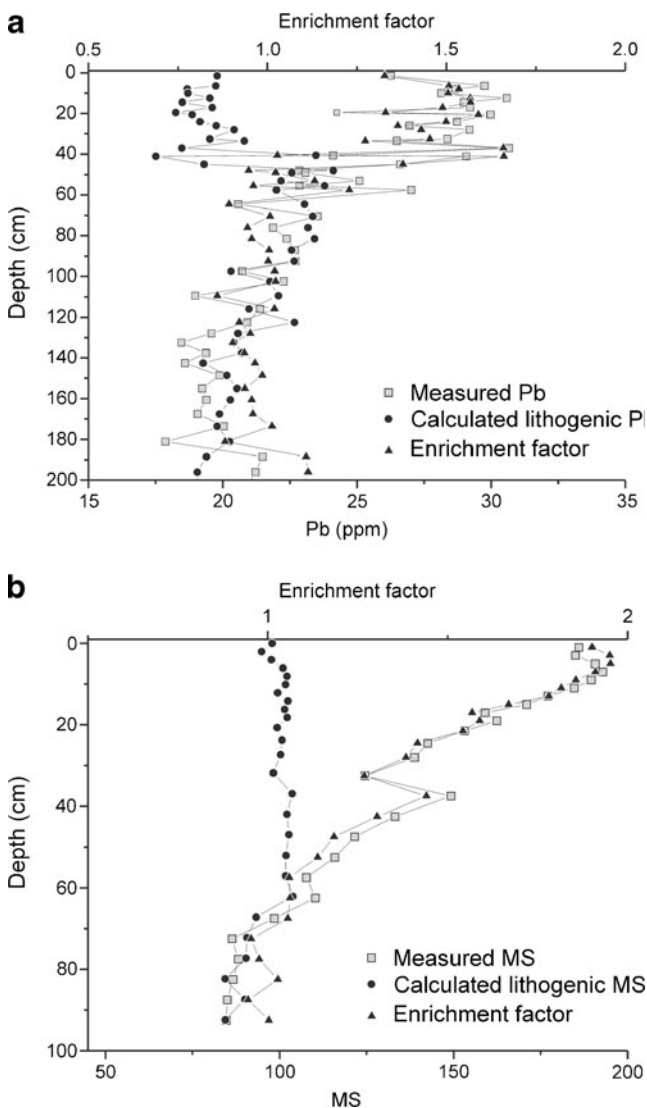
$$EF_{MS} = MS_R / MS_{LBG}$$

Fig. 3 **a** An example of calculated enrichment factor (EF) of Rb-normalised Pb concentrations in floodplain sedimentary profile TN1. **b** MS EFs for floodplain profile LP1. Units of MS are $10^{-9} m^3 kg^{-1}$

where MS_R is the actual (measured) MS value and MS_{LBG} is the calculated lithogenic background. Typical EFs for MS are shown in Fig. 3b, which depict the EFs, calculated lithogenic values and the measured values of MS from floodplain profile LP1. EFs for MS in floodplain sedimentary profiles (with maximum EF ~2.0) in the topmost part of the profile start to increase at depths of approximately 0.6–0.7 m.

Maximum values of EFs in the naturally inundated areas (distal floodplains) ranged from 1.3 to 2 for Pb and Zn, from 1.2 to 1.7 for Cu, from 1.1 to 1.2 for Cr and Ni and from 2 to 4 for MS. The EFs of trace metals and MS in regulated channel banks were calculated in the same manner as in the floodplain profiles.

3.3 Typical floodplain profiles

A typical depth profile from Morava floodplain profile M510 from Strážnické Pomoraví is depicted in Fig. 4a with Rb-normalised Pb, Zn, Cu, Cr and Ni concentrations. The depth profiles of Pb/Rb, Zn/Rb and Cu/Rb are similar to those reported in our previous studies (Grygar et al. 2010; Matys Grygar et al. 2011, 2012). The Cr/Rb values are only slightly elevated, whereas the Ni/Rb values are not and are similar to the values at greater depths.

Sampling of the profiles down to depths of 0.6 to 1.3 m, to obtain unpolluted sediment, permits the evaluation of the local lithogenic (pre-industrial) background. At depths below 1.5 m, there were clear signs of reductimorphic processes (see also Fig. 4a, depths marked by grey boxes) and in the deeper parts of the sedimentary profiles reductimorphic processes are considerable and the original contents of Fe, Mn and trace metals are substantially altered by migration. This is responsible for the immobilisation of a portion of the trace metals and for further "chaotic" scatter of their values with respect to the entire profile of values. Transformations of Fe(III) oxides by redox changes, such as the large irregular Fe oxide stains at depths below 1.3–1.5 m and ~1 mm Mn oxide concretions at depths of 0.9–1.2 m—particularly in very dense clay or in porous sandy sediments (Novakova 2009; Matys Grygar et al. 2011, 2012)—were observed in field and are evident in the "chaotic" scatter in the EDXRF logs of Mn and Fe (see Fig. 4a, Mn/Rb and Fe/Rb).

3.4 Erosion of channel banks

Floodplain sediments from erosion of channel banks in the Litovelské Pomoraví area (profiles M70 and M72) were sampled for comparison with the known eroding bank profiles in the Strážnické Pomoraví area and were found to be lithologically similar to the floodplain profiles. The only difference was in their upper part, where more sandy
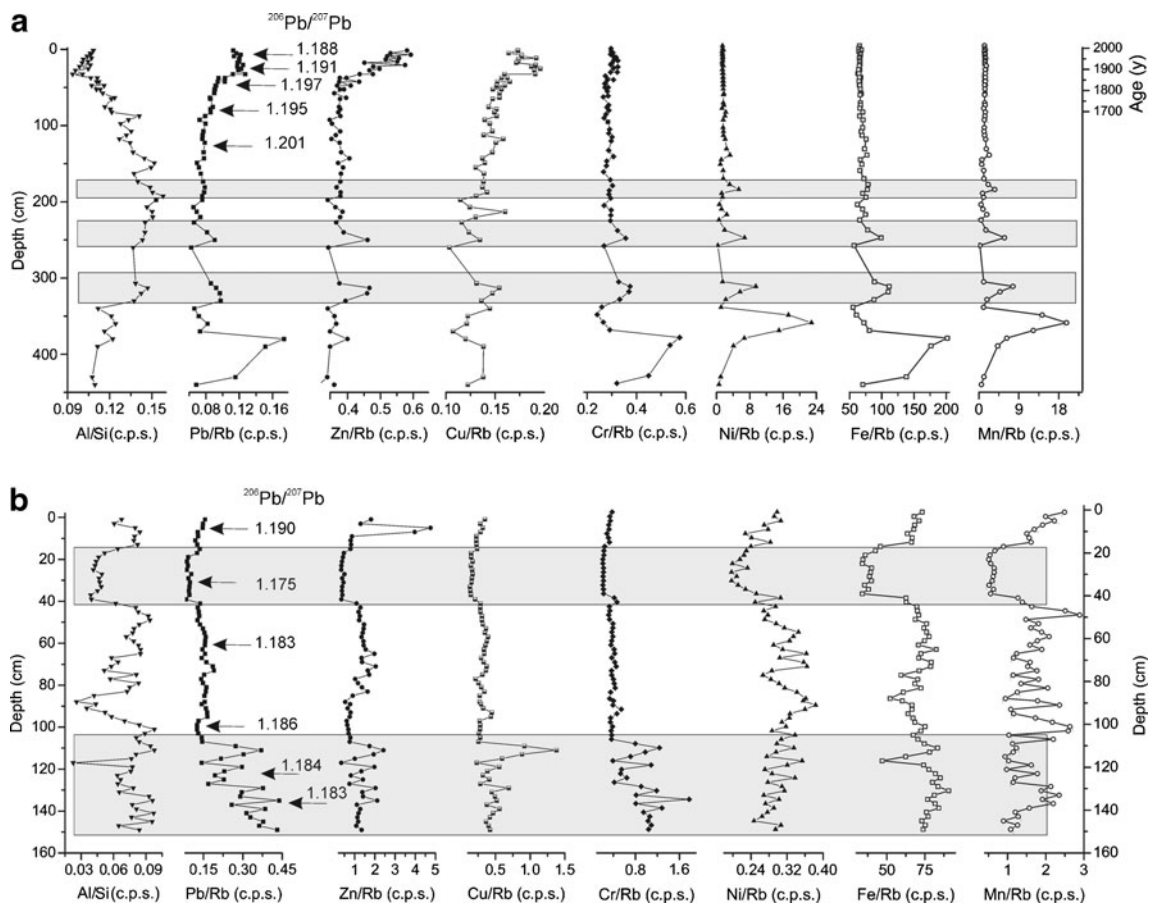
Fig. 4 a The depth profiles of Al/Si and Rb-normalised Pb, Zn, Cu, Cr, Ni, Fe, and Mn concentrations (c.p.s. signals from ED XRF) in floodplain profile M510. *Grey boxes* serve for correlation of the stratigraphically unreliable strata at depth >1.5 m, which had observed signs of gleying, confirmed by changing trace metals, and Fe and Mn concentrations. Values of ^{206}Pb/^{207}Pb isotopic ratios are marked by *arrows* near Pb/Rb log and corresponding ages of sedimentary layers, extrapolated from the age model based on ^{210}Pb dating method, are marked on the secondary *Y* axis. **b** The depth profiles of Al/Si and Rb-normalised Pb, Zn, Cu, Cr, Ni, Fe, and Mn signals from ED XRF (c.p.s.) in regulated channel bank profile OT4. Trace metal concentrations and the contents of Fe and Mn vary, corresponding to the lithological changes in the *upper part* of profile. The *bottom part* of profile is characterised by increased values of trace metals with concentrations greatly exceeding the anthropogenic values from the upper part of floodplain profiles (both parts of profile are marked by *grey boxes*). Values of ^{206}Pb/^{207}Pb isotopic ratios are marked by *arrows* near Pb/Rb log

sediments typical of levees were found. Levee sediments have already been described (e.g. Matys Grygar et al. 2011) as unreliable due to the possibility of migration of contaminants in their rather porous, unconsolidated matrix. A similar observation of trace metal migration in eroding banks was reported by Hudson-Edwards et al. (1998) and Ciszewski et al. (2008). Hence, only the middle sections of sediment profiles, without Fe and Mn fluctuations, can be used to obtain the lithogenic background values in this area.

For the calculation of EFs, the lithogenic background values were taken from the nearest, and hence, presumably the most similar, floodplains in the Zlín area (see Table 1). EFs from regulated channel bank profiles in the Zlín area have surprisingly large variations in depth profiles: 0.5–7 for Pb, 0.4–13 for Zn, 0.2–14 for Cu, 0.8–9 for Cr, 1.1–2 for Ni and 0.2–21 for MS.

The depth profiles of elements in the channel banks are much more complicated than in the floodplain sediments. In a typical regulated channel bank profile (e.g. OT4, Fig. 4b), the scattered and chaotic sharp changes in the Rb-normalised trace metal contents and also Fe/Rb and Mn/Rb ratios are evident in the entire profile and are similar to those observed in the deeper parts of the floodplain profiles, which are impacted by reductimorphic processes. Lower values of MS and low concentrations of trace metals were observed in the upper part of the profile, which has sandy layers, while the trace metal concentrations were very high in their bottommost parts, exceeding by threefold the anthropogenic values in the upper part of the floodplain profiles (see Fig. 4b, both problematic parts of the profile are marked by grey boxes). Other regulated channel bank profiles have similar features.

3.5 Regional patterns of the distribution of enrichment factors

The downstream change in the maximum EFs in naturally inundated floodplains is shown in Fig. 5a. A typical profile for the Litovelské Pomoraví area (full squares) is shown; this area has the smallest maximum EFs (EF ~1.5 for Pb, 1.3 for Zn and with maximum EF ~2.8 for MS). A profile from the Zlín area (open circles) has the highest EF values (EF ~1.65 for Pb and 1.8 for Zn, with EFs ~2.4 for MS). A typical profile for the Strážnické Pomoraví area (full

triangles) has slightly increased EFs (EF ~1.6 for Pb, 1.65 for Zn and EF ~2.6 for MS).

The downstream change in EFs can also be observed for regulated channel banks (see Fig. 5b). Profile KV1 (full squares) has extremely decreased EFs in its sandy, topmost part of the profile in comparison with the floodplain profiles (EF ~0.9 for Pb, 0.3 for Zn, 0.2 for MS). Considerable industrial contamination in the Zlín area is well demonstrated in the OT4 profile (open circles), with the highest values of EFs for both MS and trace metals in its lower part (EF ~7 for Pb and Zn, and 21 for MS). Slightly increased values are
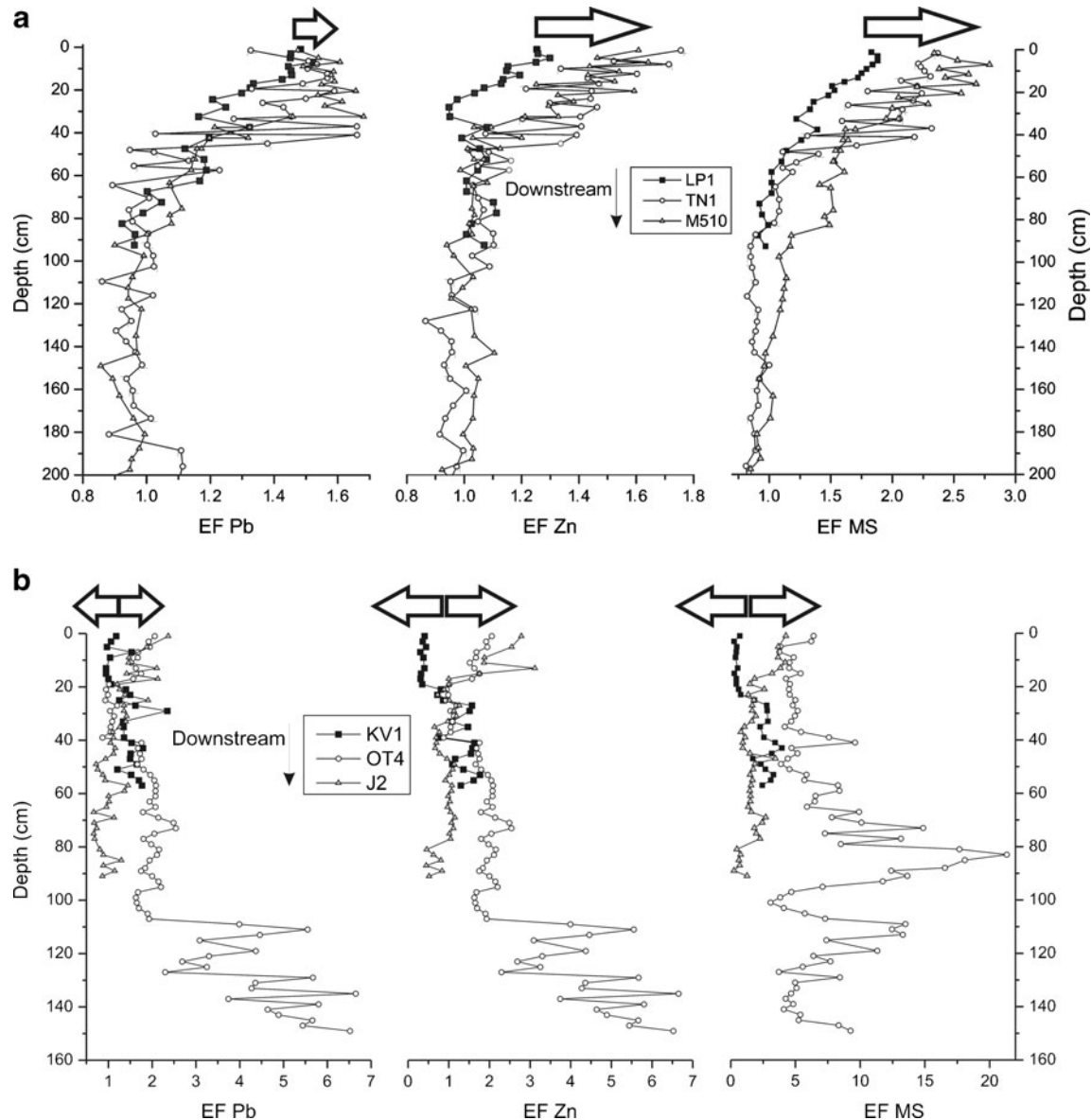

Fig. 5 a Downstream variations in EFs in floodplain sediments in the study area (increased values of EFs in the area are marked by *arrows*) using the depth profiles of Pb, Zn and MS EFs from floodplain profiles LP1 (*full squares*), situated in Litovelské Pomoraví, TN1 (*open circles*) sampled directly in the Zlín area, and M510 (*full triangles*), situated in Strážnické Pomoraví. **b** Downstream variations in EFs in regulated

channel sediments within the study area using the depth profiles of Pb, Zn and MS EFs from regulated channel banks profiles KV1 (*full squares*), situated upstream from the confluence of the Dřevnice and Morava Rivers, OT4 (*open circles*), situated in the Zlín area, and J2 (*full triangles*), situated downstream from the confluence of both rivers. Abnormally increased and decreased values of EFs are marked by *arrows*

shown in profile J2, situated downstream from the confluence of the Dřevnice and the Morava, with EF ~6 for MS, ~2.4 for Pb, and 3 for Zn. Increasing or decreasing EF values with respect to the lithogenic background values are marked by arrows in Fig. 5b.

3.6 Depth distribution of $^{206}Pb/^{207}Pb$ isotopic ratios

The $^{206}Pb/^{207}Pb$ isotopic ratios in regulated channel banks vary similarly as in the floodplain sediments. The $^{206}Pb/^{207}Pb$ ratios in typical floodplain and regulated channel bank profiles (M510 and OT4) are also shown in Fig. 4a, b. Table 2 gives a summary of the EFs and this isotopic ratio in selected typical floodplain (TN1 and M510) and regulated channel bank profiles. We distinguished three types of sediment: I) with pre-industrial values of $^{206}Pb/^{207}Pb$ (~1.201) and EFs close to 1, i.e. uncontaminated sediments; II) with lowered $^{206}Pb/^{207}Pb$ (~1.186) and EFs enhanced above the threshold limits of the background, i.e. contaminated sediments; and III) sediments with lowered $^{206}Pb/^{207}Pb$ but EFs close to 1 or <1. Type III sediments are an exception and were only found in certain strata of two cores; in the topmost layer of profile KV1 and in

the bottom part of profile J2, i.e. in sandy sedimentary layers with lowered concentrations of trace metals and magnetic particles (see also Table 2). These two profiles are suspicious because of the possibility of post-depositional mobility of particles, due to their stratigraphic inconsistency, which is confirmed by alternating layers containing sediment types I and III (see Table 2).

3.7 ^{210}Pb dating of floodplain profiles

Deposition rates of floodplain sediments in the Litovelské Pomoraví and Zlín areas were estimated using the activity of unsupported ^{210}Pb, similarly to previous work (e.g. Owens and Walling 2003; Lokas et al. 2010; Saint-Laurent et al. 2010; Bird 2011; Du and Walling 2012). In profile TN1, the activity of unsupported ^{210}Pb was calculated as the difference between the activities of ^{210}Pb and ^{214}Bi, and for the LP1 profile as the difference between the ^{210}Pb activity and the mean of the ^{214}Bi and ^{214}Pb activities. The regression line from the correlation of the natural logarithm of activities and depths, assuming constant sedimentation rate and constant initial activity of the unsupported ^{210}Pb, was plotted using

Table 2 Comparison of different types of sediments in regulated channel banks (OT4, J2, KV1 and K1) and typical floodplain sedimentary profiles TN1 and M510, characterised by different enrichment factors (EFs) of heavy metals and magnetic susceptibility (MS) and changes of Pb isotopic ratios

Profile	Depth (cm)	MS	Pb	Zn	Cu	Cr	Ni	$^{206}Pb/^{207}Pb$
OT4[b]	9	4.88	1.67	2.48	1.70	1.08	1.38	1.190
OT4[b]	33	4.70	1.09	1.12	0.75	0.45	0.62	1.175
OT4[b]	85	18.18	1.94	2.71	2.01	0.95	1.53	1.184
OT4[b]	105	4.12	1.70	1.99	2.02	1.33	1.50	1.186
OT4[b]	125	5.59	3.25	4.04	3.47	2.76	1.78	1.184
OT4[b]	145	5.27	5.66	3.30	3.03	4.93	1.24	1.183
J2[b]	5	3.70	1.88	2.55	2.04	1.48	1.53	1.191
J2[b]	15	3.22	1.42	1.76	1.36	1.19	1.01	1.189
J2[a]	29	1.68	1.36	1.13	1.25	1.01	0.83	1.195
J2[a]	55	1.70	0.93	0.92	1.05	0.96	0.85	1.202
J2[a]	77	2.28	0.69	1.05	1.18	0.98	1.15	1.205
J2[c]	89	0.27	1.15	0.84	1.04	1.06	0.91	1.192
KV1[c]	3	0.25	1.06	0.36	1.04	0.71	0.64	1.181
KV1[c]	9	0.37	1.04	0.38	0.94	0.64	0.73	1.180
KV1[c]	17	0.42	1.00	0.31	0.91	0.60	0.46	1.180
KV1[c]	39	2.57	1.36	0.75	1.27	0.94	0.74	1.183
KV1[b]	47	1.70	1.50	1.16	1.22	0.34	0.85	1.193
KV1[b]	57	2.45	1.77	1.30	1.50	1.27	1.05	1.188
K1[b]	5	5.59	1.96	2.94	2.18	1.52	1.31	1.185
K1[b]	23	4.96	2.12	3.43	1.76	1.26	1.05	1.184
K1[b]	37	3.73	1.43	1.35	1.21	0.91	0.98	1.190
K1[b]	43	7.44	2.00	1.99	1.92	0.78	0.97	1.192
TN1[b]	8	2.24	1.54	1.71	1.60	1.20	1.20	1.189
TN1[a]	81.5	1.05	0.96	1.05	1.14	1.06	1.02	1.205
M510[b]	16	2.69	1.59	1.52	1.29	1.10	1.12	1.188
M510[a]	135	1.03	0.97	1.04	1.10	1.07	1.11	1.201

[a] Type I: Uncontaminated lithological background sediments with increased $^{206}Pb/^{207}Pb$ values

[b] Type II: Contaminated sediments with decreased values of $^{206}Pb/^{207}Pb$

[c] Type III: Uncontaminated sediments with decreased values of $^{206}Pb/^{207}Pb$

the activities of the topmost points, similarly, as it has been reported previously (Matys Grygar et al. 2011). Sedimentation rates were estimated to be ~0.37 cm year^{-1} in TN1 and ~0.51 cm year^{-1} in LP1, which is consistent with the range of 0.3–0.5 cm year^{-1} reported by Grygar et al. (2010) and Matys Grygar et al. (2011) for the Strážnické Pomoraví area.

The extrapolation of the sedimentation rate obtained by ^{210}Pb to the base of the industrially contaminated sediments in profile M510 (see secondary Y axis, Fig. 4a) provides estimates of the onset of Pb/Rb contamination in 1855 and Zn/Rb in 1888, at a depth of about 0.5 m, which corresponds to the actual bases of the normalised trace metals in profile TN1 and to the data previously reported by Matys Grygar et al. (2011). The base of the increasing of other industrial contaminants, Cu and Cr, lies at a depth of approximately 0.5 m in the M510 profile. The concentrations of Ni were not elevated significantly above the lithogenic background. The results correspond to the historical development of the region. Industrial contamination started before the fall of the Austrian-Hungarian Empire in the 2nd half of the nineteenth century. Since that time, new factories (e.g. Baťa shoe factory, rubber and plastic production and the chemical industry) have been established in the Zlín area.

4 Discussion

This study substantially extends the spatial scale of our previous work in the Strážnické Pomoraví area (see Fig. 1) and confirms our previous ideas (e.g. Matys Grygar et al. 2011, 2012); even a rather weak industrial contamination signal can be unequivocally traced in the inundated floodplain profiles. EF is a useful tool if it is based on the comparison of polluted strata with deeper (=older) strata (see Table 1). This approach overcomes problems related to local differences in actual geochemical baselines (Reimann and Garrett 2005) and to crude approaches based on averaged shale or crust values (Covelli and Fontolan 1997; Martin 1997). Magnetic susceptibility measurements have been used in many previous studies (e.g. Knab et al. 2006; Babek et al. 2008) but we have introduced the potential of MS/Fe normalisation (see Fig. 2b). Obviously, MS can be handled in the same manner as trace metals. EFs in floodplain profiles and channel banks ranged from 1.5 to 2 for trace metals and 2 to 4 for MS (typical EFs of trace metals and MS are shown in Fig. 3a, b). According to the five-category system proposed by Sutherland (2000), the floodplain of the middle and lower reaches of the Morava is minimally (EFs <2) or moderately (EF ~2–5) contaminated.

This study includes analysis of sediments of the Morava River from the banks of the regulated channel, mainly from the Zlín area, the most important pollution source in the middle and lower reaches of the Morava River near the confluence of the Dřevnice and Morava Rivers (see Fig. 1). There is no preserved, naturally inundated, floodplain area just downstream from this confluence. Study of the impact of the Zlín area required the analysis of sediments from very dynamic river banks environments, which have been strongly impacted by channelization and embankment. Typically, these sediments were coarser than inundated floodplain sediments (see Fig. 2c). The lithogenic background from the inundated floodplain is still the best possible preindustrial reference for calculation of EFs in the channel bank sediments. Comparison of EFs in industrially contaminated floodplain sediments upstream (Litovelské Pomoraví) and downstream (Strážnické Pomoraví) from the Zlín area (see Fig. 5a) clearly reveals enhanced pollution by this source. This is confirmed by the more polluted channel bank sediments just downstream from that area (see Fig. 5b). The EFs of topmost channel bank sediments downstream from the confluence of the Morava and Dřevnice Rivers are slightly higher than for the inundated floodplains. However, their depth profiles are rather "chaotic" (see Fig. 5b) and thus the actual element composition of particular sedimentary strata at a given site must be evaluated cautiously. The channel sediments and sediments from close vicinity to the channel (i.e. in embanked rivers) are often used for the assessment of regional contamination or geochemical mapping (e.g. Ridgway et al. 1995; Babek et al. 2008; Devesa-Rey et al. 2009, 2010), but we consider these sediment types too complex for stratigraphic purposes. We also prefer the use of distal floodplain sediments for mapping past impacts, because they do not require abstract statistical analysis that could produce mistakes (Reimann and de Caritat 2000, 2005). Sediments sampled from easily accessible outcrops in eroding channel banks are also often used for the assessment of regional contamination. These sediments must also be treated with caution due to their substantial (or exclusive) composition of mostly sandy levee sediments and crevasse splays. Thus, their porosity (permeability) allows for the mobilization of trace metals due to better sorting and lower or no clay content (e.g. Swennen and van der Sluys 1998; Ciszewski et al. 2008; Matys Grygar et al. 2011).

The Pb isotopic composition is a useful tracer of modern industrial pollution (Ettler et al. 2004; Komarek et al. 2008). In the Czech Republic, coal combustion and the use of leaded petrol are the most important sources of atmospheric Pb, but it is not easy or impossible to distinguish their contribution only from a change in the Pb isotopic signature. Typical ^{206}Pb/^{207}Pb values ranged from 1.195–1.22 for Central European lithogenic Pb, 1.12–1.16 for European leaded gasoline (Komarek et al. 2008), and 1.17–1.24 for Pb from coal combustion (Mihaljvic et al. 2009). Preindustrial values of ^{206}Pb/^{207}Pb in the Strážnické Pomoraví area ~1.202 and values for eroding channel banks with the most contaminated sediments (1.188–1.191) were similar to the values reported in our previous work (Grygar et al.

2010). The $^{206}Pb/^{207}Pb$ ratios in Litovelské Pomoraví and the Zlín area were also similar, with "anthropogenic" values of ~1.189 and pre-industrial values of ~1.201. Except for some sediments from the core KV1 (see Table 2), there is clear link between the EFs of Pb and the shift in the $^{206}Pb/^{207}Pb$ ratio, demonstrating that Pb enrichment has a different isotope signature, being a mixture derived from coal and leaded gasoline.

The increase in the EFs of floodplain sediments downstream from the confluence of the Morava and Dřevnice Rivers due to contamination from the Zlín area demonstrates that inundated floodplains are useful environmental archives. Strážnické Pomoraví reflects the contamination from the Zlín area, with EFs of only several tens of per cent. Such a small number emphasizes the need for caution because of several phenomena that could possibly disturb the originally deposited sediments. EFs may be influenced by biogeochemical processes in the soil (Reimann and Garrett 2005) that could possibly result in EFs of Pb and Zn comparable to those obtained for the floodplain sediments of the Morava River. However, the relative importance of pedogenic processes in fluvisols depends on the sedimentation rate and consequently on the time over which the overbank fines are exposed to pedogenesis. It is hard to estimate the real importance of biogeochemical processes for a given fluvisol; each floodplain must be judged individually. The vertical migration of trace metals related to the redox cycling of Fe and Mn at depths, due to water level fluctuations, are easily recognized and the corresponding parts of the sediment profiles can be omitted (e.g. Fig. 4a and its discussion, see also Matys Grygar et al. 2012).

There are several lines of evidence that suggests that the EFs in the Morava River floodplains reflect real contamination and not pedogenic processes. Most parameters are shifted in the contaminated topmost layer, which was also observed in many previous studies (e.g. Liu et al. 2003; Ettler et al. 2004; Knab et al. 2006; Komarek et al. 2008; Novakova 2009; Grygar et al. 2010; Matys Grygar et al. 2011, 2012). The anthropogenically contaminated layer at the top of the sedimentary profile can be recognized by its elevated MS, the occurrence of strongly magnetic particles (spherules) derived from high-temperature processes (see also Fig. 6) and enhanced contents of trace metals and shifted Pb isotopic ratios. Moreover, in the "old" floodplain outside of the flood defences in the Strážnické Pomoraví area (erected in the 1930s) the EFs are lower and Pb isotope shifts are much smaller than in the still-inundated floodplain within the flood defences (Matys Grygar et al. 2011). Hence, we consider our methodology to be suitable for the floodplains of aggrading rivers with weakly contaminated watersheds and attribute the obtained EFs to contamination rather than to pedogenesis. This anthropogenic effect can thus be used as a local chronostratigraphic marker for rivers
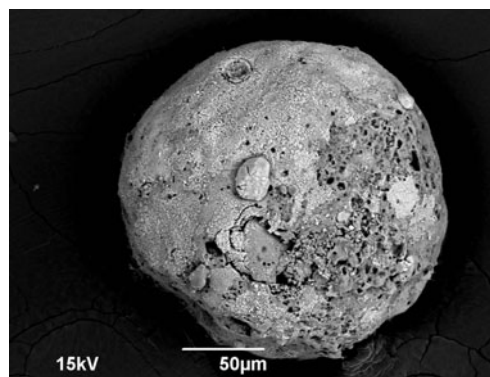

Fig. 6 An example of a magnetic particle from a depth of 112 cm from core profile OT4

(e.g. Middelkoop 2000; Rumsby 2000; Middelkoop 2002; Ciszewski 2003; Lokas et al. 2010).

Recognising the limitations mentioned above, we consider appropriately calculated EFs to be suitable as chronostratigraphic markers, similar to those described by Zalasiewicz et al. (2011) as a stratum in the sediment record indicating the onset of collective human activity. On the other hand, we are not as optimistic about the durability of this pollution marker on geological timescales. Further aggradation will inevitably disturb the original sedimentary patterns by soil redox processes. Without further aggradation, later pedogenesis and related biogeochemical processes will tend to enhance or even create a depth gradient resembling the pollution signal (Reimann and Garrett 2005).

5 Conclusions

Our results show that distal floodplain sedimentary profiles should be preferred for the reconstruction of historical regional contamination, while sediments from regulated river banks and channel sediments—that qualitatively reflect the actual, local contamination of the river system and contain up to several times higher concentrations of trace metals than overbank fines—can be used for more sensitive assessment of the local sources of contamination in the area. The metal content in river bank and channel sediments should also be compared with the average regional contamination signal, which is easily accessible from distal floodplain profiles.

Properly calculated EFs from distal floodplain sedimentary profiles are a very robust quantitative expression of the actual human influence, even in only weakly contaminated areas (with EF ~1–2) such as in overbank fines in the Morava floodplain. The weak contamination signal can be traced unequivocally in the real sediment record; it reflects the regional human impact (i.e. broad-scale industrialization and chemization of a typical Central European country). The same approach should be applicable to other regions which

are not affected by heavy industry. Hence, the contamination signal can be used as a chronostratigraphic marker for any inhabited region in the world. This methodology also allows for the monitoring of past environmental pollution and the fate of contaminants in different fluvial systems.

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