Geochemical monitoring of suspended sediment transport in a mercury-mining impacted fluvial system

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INTRODUCTION

Asturias (northern Spain) has a long legacy of mercury (Hg) mining (Luque Cabal and Gutiérrez Claverol, 2006; Ordóñez et al., 2013), which significantly impacted surrounding environments (Gallego et al., 2015; Loredo et al., 2006). Abandoned Hg mines such as El Terronal and La Peña–El Terronal left waste materials rich in Hg and arsenic (As) (Loredo et al., 2005; Rumayor et al., 2017), posing potential risks for mobility and dispersion into surface waters and sediments. Studies in the region have shown extremely elevated concentrations of As and Hg in mining wastes and fluvial sediments, often many times above natural background levels (Gallego et al., 2015). Although bed sediment surveys reveal contaminant enrichment downstream of mining sites (González-Fernández et al., 2018), they do not fully capture whether contaminant inputs remain active or how they are partitioned among sediment particle sizes. Since mobility and bioavailability of Hg and As depend strongly on particle characteristics, it is essential to investigate their distribution in suspended particulate matter under natural hydrological conditions.

MATERIALS AND METHODS

Study Area

The field study focused on the San Tirso River, a tributary of the Caudal River in Central Asturias (NE of Mieres, northern Spain) (Fig. 1a), where historic Hg extraction left a legacy of contaminated waste and altered geochemistry. Surface runoff, intensified by extreme weather events associated with climate change, facilitates the remobilization of contaminated sediments and influences downstream transport.

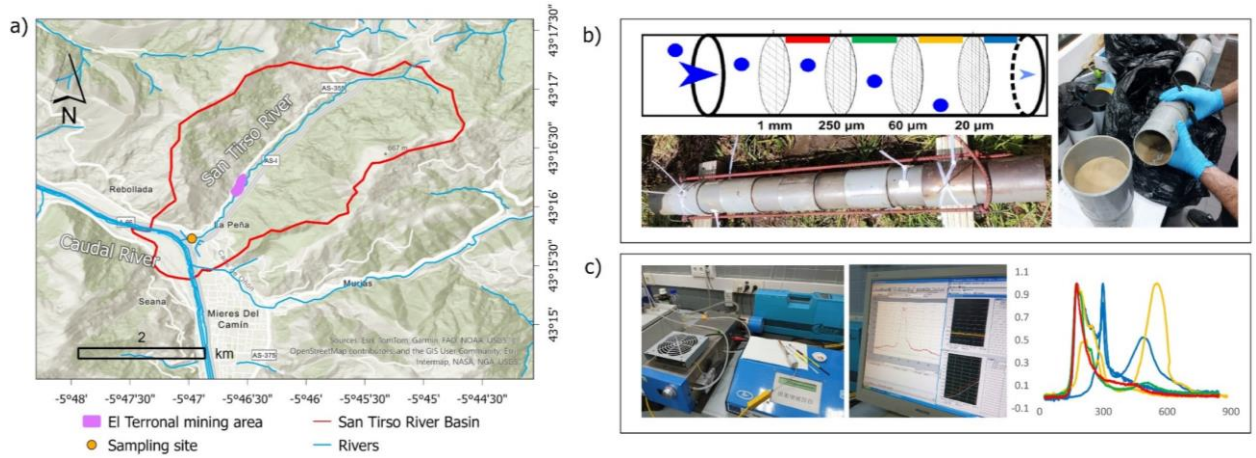

Fig 1*. (a) Location map of the study area; (b) sediment sampling mechanism; (c) mercury speciation process. Colors represent particle-size fractions (µm): red (250-1000), green (60-250), yellow (20-60), and blue (<20).*

Sediment Sampling and Analyses

A GEACOS (Granulometric passive capture of dissolved organic matter & sediment) sediment trap was used to study suspended particulate matter (Fig. 1b). The device, consisting of a modular structure with sieves of different mesh sizes, was installed on the riverbed for one month, retaining sediments in four particle-size fractions (250-1000, 60-250, 20-60, and <20 μm). Samples were air-dried and chemically analyzed. Concentrations of As and Hg were determined after acid digestion using ICP-MS and AMA, respectively. Hg speciation was performed via thermal programmed desorption (Hg-TPD) (Fig. 1c).

RESULTS AND DISCUSSION

As expected, the highest concentrations of Hg were found in the smallest particle size fraction (<20 μm). This trend was also observed with As where a strong correlation between As and Hg concentrations ($R^2 = 0.979$) indicates that these elements are transported together within the river system. On the other hand, mercury speciation analyses revealed a different distribution of Hg species depending on the particle-size (Fig. 1c). In general, it was observed that the coarse fractions (60-250 and 250-1000 μm) exhibited a single desorption band between 150 and 300°C, corresponding to HgS and Hg associated with organic matter and pyrite species (Hg-OM, Hg-FeS_2). This suggests its transport as relatively inert mineral-bound Hg associated with sediments from mine residues. However, in the finer fractions, a second band was also observed at temperatures between 450 and 600°C. This second band indicates the presence of HgO, suggesting a contribution from both natural mineral sources and potentially labile Hg forms capable of long-range transport. The results are consistent with those reported by Rumayor et al. (2017) for sediments, waste, and soils from El Terronal. Taken together, finer sediments (<20 μm) showing elevated Hg levels reflect their role in long-range transport and potential bioavailability, while the coarser fractions act as sinks for Hg bound to organic matter and sulfur species, highlighting differential transport mechanisms. These findings emphasize the importance of considering both particle size and contaminant speciation to understand the dynamics of toxic element transport in mining-impacted fluvial systems. Future analyses will further clarify the relative contributions of active contamination from mine residues in contrast to legacy sediments previously deposited in the riverbed.

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