



Geochemical background in polluted river sediments: How to separate the effects of sediment provenance and grain size with statistical rigour?



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ARTICLE INFO

Article history:

Received 21 December 2014

Received in revised form 7 July 2015

Accepted 8 July 2015

Available online 27 August 2015

Keywords:

Anthropogenic contamination

Geochemical background

Fluvial sediments

Geochemistry

Enrichment factors

Log-ratio statistics

ABSTRACT

Defining anomalies from geochemical background is a principal step in anthropogenic contamination studies and environmental risk assessment, and yet the complexity of processes affecting the composition of sediments makes this task extremely difficult. We address grain size and sediment provenance as two parameters influencing the geochemistry of contaminated fluvial sediments. We analysed 576 sediment samples from channels, floodplains, oxbow lakes, and dam reservoirs of the Morava River, Czech Republic. The geochemical data are compared with grain size and statistically processed using primary observations and log-ratios. An effective way to remove the grain size and provenance effect is to use enrichment factors calculated from least trimmed squares regression of Pb, Zn, Cu and Cr data vs. normalizing Ti, which is sensitive to grain size. Based on empirical testing, titanium proved more suitable for normalizing than did Al and Rb. Isometric log-ratio coordinates of the Pb, Zn, Cu and Cr data show a strong misfit with those defined by the enrichment factors. A log-ratio approach considering just subcompositions of elements with similar geochemical behaviour provides much better results.

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1. Introduction

Separating lithogenic background concentrations from anthropogenic impact by toxic metals constitutes a key issue in contamination studies and environmental risk assessments. Numerous ways of defining the geochemical baselines are employed in contamination studies of both soils (Jarva et al., 2010; Reimann et al., 2012; Wang et al., 2011) and sediments (Castelle et al., 2007; Gustavsson et al., 2012; Rantitsch, 2000; Vijver et al., 2008). Perhaps the simplest way to calculate enrichment in a target element is by normalizing to the global average shale or the average upper crustal concentrations (Kaushik et al., 2009; Wu et al., 2013). Normalizing toxic metals to typical “lithogenic” elements (Al or Rb) and applying such statistical procedures as multiple linear regression and factor analysis represent another common approach (Grosbois et al., 2012; Sajn et al., 2011). Other studies utilize the concept of a geochemical “baseline” derived from element concentrations from pre-industrial deposits, usually backed up by dating methods (Matys Grygar et al., 2012; Nováková et al., 2013; Vijver et al., 2008). However, this approach often suffers from subjective definition of what is considered to be the pre-industrial concentration and what is already contaminated. It has been shown, for example, that even the pre-industrial sediments can be

depleted or enriched in the target elements owing to very early diagenesis (Matys Grygar et al., 2013).

Many of these studies are based on classical statistical methods, in which outliers can have strong effect on the calculation of key statistical parameters, which in turn constitute the basis for background definition (e.g., median and regression equations in univariate and bivariate statistics, respectively). In order to smooth the influence of potential outliers on these estimates, robust statistical methods are increasingly applied in detection of outliers in various geochemical case studies (Carranza, 2010; Montero-Serrano et al., 2010; Rantitsch, 2007). In addition, the statistical processing of geochemical data is further complicated by their closed nature and possible spurious correlation between element concentrations. The log-ratio approach utilizing logarithms of element concentrations or their aggregations is becoming widely applied to overcome the closed nature of compositional data in geosciences (Pawłowsky-Glahn and Buccianti, 2011). Although this approach seems to be applicable in a range of real-world problems in geochemical mapping (Filzmoser et al., 2012; Martín-Fernández et al., 2012; Reimann et al., 2012), to our knowledge general log-ratio approach to background definition has not yet been defined.

The geochemistry of sediments is known to be strongly affected by the chemical composition of their source rocks (i.e., by provenance), which may increase even the background concentrations of toxic elements such as Cr, Ni and V (Amorosi and Sammartino, 2007; Arias et al., 2012; Swennen et al., 1998). Moreover, grain size variability, which is inherent to fluvial sedimentation in both natural and regulated

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river systems (e.g., Collinson, 1996; Hesselink et al., 2003; Miall, 1996), can account for up to 70% of the variation in the chemistry of river sediments, including both trace elements and potentially toxic elements (Sageman and Lyons, 2005; Tebbens et al., 2000). The majority of toxic metals and organic pollutants are bound to fine-grained solid particles as clay minerals and organic matter, often in the submicron size range (Förstner, 2004; Förstner and Salomons, 1980). Vertical grain size variations in sedimentary archives have proven to have strong influence on the concentrations of major and trace elements, even when normalized to lithogenic Al (Bábek et al., 2011; Sedláček et al., 2013). This contributes to even greater uncertainty about background concentration and anthropogenic impact, especially in moderately contaminated sediments (Matys Grygar et al., 2013).

In fluvial settings, which often are densely populated, a complex interplay of natural and anthropogenic processes (cf. Hudson Edwards et al., 1997) produces a wide range of depositional environments with a broad variety of sediment products. These sediments are sorted by grain size, mineral composition, organic content, chemistry of pore water, and many other factors which affect their primary chemical composition and, therefore, their geochemical baselines. The Morava River, located in the eastern Czech Republic, has a medium-size, relatively densely populated catchment which is affected by anthropogenic pollution (Bábek et al., 2008; Grygar et al., 2010; Hilscherová et al., 2007; Nováková et al., 2013).

The aim of this paper is to make insight into the effects of grain size/depositional environment and sediment provenance in defining background concentrations of toxic elements using various statistical methods. We discuss various depositional settings of the Morava River catchment which include river channels, floodplains, dam reservoirs, and natural and artificial abandoned meanders using shallow sediment cores. Stratigraphy and lithology of the core samples, including grain-size analyses, are compared with their geochemical compositions focusing upon major and trace elements, and including toxic metals (Pb, Zn, Cu and Cr). We compare various methods of geochemical background definition including simple element concentrations, element ratios and enrichment factors, and use various statistical tools including classical statistics, robust statistical methods and log-ratio analysis. Our aim is to provide insight into the definition of geochemical baseline levels and enrichment factors (EFs) and contribute to the environmental risk assessment of complex depositional fluvial environments.

2. Geographic settings

The Morava River, a left-hand tributary of the Danube River, is situated in the eastern part of the Czech Republic (Fig. 1). The river runs approximately in the North–South direction with a total length of 284 km. Its drainage area is 20,692.4 km² (within the Czech Republic) and the mean annual river discharge is nearly 110 m³ s⁻¹ close to its confluence with the Danube. Its most important tributaries include the Bečva, Dřevnice and Dyje (Thaya) rivers, the former two draining industrial areas with major sources of anthropogenic pollution. These main sources include coal combustion and road traffic as diffuse sources of Pb and Zn, agriculture, local chemical and shoe production industry as point sources of Cr, Cd and other elements and municipal sewage waters as point sources of wide spectrum of pollutants.

The Morava River is a meandering river forming extensive floodplains with vertically accreted floodplain deposits and soils (Grygar et al., 2010; Havlíček, 1994; Kadlec et al., 2009; Matys Grygar et al., 2011). Along the greater part of its course, the river was embanked during the 20th century. The main channel was shortened by about 40%, thereby giving rise to more than 180 artificial oxbow lakes which act as traps for fine-grained sediments (Bábek et al., 2008, 2011). Although the Morava River itself is not dammed, several water reservoirs have been built on its tributaries. The most important tributary reservoirs include Nové Mlýny reservoir (33.9 km² of inundated area) on the Dyje River, Brno-Kníničky (2.33 km²) on the Svratka River, and Plumlov reservoir (0.68 km²) on

the Hloučela River. The reservoirs act as traps for mostly fine-grained sediment (Sedláček et al., 2013). The largest sources of anthropogenic pollution are industrial cities (mainly from chemical and mechanical engineering, leather processing industry, and metallurgy) located along the Morava River and its tributaries, in particular Brno (population 380,000), Olomouc (102,000), Zlín (76,000), Přerov (45,000), Uherské Hradiště (25,000), and Otrokovice (18,000).

3. Material and methods

Several depositional environments within the catchment were sampled by shallow (~0.6 to ~2.6 m deep) drill cores at 15 sites (Fig. 1). Sampling included river channels (three drill cores: KV1, OT4 and J2), floodplains (three cores: TN4, TN5 and TN6), abandoned meanders (two cores: CH4 from the Kurfürst meander near Olomouc and CRT2 from the Čert'ák meander near Uherské Hradiště), and dammed reservoirs (seven cores: NM1, NM4 and NM8 from the Nové Mlýny reservoir; BP1, BP2 and BP5 from the Brno reservoir; P2 from the Plumlov dam). River channel cores were taken from long, narrow point bars of regulated parts of river channels. Floodplain cores were taken from floodplain forests at ~300 m (TN6), ~550 m (TN4) and ~1250 m (TN5) distance from the major channel, which are inundated during Q₂₀ floods (Brázdil et al., 2011). Meander cores were taken in proximal parts of abandoned meanders, within 200 m distance from the main channel. Reservoir cores were taken from various parts of the reservoirs, close to the dam (P2, BP5) or in upstream parts of the reservoirs (BP1, BP2, NM1) (Fig. 1).

The cores were drilled using an Eijkelkamp percussion drilling set (the Netherlands) (channels, floodplains) and a Multisampler piston-core sampler (Eijkelkamp) (abandoned meanders, reservoirs). The cores were described and sampled with a 1–5 cm vertical interval depending on the required stratigraphic resolution: finely laminated dam reservoir sediments were sampled with higher resolution (1–2 cm) while homogeneous, bioturbated floodplain sediments were sampled with lower resolution (up to 5 cm). The samples were dried at 50 °C, stored in plastic bags, then further prepared for energy-dispersive X-ray fluorescence (EDXRF) analysis (576 samples). Grain size of 70 samples (<5 g) was analysed by laser diffraction in wet dispersion using a Fritsch Analysette 22 MicroTec plus laser particle sizer with measuring range from 0.08 to 2000 µm (102 channels). The large measuring range is obtained by utilizing two lasers with different wavelengths: a green laser for the small particle range and an IR laser for measuring larger particles. No correction for potential underestimation of the clay fraction due to non-sphericity of measured particles (cf. Konert and Vandenberghe, 1997) was performed. We use the cumulative sum of clay and silt fraction (<62.5 µm) as the main grain size proxy while the laser size overestimation affects much smaller grains (between 2 and 8 µm; Konert and Vandenberghe, 1997). Partial grain size shifts, if any, affect only a small part of the sum. Grain size distribution of an additional 18 samples was analysed by wet sieving using a Fritsch Analysette vibration sieve and a set of calibrated sieves from 32 to 8000 µm. For each wet-sieving analysis, several juxtaposed samples were pooled in order to obtain sufficient sediment volume. Grain size classes and subclasses of the Wenworth scale (clay, silt, sand and gravel) are used throughout this paper.

EDXRF analysis of powdered sediments was performed using a PANalytical MiniPal 4.0 spectrometer (PANalytical, the Netherlands) with Rh lamp and Peltier-cooled Si PIN detector. Powdered samples were stored in plastic cells sealed by Mylar foil with ~25 mm diameter. Fifteen elements were analysed for each sample: Al, Ca, Cu, Fe, K, Mn, Ni, P, Pb, Rb, Si, Sr, Ti, Zn and Zr. Signals of Al and Si were acquired at 4 kV/200 µA with a Kapton filter under He flush (99.996% purity); Zn, Mn and Fe at 20 kV/100 µA with an Al filter in air; and Rb and Pb at 30 kV/200 µA with an Ag filter in air (Matys Grygar et al., 2012). Total analysis time was set at 800 s per sample. EDXRF analytical results for selected elements (in units of counts per second [cps]) were calibrated

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