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Revisiting geochemical methods of distinguishing natural concentrations and pollution by risk elements in fluvial sediments

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ABSTRACT

This paper provides an overview of the natural variability of the element composition of fluvial sediments, paying particular attention to As, Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Ti, and Zn. The primary factors controlling the sediment composition are source rocks in the river catchment, the extent of their weathering, the sorting of so-formed solids during transport through the catchment, and their chemical transformations, in particular reductive/oxidative-driven processes, particularly affecting the finest particles in the fluvial systems. Those factors result in grain-size control as the major source of variation of the sediment's chemical composition; they also change element patterns (ratios, associations) in the finest sediment components compared to Earth's upper crust. Grain-size control of element composition (the grain-size effect) is suppressed by geochemical normalization and is best treated through geochemical background functions applied to analyses of bulk samples. Robust regression should be preferred for inter-element relationships in fluvial sediments. Conversely, the evaluation of element concentrations in sediments neglecting grain size or using particle-size separation (e.g., sieving to submillimetre size fractions) to separate only a minor weight fraction of the sediment should be avoided in research. Improper data processing and a lack of respect for natural variability may prevent the recognition of anthropogenic pollution. The use of inappropriate statistic tools in this task, such as the mean $\pm 2\sigma$,boxplots, and ordinary least-squares' regression, is primarily hindered by the lack of a Gaussian distribution of element concentrations in real collections of fluvial sediments and neglect of a suite of natural factors inherent to fluvial sediments. The applicability of geochemical background concepts is discussed at three levels of approaching reality: (1) a normalization of target element concentrations M using reference element M_{REF}, M/M_{REF}, where M_{REF} is typically Al, Fe, Ti, or Rb; (2) a comparison of normalized concentrations with normalized mean upper crustal concentrations by double normalization producing enrichment factors, $EF = (M/M_{REF})_{sample}/(M/M_{REF})_{UCC}$, where UCC refers to the mean composition of the upper continental crust; and (3) empirical geochemical background functions predicting background concentration M_{GB} and producing local enrichment factor $LEF = M/M_{GB}$. The latter of these three approaches is recommended as it performs well also in immature sediments (unlike double normalization with Al as M_{REF}) and considers the specificity of individual river catchments. The empirical background functions (linear, non-linear, with variable intercepts) derived from unpolluted and post-depositionally unaffected sediments and LEF are effective in avoiding the grain-size bias of enrichment factors typical of the commonest method of double normalization with Al as M_{REF}. An overview is provided regarding exogenic processes that produce element patterns different from those of the catchment rocks and thus biasing EF obtained by double normalization. The processes' consequences for fine chemical weathering products include the following: (1) the natural enrichment of elements, such as Cd, Cu, Fe, Mn, Pb, and Zn in fine fluvial sediments as compared to parent rocks and (2) the formation or strengthening of the risk elements' association with Fe. We hypothesize that both phenomena result from the preferential chemical weathering of felsic minerals and biogeochemical processes in catchment and fluvial systems. The list of risk elements naturally enriched in the finest fluvial sediments is not complete and probably also include As, Bi, Hg, and Sb; the phenomena responsible for that deserve further research.

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1. Introduction: human impact and natural variability

Human impact on element fluxes in river systems has been addressed in a range of scales, extending from global estimates (Martin and Meybeck, 1979; Viers et al., 2009) to numerous case studies in individual rivers or river reaches. Unless the human-induced element concentrations or fluxes overwhelm the natural ones—which is fortunately rather exceptional and typically limited to small catchments involving ore mining and smelting—it remains a challenge to distinguish between the human and natural portions of risk elements in sediments and soils. The risk elements addressed in this review are those conventionally denoted “heavy metals” (typically Cd, Cu, Hg, Pb, Zn) and other elements potentially harmful in aquatic environment such as As. The assignment of element enrichment to human impact has been a topic of recent, vivid discussions, e.g., in the cases of Hg enrichment in soils and sediments in Amazonia (Lechler et al., 2000) and sediments of Arctic lakes (Goodsite et al., 2013) and in the cases of Pb and some further elements in forest humus (Reimann et al., 2008a, 2008b; Sucharová et al., 2012). In most catchments without metal mining and heavy industry and at regional to global scales, the anthropogenic contribution to risk-element concentrations is comparable to natural variability (Matys Grygar et al., 2011; Matys Grygar et al., 2013; Guo and Yang, 2016), except in the case of rivers bordered by a nearly continuous chain of persistent pollution sources, such as in some Central and Western European rivers (Macklin et al., 1994; Grosbois et al., 2012). Consequently, knowledge of natural concentrations, i.e., the hypothetical composition of any unpolluted sediment sample, is of crucial importance. The natural variability of Earth's surface has been addressed in studies on average composition of Earth's crust (e.g., Hu and Gao, 2008; Rudnick and Gao, 2003), soil and sediment geochemical mapping (e.g., De Vos et al., 2006; Reimann and de Caritat, 1998; Reimann et al., 2012), element fluxes through river systems (Bouchez et al., 2011; Garzanti et al., 2011; Martin and Meybeck, 1979; Singh et al., 2005; Viers et al., 2009; Vital and Stattegger, 2000), and sediment provenance studies (Koiter et al., 2013). In local and regional case studies, it is also important to consider the actual geology/geochemistry of parent rocks (Amorosi and Sammartino, 2007; Tapia et al., 2012; Viers et al., 2009); on continental scales, long-term history and climate must be taken into account (Reimann et al., 2012). Considerable efforts to understand the chemical variability of Earth's surface, including fluvial sediments, have recently resulted in valuable analytical datasets that can now be summarized and interpreted. We are persuaded that the only way to distinguish anthropogenic impact on sediment composition is to understand its natural variability and consider fluvial processes; regardless of how trivial those requirements seem, in some studies aimed at identifying pollution, they have not been implemented (Pavlović et al., 2016 and discussion in Matys Grygar, 2016). Fluvial sediment pollution is sometimes evaluated without consideration of local or global natural concentrations and sediment lithology (Navrátil et al., 2008; Comero et al., 2014). One goal of this review is to summarize the knowledge essential to improve that state.

The terms “natural background” and “background” are of crucial importance to this paper. The word background is commonly used with a scale of adjectives that have produced numerous definitions listed by Reimann and Garrett (2005) and Gałuszka (2007). Common adjectives used with background in sediments and soils are “geochemical” or “geogenic”; the synonym “baseline” has also been used. We use the term background to mean the concentration of an element in any sediment sample as if there was no anthropogenic pollution at play; it corresponds to definition No. 8 in the review by Reimann and Garrett (2005). An inherent part of such a simple definition is that it did not provide hints about the phenomena controlling the element composition of sediments. This paper is an overview of those controlling mechanisms in the fluvial domain. Our overview is based on datasets with sediment composition of several non-polluted or marginally polluted fluvial systems described in Appendix A.

2. Geochemical background functions

2.1. Geochemical treatment of grain-size and dilution effects

The settling of particles from flowing water, i.e., the distribution of solid particles between suspended load and bedload (Singh et al., 2005; Vital and Stattegger, 2000) and the variable lithology of deposits in individual fluvial environments (Bábek et al., 2015) are the primary factors driving the variability of risk-element concentrations in fluvial sediments. In at least partially chemically weathered (moderately mature) sediments, the concentrations of all elements vary with the actual sediment grain size (Borovec, 2000; Bouchez et al., 2011; Garzanti et al., 2011; Zhou et al., 2015) (Fig. 1). The Al/Si ratio in Fig. 1 is a proxy for sediment grain size (Bábek et al., 2015; Bouchez et al., 2011; Grygar et al., 2010; Limmer et al., 2012). Thus, there is no “conservative”