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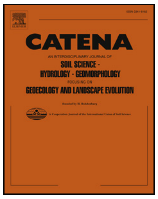

Geochemical mapping in polluted floodplains using in situ X-ray fluorescence analysis, geophysical imaging, and statistics: Surprising complexity of floodplain pollution hotspot

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ABSTRACT

This study is focused on a pollution hotspot in a floodplain impacted by uranium mining in the second half of the 20th century. To image the internal structure of the hotspot, we performed surface gamma activity mapping, in situ X-ray fluorescence spectroscopic analysis (XRF) using a portable instrument and manually obtained sediment cores, and electric resistivity imaging of the shallow subsurface with the help of electric resistivity tomography (ERT) and dipole electromagnetic profiling (DEMP). We used two approaches aimed at deciphering the origin of the pollution hotspot: (i) surface pollution mapping and (ii) identification of the deeper lying lithogenetic units. The description of the floodplain subsurface was supported by optically stimulated luminescence (OSL) dating. The surface mapping approach was found insufficient to visualise the hotspot and understand its origin. We recognised deposition non-linear in time (or temporally independent) of younger overbank fines, including mining pollutants over considerably older channel sediments. Our work documents the value of dense geochemical mapping for documentation of fluvial pollution (accessible by portable XRF) as well as the need to understand the structure of the floodplain subsurface (accessible by electric resistivity imaging) and thereby rationalise the hotspot internal structure.

1. Introduction

Portable (also denoted as mobile, handheld, or field-portable) analytical methods, including in situ analyses (without any sample pretreatment), are increasingly attractive in sedimentary and environmental research (Gałuszka et al., 2015; Horta et al., 2015; Ryan et al., 2017). Regardless of some limitations inherent in that approach, it allows the unprecedentedly dense imaging of spatially complex systems such as abandoned mining sites (Burlakovs et al., 2015; Migaszewski et al., 2015), landfills and abandoned sites (Gutierrez-Gines et al., 2013), urbanised areas (Parsons et al., 2013; Weindorf et al., 2012) and polluted floodplains (Brumbaugh et al., 2013; Hürkamp et al., 2009; Grygar et al., 2010). Over the last decade, portable XRF (X-ray fluorescence) spectrometers have achieved higher quality suitable for geological research and environmental monitoring. They also allow progress in further areas where large analytical datasets are required and/or monotonous fine sediments or soils are studied (Rowe et al., 2012). XRF scanning on split sediment cores is another version of XRF analysis without conventional sample pretreatment (Hennekam and de Lange, 2012; Jones et al., 2012; Löwemark et al., 2011; Peros et al., 2017).

Another emerging method, which has in practice proven its efficiency in saving time for sampling and sample processing, is geophysical imaging using DEMP or ERT. These methods are based on the electrical resistivity of a shallow subsurface, which is a complex function of soil/rock textural properties, surface conductance of clay particles, water saturation, fluid conductance (~salinity), and temperature (Corwin and Lesch, 2005; Endres and Knight, 1993; Revil and Glover, 1998; Rey et al., 2006). Resistivity imaging is particularly attractive for archaeologists searching for buried sites and cultural materials (Conyers et al., 2008; Nowaczinski et al., 2015) and in geomorphology for the localisation and recognition of subsurface structures, especially in larger areas (Schrott and Sass, 2008). The most common targets for geophysical imaging are alluvial fans, permafrost, and landslides (Bichler et al., 2004; Gourry et al., 2003; Hauck and Mühll, 2003; Jiang and Wu, 2016; Klug et al., 2017). Geophysical methods can be used for the localisation of sedimentary bodies whose topographical features are

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masked by a vegetation cover. In our opinion, the power of shallow subsurface imaging is underestimated in current research; only a few connections have been made between geophysical methods and geochemical mapping (Khalil et al., 2013).

This paper reports on the use of portable XRF and resistivity imaging by ERT and DEMP in describing a pollution hotspot in a floodplain of a river with a laterally unstable channel. The thickness of the top polluted strata is spatially quite variable in the target area for reasons that have yet been poorly understood (Hošek, 2015); the hotspot definitely does not resemble a homogeneous "blanket" of polluted overbank fines that might be expected for flat floodplain surfaces. We hypothesise that the observed spatial complexity is in fact quite typical for all pollution hotspots in fluvial systems (Lecce and Pavlowsky, 2014), but is rarely revealed because of insufficiently detailed mapping. The main aim of this paper was to find a more efficient approach to studying floodplains. Portable analytical and geophysical methods have been considerably improved in recent years and now allow the deciphering of pollutant distributions easier and faster than ever before. Nonetheless, it is still necessary to verify the data thus obtained by the examination and analysis of drill cores. We show how portable analytical instruments and resistivity imaging can facilitate research in pollution hotspots and how a multidisciplinary approach can allow the interpretation of results.

2. Study area and methods

2.1. *The Ploučnice River and its pollution history*

The Ploučnice River, a right bank tributary of the Labe (Elbe) River, is 106 km long and drains 1194 km^2 of north Bohemia in the Czech Republic (Fig. 1). In the city of Mimoň (just upstream from the study site, Fig. 1), its subcatchment area is 270 km^2, and its mean annual discharge is 2.6 m^3/s. The source rocks in the catchment of the study site are mainly Cretaceous sandstones, siltstones and marls; a minor proportion of sediments is derived from isolated bodies of Cenozoic volcanic rocks (Majerová et al., 2013).

The Ploučnice valley in the studied area (Fig. 1) has a river slope of 0.6–1‰ and a floodplain width of 100–200 m; the channel actively meanders with occasional channel avulsions (Matys Grygar et al., 2016). The bedrock consists of mature Cretaceous sandstones of the Jizera Formation. The inundation of the studied floodplain is more or less annual; floods are currently mainly caused by summer local precipitation extremes.

The studied area in Boreček, which at first glance might seem to be flat and uniform, shows certain topographic features after closer examination. The Ploučnice River has a laterally unstable channel, as it is embedded in a sandy material. The channel in the Boreček area has exhibited some lateral shifts from the 1840s but not active meandering; as a result of two chute cut-offs two floodplain islands were formed between 1994 and 1999 (Fig. 1B). The target area with the hotspot is approximately 150 m × 100 m; it is bordered by the Ploučnice River on the north, west and south and by an abandoned floodplain and a higher terrace level and older meander remnants on the east.

Several topographic levels (geoforms) can be distinguished on the valley bottom near the study area. The pollution hotspot is situated at an altitude of ca. 266.7–266.9 m a.s.l., which level was denoted as the active floodplain (Fig. 1B). The main forms of this level are the active channel of the Ploučnice River and its side (secondary) channel. These channels are bordered by active point-bars and fluvial levees, whilst farther from the channel the deep-lying distal floodplain is located. These forms are flooded quite frequently because of its lowest altitude; in almost all fieldwork we observed the consequences of recent flooding at that floodplain level such as fresh mud on vegetation and floating debris on the surface. The sandy sediments at depths of ~1.3 m (approximately at the level of the current channel bottom) were dated to the Middle and Late Holocene (Table 3, OSL4 to OSL6). Several shallow depressions can be distinguished in the centre of the hotspot in the DTM (Fig. 1B). The sediment is very fine in the top 50 cm in those lower-altitude areas, with typical Al/Si weight ratios above 0.19 (proxy for sediment size, see Matys Grygar and Popelka, 2016 and references therein). A point-bar, the coarsest sedimentary body in the shallow subsurface of the active floodplain, is located in the north-western part of the hotspot.

In the eastern part of the target area, there is an abandoned, higher floodplain level with a medium altitude of 267–267.5 m a.s.l. (Fig. 2, geoform 5); it is inundated by a 50-year recurrence discharge (Q50). On this floodplain level the remnants of two large paleo-channels could be identified. The OSL samples were taken from the last point-bar of the paleo-channel, thus it reflects the end of the activity of this channel. The dating refers to Late Holocene age (Table 3, OSL1). Between this the Late Holocene floodplain level and the active floodplain stretches the narrow side channel shown in Fig. 2. The deposits near the side channel and in the abandoned floodplain mostly consist of sand and silt with a minor clay fraction.

The highest level of the floodplain is represented by a fluvial terrace (267.6–268.0 m a.s.l.) (Fig. 2, geoform 3) that can be flooded only by discharges higher than Q100. The terrace deposits consist of pebbles, gravel and sand with admixtures of silt.

The Ploučnice River was severely impacted by uranium mining between 1967 and 1996; pollution of the Ploučnice fluvial system followed nearly immediately after the start of mining (Matys Grygar et al., 2014; Slezák, 2000). Approximately $4.1{\cdot}10^6$ t of H_2SO_4 and $3.2{\cdot}10^5$ t of HNO_3 were pumped underground (Hanslík, 2002; Kafka, 2003; Kühn, 1996). The main contaminants were ^{226}Ra (the main gamma emitting radionuclide in the polluted areas) and U; less striking but relevant in terms of amounts were the free acids Zn and Ni (Kafka, 2003). The overflow of acidic leachates from the underground chemical leaching to a nearby underground mine resulted in such large volumes of mine waters that they exceeded the capacity of the waste water treatment technologies available at the beginning of mining. Ra^{2+} ions are soluble in ambient water and would not be retained in the floodplain sediments; however, the waste waters from mining were treated by $BaCl_2$ to convert most ^{226}Ra ions to chemically stable and insoluble radiobarite (Ba,Ra)SO_4, a solid with a large gravimetric density. Former researchers Hanslík (2002), Kühn (1997) and Moucha (1990) stated that a summer storm in 1981 caused a flood and the transport of considerable amounts of particulate radionuclides from the mining area to the Ploučnice River system downstream from the city of Mimoň.

The pollution from the mining area ended in the second half of the 1980s when hydrodynamic barriers (series of drill cores controlling the underground movements of fluids) stopped overflows of the solutions from the underground leaching fields and a sewage disposal plant was built and placed in operation. Soon after those measures, the decision was made to reduce uranium mining (Kafka, 2003; Slezák, 2000). Even then, continuous floodplain reworking has spread secondary pollution farther downstream and from the channel belt more towards the floodplain (Matys Grygar et al., 2014). Analogously, the channel bank erosion in unpolluted upstream reaches has brought less polluted sediments over the most polluted places such as the Boreček hotspot (Hošek, 2015; Matys Grygar et al., 2014).

The current pollution status of the floodplain (concentration, spatial patterns) is insufficiently documented. The low-resolution airborne gamma spectrometry survey (with a 250-m spatial grid) performed in the 1990s (Gnojek et al., 2005) revealed several pollution hotspots in the Ploučnice floodplain between the cities of Mimoň and Česká Lípa (Fig. 1A). Floodplain sediments in Boreček were cored in one hotspot and analysed for risk elements in the early 1990s (Kühn, 1996) and Ploučnice channel sediments were analysed 10 years later (Hrdoušek, 2005; Kolář, 2004); all those studies showed considerable pollution in spatially complex patterns.