Sediment origin and dispersal dynamics in the Lower Danube Basin

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1 Introduction

Within mining-affected river systems, identifying the sources of contaminant metals is a prerequisite for developing effective catchment management and remediation strategies. This is of particular importance in large river catchments, where metal inputs are generally received from a variety of different sources (Gelinas & Schmit 1997), and particularly where the catchment includes more than one country. The Danube River Basin represents Europe's second largest international drainage basin, covering an area of 817,000 km^2 and contains a large number of base and precious metal deposits (Heinrich & Neubauer 2002) that have been exploited since pre-Roman Times (Rice et al. 2007). Previous work in the Lower Danube system has identified the environmental impacts associated with historical and contemporary mining activity in Romania (Bird et al. 2005; Bird et al. 2008), Bulgaria (Bird et al. 2010), Serbia (Korac & Kamberovic 2006) and Hungary (Odor et al. 1998); however, there has been little or no attempt to establish and quantify patterns of contaminant-metal dispersal within the wider lower Danube Basin (Figure 1).

It has been noted by a number of studies that total metal concentrations alone are insufficient when attempting to document dispersal and deposition of contaminants (e.g. Ettler et al. 2004). In an attempt to overcome this problem, Pb isotopes have become increasingly used as geochemical tracers in environmental studies (Komárek et al. 2008); however, relatively few have sought to apply their use to the identifying and modelling patterns of contaminant dispersal in fluvial sediments. Four Pb isotopes can be utilized as geochemical tracers: ^{204}Pb, which is a stable, and the long-lived radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb, which are the daughter products of the decay of ^{238}U, ^{235}U and ^{132}Th, respectively. This study utilizes Pb isotope and multi-element geochemical data to assess the fluvial dispersal of sediment-associated metals within tributary catchments of the River Danube and within the River Danube itself.

2 Materials and methods

River channel sediment samples were collected from the River Danube and Romanian and Bulgarian tributaries at low river stage from exposed bar surfaces. Samples of mining and smelting waste were also collected from spoil tips, waste dumps and tailings ponds. Sub-samples of the <63 µm fraction were digested in concentrated HNO_3 at 100°C for 1 hour and As, Cd, Cu, Pb and Zn concentrations determined using ICP-MS. Lead isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb were determined in samples using a Thermo-Finnigan Element2 Magnetic Sector ICP-MS. Analytical accuracy versus the NIST981 standard was 0.28 % ($^{206/204}Pb$), 0.17 % ($^{207/206}Pb$) and 0.44 % ($^{208/206}Pb$).

3 Results and discussion

Metal and As levels in Hungarian, Bulgarian and Romanian tributaries and in the Lower Danube River itself have been reported by Bird et al. (2003; 2010; 2005). It has been found that most significant and spatially-extensive metal enrichment occurs in river sediments, with enrichment patterns mirroring major mineralization types. For example, Cu mineralization in the Timok (Serbia) and Panagyurishte (Bulgaria) ore

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districts is reflected by enrichment of Cu in the Timok (310-500 mg kg^{-1}) and Iskar (17-5500 mg kg^{-1}) catchments and in the River Danube (8-280 mg kg^{-1}).

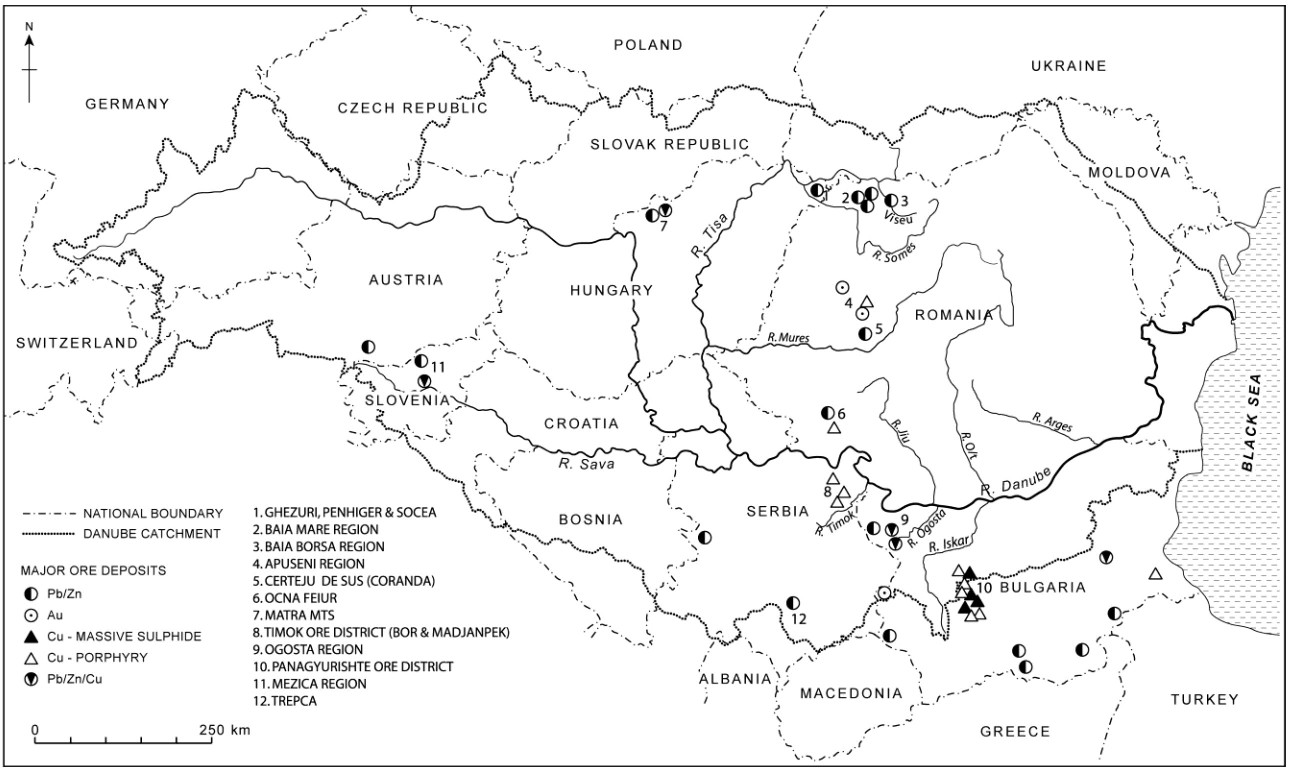

Figure 1. *Map of the Danube drainage basin showing major rivers and locations of metal ore deposits.*

Given that Pb isotopic signatures in mineral deposits will vary spatially due to differing ages of mineralization and geochemical composition, it is possible to differentiate between ore bodies within the Lower Danube Basin based upon bivariate relationships between $^{208/204}$Pb and $^{206/204}$Pb isotope ratios (Figure 2). Furthermore it is possible to differentiate between ore-bodies and potential contaminant sources can be seen within a single country, for example, the isotopic signatures within the West Balkan Metallogenic Zone of NW Bulgaria and the Elatsite deposit within the Panagyurishte ore district, show statistically-significant ($\alpha = 0.05$) isotopic variation, despite being just 60 km apart.

The sediment-metal load of mining-affected river systems will therefore reflect inputs from natural bedrock weathering and key anthropogenic sources such as mined ore deposits, which commonly have a different Pb isotopic signature from the surrounding bedrock. Similar to the Pb isotopic signatures for ore deposits, it is also possible to differentiate between the isotopic signatures determined in river channel sediments of mining-affected river catchments within the Lower Danube catchment (Figure 3). For example, the signatures for isotopes determined in Romanian ore deposits, are mirrored in river channel sediments, with those for the River Someş catchment, which drains the Baia Mare region, exhibiting lower $^{208/206}$Pb (2.0662-2.0740) and $^{207/206}$Pb (0.8323-0.8378) ratios than other Romanian catchments.

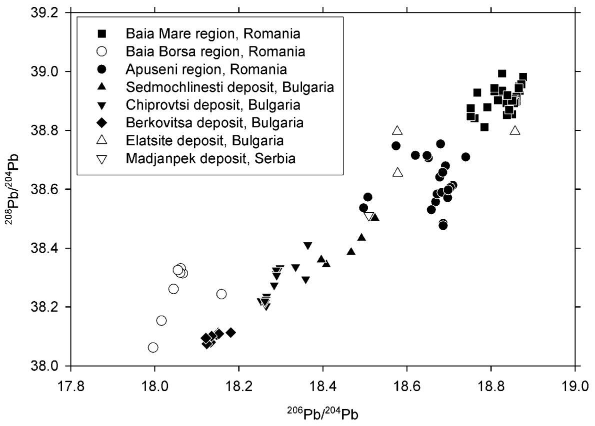

Figure 2. *Pb isotope signatures for ore deposits*

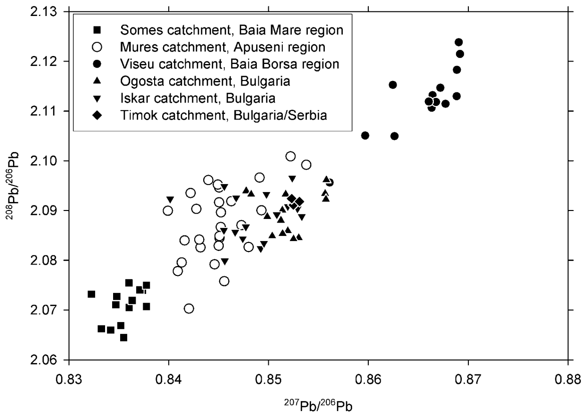

Figure 3. *Pb isotope signatures for river sediments*

In small river catchments (10 – 100 km^2), with a limited number of potential contaminant sources, binary mixing models can be used to quantify Pb contributions to river sediments, based upon Pb isotope signatures in river sediments forming a strong linear trend between two end-members, which are taken to be the primary Pb sources. However, given the greater number of potential Pb sources within larger river systems, such as the Lower Danube Basin, Pb isotopic signatures often do not form strong linear trends. For example r^2 values for bivariate $^{207/206}$Pb and $^{208/206}$Pb relationships in river sediments from the Rivers Ogosta, Iskar and Danube are 0.28, 0.49 and 0.54, respectively.

In order to determine sediment provenance in the lower Danube Basin, a composite fingerprinting technique was used to discriminate between sediment sources using multi-element geochemical data and Pb isotopic signatures as diagnostic properties (cf Rowan et al. 2000). Relative sediment contributions from source groups were quantified using a multivariate mixing model (cf Walling et al. 1999). The composite fingerprinting approach and multivariate mixing model was employed in two stages. Firstly within mining-affected tributary catchments of the Lower River Danube (notably the Ogosta and Iskar), to identify key contaminant sources (Figure 4), and secondly using tributary catchments as source groups in order to quantify their relative contributions of contaminant metals to the River Danube (Figure 5).

Within mining-affected catchments, the use of a multivariate mixing model allows key sediment sources to be identified, which may in turn assist in the interpretation of spatial patterns in metal concentrations. For example in the Upper River Ogosta, sediments represent an even mix of material from the Chiprovtsi and Dalgodelska regions, both of which contain a legacy of historic metal mining and are supplying sediment that is particularly enriched in As (Figure 4). With increasing distance downstream the relative importance of mining-affected sediment sources reduces, however at its confluence with the River Danube, approximately 47 % of channel sediment in the River Ogosta is sourced from mining-affected tributaries within the Ogosta catchment. With respect to sediment delivery to the River Danube, data from the mixing model indicate the notable influence of tributary streams upon sediment geochemistry in the River Danube within relatively short distances downstream of Danube/tributary confluences (Figure 5). Whilst a majority of sediment in the Lower Danube is believed to originate from upstream of the Timok/Danube confluence, relative contributions from Romanian and Bulgarian tributaries account for 2-27 % of sediment load, with peak contributions generally occurring within 20 km river confluences; followed by a subsequent downstream reduction due to mixing and physical dilution with inputs from other tributaries (Figure 5). In terms of sediment-bound metal levels in the Lower Danube, the mixing model data provide further evidence of the importance of mining-affected tributaries in Bulgaria.

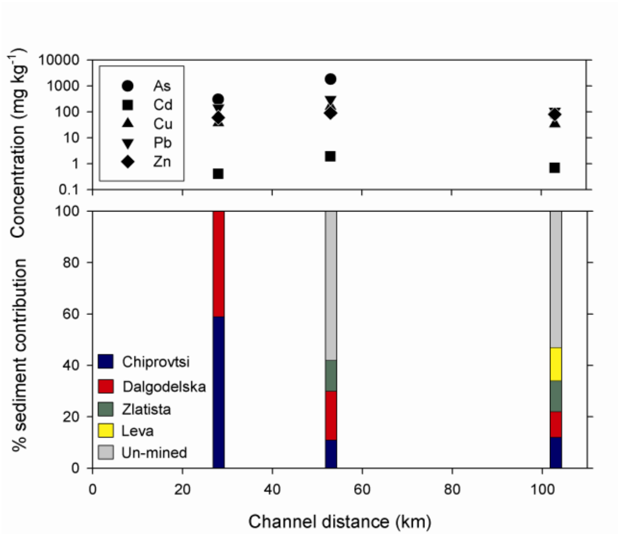

__Figure 4.__ Sediment-bound metal and As levels in the River Ogosta plotted with percentage sediment contributions from mined and non-mined tributaries. Channel distance is calculated from the source of the River Ogosta.

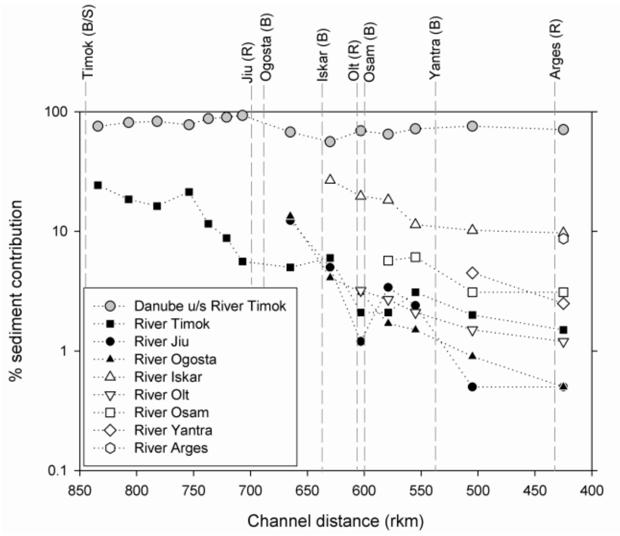

__Figure 5.__ Relationships between distance in Danube river kilometres (rkm) along the Lower Danube River and percentage sediment contributions from Romanian (R), Bulgarian (B) and Serbian (S) tributary catchments.

For example, sediment delivered from the River Timok, which accounts for 12-20 % of the sediment supply to the River Danube between 834 and 737 rkm, contemporaneous with the locations of Cu enrichment in Danubian River sediment (250-280 mg kg^{-1}). Sediment delivered by the River Timok is enriched in Cu due to Cu mining and metallurgy at Bor in Eastern Serbia.

4 Floodplain records of contamination

Floodplain sediments represent an important sink for sediment-associated contaminant-metals that are dispersed within fluvial systems. Vertically-accreted sedimentary records provide the opportunity to establish a record of metal dispersal and deposition that can be used to reconstruct a contamination history for the Lower Danube drainage basin. Establishing patterns of contaminant dispersal in a large multi-national drainage basin such as the Danube, which has a long history of mining activity, is key to establishing: 1) the magnitude of contaminant-metal loading to alluvial sediment stores, 2) temporal changes in the origin of sediment-associated metal dispersal, and 3) the potential implications for remobilization of metals within alluvial deposits under changing flood frequency and magnitude.

Floodplain sediment cores collected from the Romanian bank of the Lower Danube River indicate that highest metal levels occur within the upper 1 m of the sediment profile. XRF intensity values determined through ITRAX core scanning of 4-5m long floodplain cores (Figure 6) indicate peak Cu and Zn levels in the upper 70 cm of the Danube floodplain. Concentrations of Cu (63-130 mg kg^{-1}), Pb (30-50 mg kg^{-1}) and Zn (60-115 mg kg^{-1}) in the upper 70 cm, are 2-4 times greater than those at lower depths (Figure 7), but are generally no higher than those measured in contemporary river channel sediments. Preliminary Pb isotope analysis indicates that, in addition to lower metal levels, floodplain sediment at depth may have lower $^{207/206}$Pb ratios, which are potentially indicative of a different Pb origin to those in more contemporary sediments. Further work is required to establish a chronology for the floodplain sediments and to investigate down-profile variations in Pb isotope signatures.

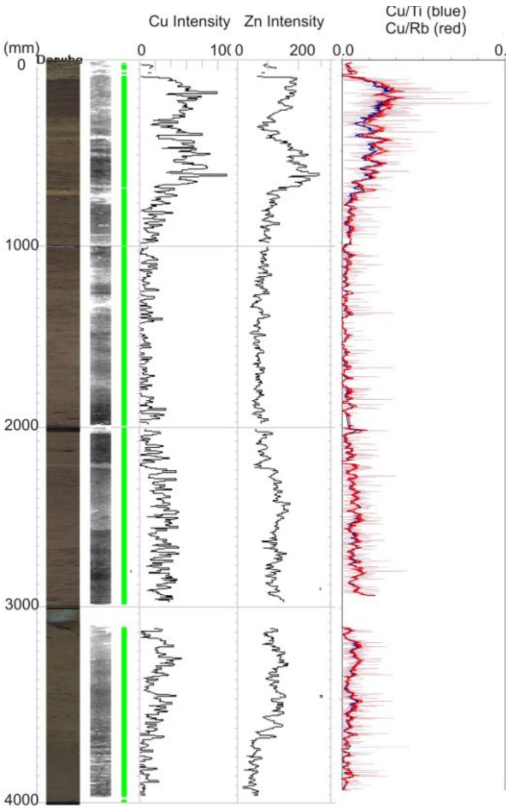

Figure 6. *ITRAX XRF profiles for Cu and Zn intensities and Cu/Ti and Cu/Rb ratios in a floodplain core from the Danube floodplain at Giurgui, Romania*

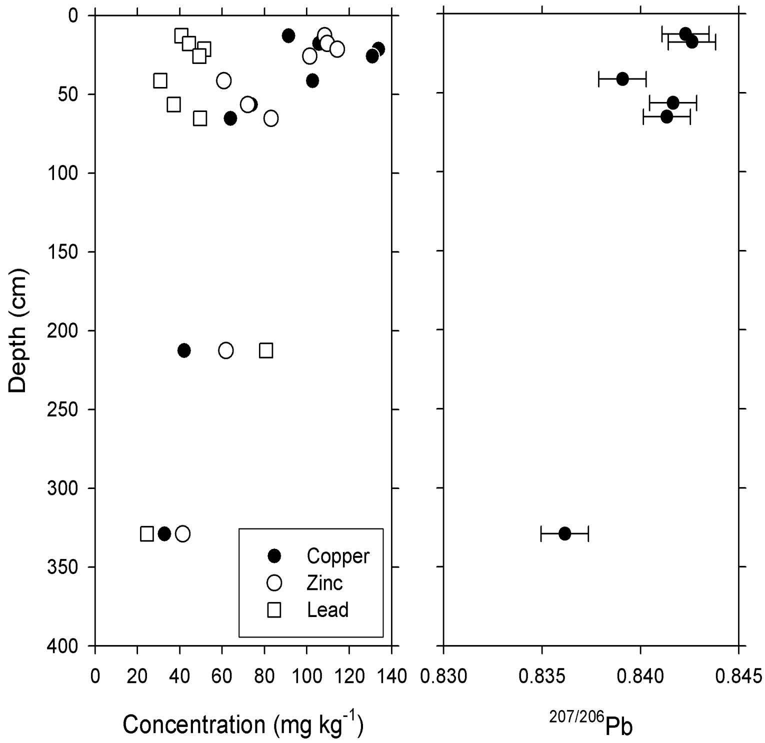

Figure 7. *Cu, Pb and Zn concentrations and $^{207/206}$Pb isotope ratios in a floodplain core from the Danube floodplain at Giurgui, Romania.*

5 Conclusions and implications for catchment management

Collation of Pb isotope data determined for metal ore deposits in the Lower Danube drainage basin, notably Bulgaria, Romania and Serbia indicate that definable differences in isotopic signatures occur for between a number of mineralised regions, both within and between countries. Furthermore, it has been possible to characterize river catchments within the Lower Danube Basin based upon bivariate relationships between Pb isotope ratios. Within mining-affected river catchments, Pb isotopic data collected for river channel sediments and mine and metallurgical waste have identified tailings, AMD and smelter waste as being key point sources of Pb and other contaminant metals to the metal load of rivers within the Lower Danube Basin.

The use of Pb isotope data in conjunction with a multivariate mixing model allows key contaminant sources within mining-affected river catchments to be identified, which may in turn inform remediation and management practices. The need to develop effective catchment management techniques is increasingly apparent given the implementation of the EU Water Framework Directive (EU WFD), which seeks to take a river basin-scale, ecologically-based approach to safeguarding water quality and protecting and improving aquatic ecosystems.

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