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

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ABSTRACT

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

1. Introduction

Knowledge of the manner in which pollution is distributed in a fluvial sediment record and how it behaves there helps in developing a better understanding of fluvial systems. The value of such approach has recently been demonstrated by the huge impact of methods based on the purely anthropogenic unstable isotope ^{137}Cs, whose presence can provide isochrones in sediment bodies (Walling and He, 1998). Chemical pollution of fluvial systems can also yield such isochrones, and its experimental characterisation can be less experimentally demanding than that of ^{137}Cs. Certain pollutants may be more stable in sediment profiles than ^{137}Cs, which migrates through coarser sediments with a low illite content. The pollution-based isochrones have been proven relevant for practical fluvial geomorphology and *vice versa*: the contaminant distribution in floodplains is a function of geomorphologic evolution (Macklin et al., 1994; Hudson-Edwards et al., 1999; Notebaert et al., 2011; Matys Grygar et al., 2011). The use of floodplain sediments for reconstructing the development of historical pollution has already demonstrated its potential in influential case studies of long-term historical pollution of European rivers (Hudson-Edwards et al., 1999; Swennen and Van der Sluys, 2002). That approach has been developed further for evaluating pollution changes during the 20th century (Meybeck et al., 2007;

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Nguyen et al., 2009; Grosbois et al., 2012; Matys Grygar et al., 2012; Zachmann et al., 2013; Majerová et al., 2013). For each such sedimentary record, possible lags or other anomalies in the primary pollution signal are of crucial importance. Knowledge of the dynamics of the pollutant transport through the fluvial system with good temporal resolution is particularly important when the impacts of catastrophic pollution events and subsequent remediation measures are evaluated (Fleit and Lakatos, 2003; Osán et al., 2007; Turner et al., 2008; Bird et al., 2008; Nguyen et al., 2009).

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

2. Study area

2.1. Ploučnice River

The Ploučnice River (Fig. 1) is a right-side tributary of the Labe/Elbe River (length: 106 km; catchment area: 1194 km^2). The mean annual discharge at Mimoň is 2.30 m^3/s, and the channel slope is approximately 0.6‰. It is a medium-energy meandering river in a confined valley with medium-grained cohesive to noncohesive floodplain sediments. The area (ca. 100×400 m) studied in detail is located south of the village of Boreček, alongside the middle reach of the river. In this area, the active floodplain is narrow (100–150 m), as the river is located in a valley bounded by Turonian to Coniacian sandstones (Kühn, 1996) and Late Glacial/early Holocene fluvial deposits (Sádlo et al., 2013). The Ploučnice River has a meandering and anastomosing pattern on the floodplain, and the channel is ca. 5 m wide on average.

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

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

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

2.2. Uranium mining and resulting pollution

In the Stráž pod Ralskem area, uranium was mined by conventional methods (underground haulage) and by underground chemical leaching (Kafka, 2003). Main U-bearing minerals are uraninite and hydrozircon; they occur in silty-sandy sediments. The conventional uranium mines were located in Hamr na Jezeře and Břevniště (Fig. 1). They operated since the middle 1970s, with a peak in the 1980s (800–900 t/year). There was a decline after 1989, and the mining was terminated in 1994. Mine waters were the primary source of pollutants, which included heavy metals (particularly Ni and Zn), SO_4^{2-}, acid and radioactive nuclides (U, ^{226}Ra). The treating and cleaning of the polluted water were limited by its huge volume (Kafka, 2003). At the beginning of the mining, the mine water was only treated by anion exchangers to remove U and by addition of $BaCl_2$ to precipitate radiobarite $(Ra,Ba)SO_4$. The primary pollution escaping to the Ploučnice system was minimised (terminated) at the end of the 1980s