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MERCURY DISPERSION FROM THE MT. AMIATA MINING DISTRICT TO THE UPPER REACH OF THE PAGLIA RIVER (CENTRAL ITALY): A GEOMORPHOLOGICAL-GEOCHEMICAL APPROACH DEFINES THE INTERACTION BETWEEN RIVER DEPOSITS AND MINING ACTIVITY

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ABSTRACT: The Paglia River drains the Mt. Amiata Mercury District (the 3rd most important district worldwide exploited from 1880 to 1980) before becoming a tributary of the Tiber River. A combined geochemical-geomorphological approach was applied to understand Hg distribution in the fluvial morphological units (MUs). The Hg mean values in the terraces (here after indicated as Tn) seem to be linked to the mining activity: T1, formed before the activity, has values within the local background (2÷6 mg/kg); T2, T3 and T5, formed either at the beginning or in the final phases, have values lower than 9 mg/kg; T4, formed during the peak activity, has 26 mg/kg. The current baseflow channel and bar have mean value of 9 mg/kg. The high value of the modern floodplains (19 mg/kg) could be related to intense flood events causing greater erosion of contaminated MUs upstream. The total contained mass of Hg in the studied stretch is estimated at 63 tonnes.

KEYWORDS: Fluvial sediments, fluvial dynamics, morphological units, Hg contamination

1. INTRODUCTION

Between the 1880s and 1980s, the Mt. Amiata Mining District (MAMD), located in Southern Tuscany (Italy), produced about 102,000 tonnes of Hg and released into the environment not less than 30,000 tonnes of Hg (Benvenuti & Costagliola, 2016, and references therein). MAMD is located within the catchment of the Paglia River, the main tributary of the Tiber River, which flows directly into the Mediterranean Sea. In this study, an integrated geomorphological and geochemical approach was used to interpret and understand temporal and spatial contaminant distribution in the upper catchment of the Paglia River.

The analysed stretch of the Paglia River extends over about 43 km from the source near Abbadia San Salvatore, where the most important Hg mine of the district was located, to Allerona Scalo in Umbria (Fig. 1). The area of interest covers about 720 km^2, straddling Southern Tuscany, Northern Lazio and Central Umbria. The shape of the basin and the hydrographic net are mainly linked to the structural characteristics of two grabens: Radicofani and Paglia-Tiber (Fig. 1). The main lithologies cropping out along the Paglia River belong to a Quaternary continental deposit complex (Marroni et al., 2015), characterized by: (1) Holocene fluvial deposits (pebbles in a mainly sandy-silty matrix), the Paglia River cuts through its alluvial deposits locally forming various orders of terraces; and (2) Pleistocene fluvial-lacustrine deposits (mainly conglomerates with sandy-silty beds and levels). These last deposits are arranged on large terraced surfaces located at altitudes from 5 to 20 m above the current course of the Paglia River (e.g. Pleistocene terrace in Fig. 1).

2. METHODS AND DATA COLLECTION

The Paglia River is a relatively high-energy, dynamic river, characterized by a sequence of channel adjustments in its catchment, occurred during the period of mining activity and during the last decades. To understand this evolution, the multi-scale approach developed by Rinaldi et al. (2013, 2015) and Gurnell et al. (2016) was used. On this basis a series of Landscape Units (LUs), segments and reaches were identified (Fig.1). The lower hierarchical spatial order is the Morphological Unit (MU), *i.e.* an area within the floodplain channel containing a landform created by erosion or deposition of sediment, sometimes in association with vegetation.

A multi-temporal analysis of the Paglia River changes was performed to evaluate the evolution of channels and floodplains, and to try and date the recent terraces and modern floodplains formed during the time interval from the beginning of mining activity to present. This analysis was restricted to the following three key years: (1) the first topographic maps produced by the IGM (Istituto Geografico Militare) dating from 1883 (scale 1:50,000), coinciding with the initial period of MAMD activity; (2) aerial photos from 1954 (IGM GAI, scale 1:33,000) corresponding to the highest production period of MAMD activity; (3) aerial photos from 2012 (Environmental Ministry, scale 1:10,000), corresponding to the available most recent and best resolution aerial photos. Maps and aerial photos were processed by GIS

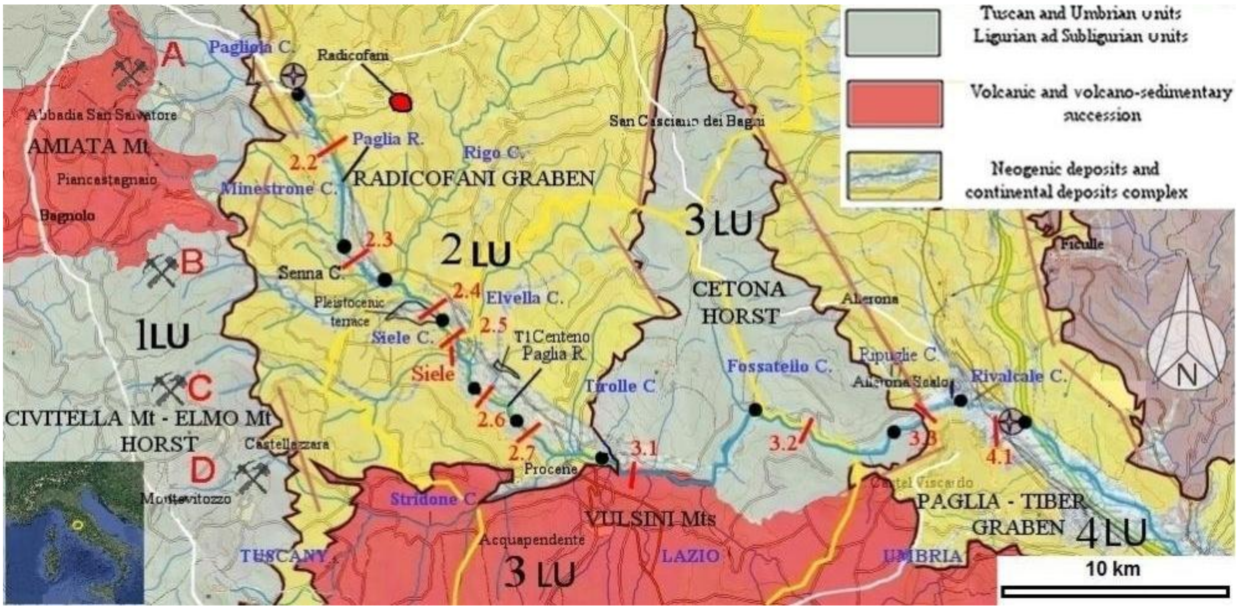

Fig. 1 - Geology of the upper part of the Paglia River catchment (delimited by a white line) after Colica (2017). The analyzed Paglia River stretch is between the points with stars. Landscape Units (LUs; their limits are highlighted with a black line): 1LU) Mountain areas with volcanic and volcano-sedimentary successions and Ligurian and Subligurian Units; 2LU) Hilly areas with Neogene deposits and continental deposits complex; 3LU) Mainly hilly areas with Ligurian and Subligurian Units and volcanic and volcano-sedimentary successions; 4LU) Intermontane plain unit with Neogene deposits and continental deposits complex. The transects are indicated by red segments and numbers. The black points indicate the beginning of the reaches along the Paglia River (same numbers of transects). Siele is the transect along the Siele Creek. The capital red letters indicate the mining areas: A) Abbadia San Salvatore; B) Casa di Paolo - Senna mine - Cerro del Tasca; C) Siele - Carpine; D) Cornacchino. Regional boundaries are reported in yellow.

analysis (using ArcGis 9.3). Multitemporal analysis of channel changes was then used to support interpretation and classification of the MUs related to the channel evolution occurring during the investigated period. This GIS-based analysis was validated by field surveys.

2.1. Geomorphological field characterization of sampling transects

A sampling transect was identified for each fluvial reach. A total of 11 sampling transects were selected (10 along the Paglia River and 1 along Siele Creek, a tributary of Paglia R.; Fig. 1). The MUs are classified (according to Rinaldi et al., 2016) within two broad spatial domains, bankfull channel (baseflow channel - C and bars -B) and floodplain. The latter is strongly influenced by recent channel dynamics. The channel incision and narrowing of the Paglia River, occurred approximately during the last 150 years, determined the formation of a series of 'recent terraces' (T2, T3, T4 and T5), *i.e.*, former historical levels of floodplain that became a terrace because of bed incision; whereas the most recent alluvial, flat surface adjacent to the river created by lateral and vertical accretion under the present river flow and sediment regime is here classified as 'modern floodplain' (FP - see Belletti et al., 2016). For each transect, a profile representing the distribution, lateral extension and elevation of the different MUs was obtained. The lengths (parallel and perpendicular to the watercourse) of each MU along each transect were measured on aerial photos and maps.

In order to get an estimation of the volumes of overbank fine sediments accumulated within the wide channel of 1883, the thickness of the overbank fine sediments overlying the gravel bed deposits was estimated by a hand borer. Then the area of each polygon of the different MUs deposited after 1883 was measured by GIS, and the volume of fine sediment was calculated as a product of area and thickness. The volume of fine sediment accumulated within the channel bed of 1883 was calculated for each reach, and it was then used to get an estimation of the volumes of contaminants stocked within these MUs.

2.2. Geochemical sampling and analysis

A total of 102 samples of sediments were collected, including 82 samples from the transects along the Paglia River, 7 samples from the Siele transect, and 13 samples outside the studied transects from presumably pre-mining deposits (see below), to establish a comparison between pre- and post-mining conditions. Following preliminary tests, it was ascertained that the <250 μm fraction likely contains nearly all Hg of the bulk sample; this fraction was digested with aqua regia in a microwave oven, and the resulting solution was analysed by means of ICP-OES.

3. RESULTS

3.1. Channel and floodplain evolution

Considering channel widths of the three reference years in this study (1883, 1954, 2012), it appears that the Paglia River suffered significant channel narrowing

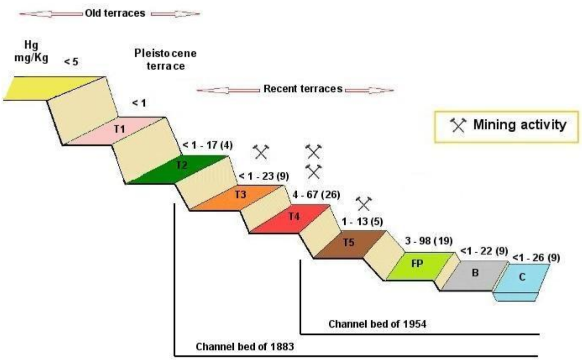

Fig. 2 - Range and mean values of Hg concentrations (mg/kg) in the different MUs along the Paglia River, modified from Colica (2017)

over time, with an average reduction in channel width of about 64% between 1883 and 1954, and a further reduction of about 70% between 1954 and 2012. Channel narrowing occurred in combination with a change in the overall morphological pattern, from a braided (1883) to a single-thread, sinuous morphology (2012). The causes of these changes are a combination of land use changes (*i.e.*, afforestation) at catchment scale with intensive sediment mining (see e.g. Scorpio & Rosskopf, 2016).

3.2. Geomorphic characterization and interpretation of sampling transects

A sequence of terraces was generated by bed incision and narrowing (Fig. 2): old terrace (T1) (i.e. formed before the last 150 years), corresponding to an alluvial surface that is already recognized as higher than the floodplain in the maps of 1883; recent terrace (T2), interpreted as the modern floodplain in the maps of 1883, corresponding to the alluvial flat surface adjacent to the channel bed of 1883; recent terrace (T3), formed between 1883 and 1954, corresponding to a flat surface at an intermediate elevation between T2 and T4, interpreted as a recent terrace in the aerial photos of 1954; recent terrace (T4), formed after 1954, corresponding to the modern floodplain recognized in the aerial photos of 1954; recent terrace (T5), formed between 1954 and 2012, corresponding to a flat surface at an intermediate elevation between T4 and the modern floodplain (FP). The FP is the lowest flat and vegetated surface adjacent to the river bed, recognized in the aerial photos of 2012 and during the field survey as the channel bars (B) and baseflow channel (C). As can be seen in Fig. 2, some MUs that are present within the 1883 channel bed were formed during MAMD mining activity: T3 during the initial phase, T4 during the maximum period of activity (1950s-60s), T5 during the final and closing stages (1980s) and possibly also after (but before 2012).

3.3. Geochemical data

Fig. 3 reports the Hg concentration in the MUs in the transects along the Paglia River. Samples from pre-mining deposits are characterized by Hg concentrations comparable with the background estimate of the Amiata area (2-6 mg/kg; Rimondi et al., 2015). By contrast, many samples in all other MUs show Hg contents well above this background and above the Italian legal limit of 5 mg/kg (DL 152/2006) for industrial soil. In particular, high values of Hg concentration are shown in the following MUs: T4 (Hg> 30 mg/kg along transects 2.2, 2.5 and 2.6), FP (> 30 mg/kg along transects 2.2 and 2.3) and C (> 20 mg/kg along transects 2.6 and 2.7). The highest mean Hg value was observed in recent T4 terraces. The highest values of Hg concentration per MUs were found along the Siele transect: C (29.4 mg/kg), B (mean value 79.2 mg/kg), FP (mean value 183.7 mg/kg) and T4 (mean value 92 mg/kg).

3.4. Total Hg masses

From the volumes of river sediments accumulated in the reaches and Hg concentrations, we estimate a total bulk value of 63 tonnes of Hg in the studied stretch (Colica et al., 2016). The highest contents are found in T4 (39 tonnes), followed by FP (19 tonnes), T3 (4 tonnes) and T5 (1 tonne). Considering the single reaches, reach 3.1 shows the largest amount of Hg (25 tonnes), followed by reaches 2.3 (12 tonnes), 2.5 (10 tonnes) and 2.6, 2.7 and 4.1 (each containing 4 tonnes of Hg).

3.5. The major flood event of February 2016

At the end of February 2016, a major flood event along the Paglia R. caused the deposition of overbank deposits on top of pre-existing MUs. These deposits have Hg values in the 5-40 mg/kg range (stars in Fig. 3) and a mean value of 21 mg/kg, similar to that of the FP (19 mg/kg). Comparing these data with those collected from the major flood of November 2012 (Pattelli et al., 2014; circles in Fig. 3), it is evident that large quantities of Hg-contaminated sediments have been transported during major flood events. Specifically, the Hg concentration in transect 2.2 is about four times higher in the 2016 event compared to that of 2012.

4. DISCUSSION

On the basis of the geomorphologic-geochemical analysis, it can be stated that current and recent MUs in the Paglia River basin are locally heavily contaminated by Hg. In particular, the most contaminated MU T4 was formed during the peak of the MAMD mining activity.

On the other hand, the high Hg values of FPs could be due both to the last flood events, which deposited abundant amounts of sediment and contaminated materials along the river banks, and to the recent local partial enlargement of some reaches of the Paglia River.

The T3 unit was presumably formed around the beginning of the MAMD mining activity and immediately prior to the peak activity period. In this MU Hg content is less than the two previous cases, but the total Hg bulk is about 4 times higher than in T5; this last unit, formed after 1954 and before 2012, contains sediment with low Hg content, probably as a result of the closure of the mining activities in the 1980s.

It is important to highlight how the erosion of some MUs can result in a high environmental risk due to their high mass of contaminants. It should also be noted that the eventual securing of these MUs areas must take into

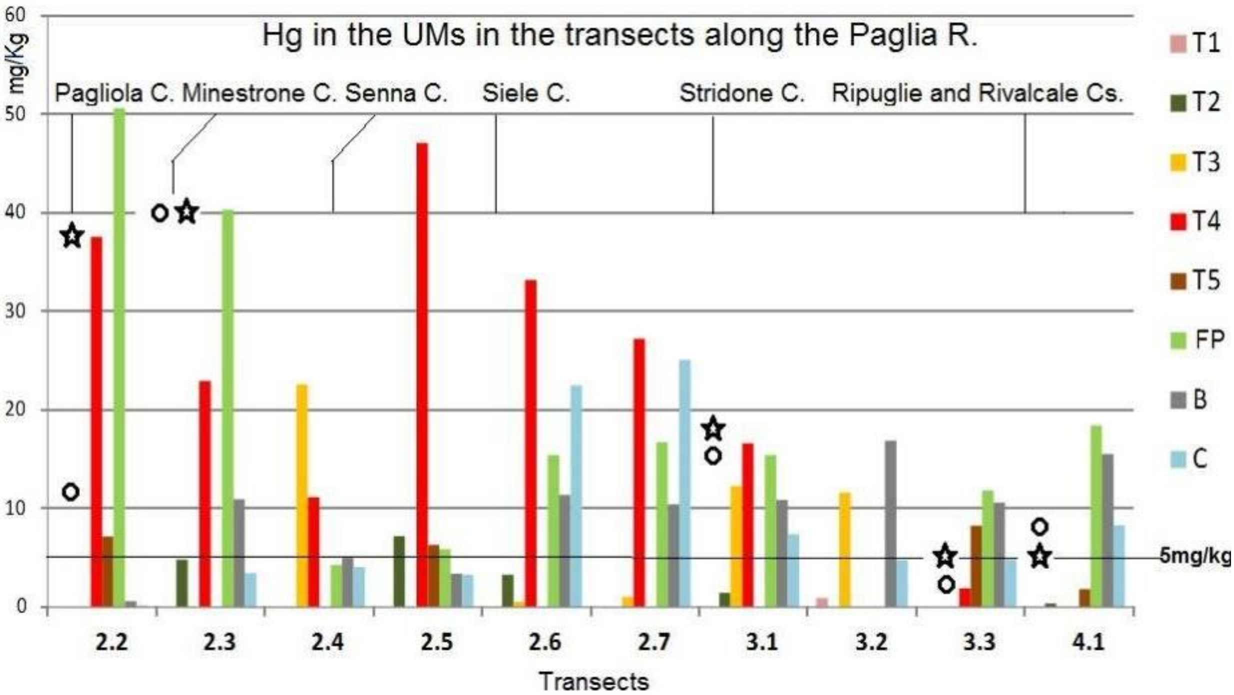

Fig. 3 - Hg concentrations in MUs along the Paglia River transects with locations of the tributaries - after Colica (2017). The Italian legal limit (5 mg/kg; DL 152/2006) for Hg in industrial soil is reported. The values are the mean of the Hg concentration in the two banks. Hg concentrations in the overbank deposits after the major flood events of February 2016 (stars) and November 2012 (circles) are here reported.

account that in every major flood event large quantities of heavy Hg contaminated sediments might be transported and redeposited on the pre-existing MUs.

The influence of the Paglia River tributaries appears to be fundamental in the supply of Hg-contaminated sediments (Fig. 3). In particular, the Pagliola Creek drains the mining area of Abbadia San Salvatore and, despite the ongoing reclamation in this area, it carries high Hg concentrations in fluvial sediments during flood events (*e.g.*, FP of transect 2.2 contains 98 mg/kg Hg). Indeed, the deposits of the baseflow channel (C) and bar (B) sampled during a period without intense floods (2013-2014) show Hg contents less than 1 mg/kg. The presence of high Hg values in recent T4 terraces (Fig. 3; transect 2.2) may also be due to the presence of more contaminated sediments in the 1954 FP, following the period of maximum activity in the Abbadia San Salvatore mining area.

The Siele Creek drains the Siele-Carpine mining area. Although reclamation was completed in 2001, the Siele transect shows the highest Hg concentrations in various MUs (*e.g.*, samples C, B, FP and T4). The contribution of highly polluted sediments from the Siele Creek to the Paglia River is clearly recorded in the Hg contents of C and B from transect 2.6 (Fig. 3). This phenomenon also occurred during the formation of recent and past FPs (*e.g.*, Hg values in T4 terraces). The presence of high Hg concentration in T4 at transect 2.5 (Fig. 3) is due to the 1954 local existence of an extended FP in which Hg-contaminated river sediments could accumulate more easily.

5. CONCLUSIONS

Based on the above geomorphologic-geochemical approach, variable, locally elevated Hg concentrations in the Paglia River sediments, belonging to the various MUs, were found in both the transects and along the watercourse. The total mass of Hg in the different MUs also varies considerably. This variability is conditioned both by past and current fluvial dynamics and, until the 1980s, by MAMD activity, whose effects are still affecting the fluvial environment. The total mass of Hg in MUs of the analysed Paglia River stretch (43 km) is estimated to at least 63 tonnes. During major flood events, the Paglia River appears to carry sediments with high concentrations of Hg. The tributaries of Paglia River contribute to this process, in particular the Pagliola Creek, which drains the mining area of Abbadia San Salvatore, and the Siele Creek, which drains the Siele-Carpine mining area. This latter creek carries sediments with the highest concentrations of Hg in all current flow conditions. The course of the Paglia River has undergone and is undergoing strong fluvial dynamics; particularly, since 1883 there has been a gradual incision. The most recent MUs can be eroded, and thus become secondary sources of contamination. However, a recent reversal fluvial trend, a partial enlargement of some reaches, was locally observed. Where this last phenomenon occurs, there are favorable conditions for a greater accumulation of contaminated sediments. Knowledge of Paglia River dynamics and of its current and past MUs is crucial for identifying areas with greater environmental risk. The survey methodology that combines geomorphologic and geochemical aspects is apparently a very effective tool for identifying these MUs, understanding current and potential environmental hazards and conducting future monitoring that may have relevance for restoration measures of the affected matrices.

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