INNOVATIVE METHODOLOGIES FOR EROSION RISK ANALYSIS IN AREAS CONTAMINATED BY INDUSTRIAL ACTIVITY: APPLICATION AT MONTE AMIATA MINING DISTRICT (SOUTHERN TUSCANY)

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INTRODUCTION

The global industrial activity, that has grown exponentially in recent years, has generated a huge amount of toxic metals thus representing a source of pollution because the sediments contaminated by these activities have affected the surrounding areas and the nearby river systems (Miller, 1997). The important role of geomorphic fluvial processes and dynamics in controlling mining waste transport and storage in river systems has been widely demonstrated in several studies (Graf *et al*., 1991; Macklin, 1992; Miller, 1997; Miller *et al*., 1999; Macklin *et al*., 2003). Among the various toxic metals, mercury is of particular concern as it is present in a large variety of chemical forms and most of its compounds are toxic even at low quantities (Chowdhury & Chandra, 1986). The Mediterranean region hosts about 65% of the world's cinnabar (HgS) deposits (Bargagli *et al*., 1986). Due to the drainage of mercuriferous mining areas, large amounts of Hg contaminated hydrographic systems (Gosar *et al*., 1997) impacting the biota and the downstream riverine ecosystems for long periods, even after the closure of the mine (Gray *et al*., 2004, 2010, 2014). Mining landfills may exhibit high concentrations of Hg (Rimondi *et al*., 2014a, 2014b, 2015) and particularly calcine (*i.e*., the residual part of the combustion process of mercuriferous mineralization) may have Hg concentrations ranging from 10 to 800 mg/kg (Rytuba, 2003). Between the 1860s and 1980s, the Mount Amiata Mining District (MAMD), located in southern Tuscany (Italy) produced about 102,000 ton of Hg and released into the environment 44,000 ton of Hg (34,000 ton from calcines and 10,000 ton from Hg emitted from smoke created during the cinnabar roasting phase; Bombace *et al*., 1973; Ferrara *et al*., 1998) and, in addition, other toxic elements, including As. MAMD is located within the catchment of the Paglia river, the main tributary of the Tiber river, which flows directly into the Mediterranean Sea. Rimondi *et al*. (2012) showed that, although more than thirty years have passed since the mining activity came to a complete halt, Hg-rich processing residues and abandoned mine structures still constitute a source of environmental pollution. In this paper, an integrated geomorphological and geochemical approach combining various data sources, observations and analyses is used to interpret and understand temporal and spatial contaminant distribution in the upper catchment of the Paglia river.

STUDY AREA

General setting of the upper part of Paglia river catchment

The upper part of the hydrographic basin of the Paglia river extends over an area of about 720 km^2, covering southern Tuscany, northern Lazio and central Umbria (Fig. 1). The shape of the basin and the hydrographic net are mainly closely linked to the structural characteristics of the two grabens present in this area: Radicofani (NNW; Liotta, 1996; Barchi *et al.*, 1998) and the Paglia-Tiber (SSE; Funiciello *et al.*, 1981; Fig. 1). The hydrographic basin is also morphologically influenced to the N by the Radicofani volcano and Mt. Cetona Horst, to the NW by the Mt. Amiata volcanic structure, to the W by the Mt. Civitella - Mt. Elmo Horst and to the S by the Vulsini volcano. The area is characterized (stratigraphicaly upwards; Fig. 1) by Tuscan and Umbrian units, Ligurian and Subligurial units (Girotti & Mancini, 2003; Marroni *et al.*, 2015), Neogenic deposits (Liotta, 1996; Marroni *et al.*, 2015), Volcanic and volcano-sedimentary successions (Quaternary), formed by Mt. Amiata (Marroni *et al.*, 2015) and Radicofani complexes (Conticelli *et al.*, 2011) in the northern part and the Vulsini complex in the south, as well as the Continental deposit complex (Quaternary). This is characterized by: (1) Holocenic fluvial deposits: are present along the Paglia river valleys and its main tributaries consisting of pebbles in a mainly sandy-silty matrix. The Paglia river engraves its alluvial deposits sometimes forming various orders of terraces; (2) Pleistocene deposits: fluvial-lacustrine deposits, mainly formed by conglomerates with sandy-silty beds and levels. These deposits are arranged on large terraced surfaces located at higher altitudes varying from 5 to 20 m compared to the current course of the Paglia river (see Pleistocene terrace; Fig. 1). The analyzed stretch of the Paglia river watercourse extends over about 43 km from the source (about 4 km W of Abbadia San Salvatore; Fig. 1), where the Cacarello creek joins the Pagliola creek, to Allerona Scalo (in central Umbria; Fig.1).

Fig. 1 - Geology of the upper part of the Paglia river catchment (delimited by a white line). 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 Neogenic 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 letters in red 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.

Overview of mining activity and contamination problems

In the MAMD, Hg genesis is considered to be due to the phenomenon of mobilization and concentration linked to hydrothermal systems present in southern Tuscany during the Pliocene-Quaternary followed by secondary enrichment during the Pleistocene periods (Morteani *et al*., 2011, Rimondi *et al*., 2015; Gasparrini *et al*., 2013). Cinnabar is the prevalent mineral whereas metacinnabar and native Hg are fairly rare; As sulfides (realgar and orpiment) are quite common. Mercury mining activity extensively began in the mid-1800s. In that period, 42 mines and numerous mining research areas were present (Bombace *et al*., 1973). Out of all these mines, only the main ones remained; among them those, within the basin of the Paglia river (Fig. 1), the main mine are (from North to South): Abbadia San Salvatore, Casa di Paolo-Miniere del Senna-Cerro del Tasca, Siele-Carpine and Cornacchino (Table 1).

Hg contamination in the Paglia river basin (Table 2) is mainly related to the presence of calcine near the mining area (Gray *et al*., 2010; Rimondi *et al*., 2012, 2014a, 2014b), contaminated soil (Fantozzi *et al*., 2013; Rimondi *et al*., 2012) and also contaminated fluvial sediments.

Table 1 - Main features of Hg mines in the MAMD (according to www.mindata.org, Inventario del Patrimonio Minerario e Mineralogico in Toscana (1991) and www.parcoamiata.com).

Mining areas	Hg minerals	Tectono-stratigraphic Units	Period of main mining activity	Hydrographic watershed
Abbadia San Salvatore (SI)	Cinnabar, metacinnabar, Hg	Tuscan, Ligurian and Volcanic seq.	1847,1873-1892, 1901-1981	Pagliola Creek ($27\ km^2$)
Casa di Paolo - Cerro del Tasca -Miniera del Senna (SI)	Cinnabar, metacinnabar	Ligurian	1846-1855, 1876-1971	Minestrone Creek and Senna Creek (total area: $59\ km^2$)
Siele- Carpine (SI)	Cinnabar, metacinnabar	Ligurian	1846-1981	Siele Creek ($34\ km^2$)
Cornacchino (GR)	Cinnabar	Tuscan		Stridone Creek ($98\ km^2$)

The latter are reported along the Paglia river by Bombace *et al.* (1973) and Gray *et al.* (2014) and along the fluvial terraces of the Pagliola Creek (Rimondi, 2013). The Hg concentrations (Table 2) are usually over the legal limit of 1 mg/kg (for public, private and residential use; Italian Legislative Decree 152/2006) and sometimes also over the legal limit of 5 mg/kg for commercial and industrial sites.

Table 2 - Range of Hg concentrations in calcines, soils and fluvial deposits of the Paglia river and tributaries (Pagliola ceek).

Hg in calcine, soils and fluvial sediments	Hg (mg/kg)
Calcines from the Abbadia San Salvatore mining area (Rimondi *et al.*, 2012, 2014 a, 2014b)	25÷1,500
Soils from the Abbadia San Salvatore mining area (Rimondi *et al.*, 2012)	150÷400
Soils from the Abbadia San Salvatore mining area (Fantozzi *et al.*, 2013)	100÷800
Fluvial terraces of the Pagliola Creek (Rimondi, 2013)	1÷2,103
Sediments from the Paglia river (Bombace *et al.*, 1973)	0.6÷10.5
Sediments from the Paglia river between Allerona Scalo and Orvieto (Gray *et al.*, 2014)	0.4÷1.9

METHODS AND DATA COLLECTION

The spatial units

An integrated geomorphological and geochemical approach was used to study contaminant (Hg, As) distribution. 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) was used. A series of Landscape Units (LUs) were settled on, on the basis of the catchment scale controls, such as geology and physiographic characteristics. Segments were delineated by the intersection of the Paglia river with the LUs and on the basis of major changes in valley gradient, catchment area, confluences of major tributaries, and lateral confinement. Within each segment, several different reaches were identified (Rinaldi *et al.*, 2013, 2015; Gurnell *et al.*, 2016) on the basis of valley setting, confinement typology, channel morphology (*e.g.*, sinuous, meandering, etc.) and presence of river tributaries. The lower hierarchical spatial order is the Morphological Unit

(MU) *i.e.*, area within the floodplain channel containing a landform created by erosion or deposition of sediment, sometimes in association with vegetation.

Multitemporal analysis of channel changes

A multi-temporal analysis of the Paglia river changes was also performed to evaluate the evolution of channels and floodplains and to try to date the recent terraces and modern floodplains formed during the time interval from the beginning of mining activity to present. In this study, multi-temporal 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 analysis (using ArcGis 9.3). Limitations and errors related to georectification and digitizing of channel morphological features are in accordance with the work by Hughes *et al.* (2006) and Surian *et al.* (2009). Multitemporal analysis of channel changes was then used to support interpretation and classification of the MUs (floodplain and recent terraces) related to the channel evolution occurring during the investigated period.

Geomorphological field characterization of sampling transects

A sampling transect was identified for each reach, based on accessibility of the field site and on representativeness of the typical assemblage of MUs observed within the reach. A total of 11 sampling transects were selected (10 along the Paglia river and 1 along Siele creek; 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 are strongly influenced by recent channel dynamics. The channel incision and narrowing of the Paglia river, occurred approximately during the last 150 years, have determined the formation of a series of 'recent terraces' (T2, T3, T4 and T5), *i.e.*, former historical levels of floodplain that has become 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), according to the GUS (Belletti *et al*., 2016). 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.

Geochemical sampling and analysis

The sampling was conducted on 102 samples, picking up about 1 kg of sediment for each sample formed by the sum of 5 sub-samples taken within a 5 m square area around the sampling point selected. The sampling of fine sediments was conducted with a hand borer (see above). The fraction of the samples less than 250 μm was tested during this study to be sure it contained 100% of the Hg and As present in the sample and then was analysed by means of ICP-OES chemical analysis.

RESULTS

Segmentation of the sub-catchment in spatial units

Based on Rinaldi *et al.* (2013, 2015, 2016) and Gurnell (2016) LUs, segments and reaches of the Paglia river have been identified (Fig. 1). Particularly, four LUs are present: 1LU) mountain areas, from 600 up to

1,738 m a.s.l., occupying the upper portion of the catchment, characterized by volcanic and volcano-sedimentary sequences of the Mt. Amiata and Radicofani and Ligurian and Subligurian Units; 2LU) hilly areas, below 600 m a.s.l., characterized by prevailing Neogene sedimentary deposits located in the Radicofani Graben; 3LU) mainly hilly areas, below 600 m a.s.l., characterized by Ligurian and Subligurian Units and Volcanic and volcano-sedimentary sequences located on the Mt. Cetona Horst and along the Vulsini Mts.; 4LU) intermontane plain unit, comprising a relatively high plain and including some low hilly portions, situated along the Paglia river main stem, mainly characterized by Neogene sedimentary deposits located in the Paglia-Tiber Graben. By intersecting the Paglia river with the LUs, four segments were identified. In these, a total of 10 reaches were defined and within each reach, a transect with the same reference numbers was selected (Fig. 1; Table 3). Only the Siele transect is located along a tributary (Siele Creek), developing mainly 2LU (Fig. 1).

Table 3 - Characteristics reaches of the Paglia River derived from their delineation. L: reach length; LU: Landscape Unit; VC: Valley Confinement (Co: confined; PC: partly confined; U: unconfined); CD: Confinement Degree; CI: Confinement Index; SI: Sinuous Index after Rinaldi *et al*. (2015). Incidence: tributary catchment area/basin area of the Paglia River calculated to the confluence of the tributary. BRT: Basic River Typology according to Rinaldi *et al*. (2015); 1: single thread; 2: straight, 3: sinuous.

Reaches	L (km)	LU	VC	CD (%)	CI	SI	Incidence	BRT
2.2	6.1	2	PC	27.5	4.5	1.05	Pagliola Creek - 79%, Cacarello Creek - 21%	1-2
2.3	3	2	PC	15.4	5.9	1.10	Minestrone Creek - 22%	3
2.4	1.7	2	PC	19.2	3.75	1.10	Senna Creek - 28%, Rigo Creek - 8.4%	3
2.5	3.4	2	U	3.5	1.9	1.2		3
2.6	3.5	2	U	9	7	1.25	Siele Creek - 16.1%, Elvella Creek - 17%	3
2.7	5	2	PC	10	2.3	1.11		3
3.1	7	3	PC	49	4.38	1.3	Stridone Creek - 20.9%	3
3.2	6.5	3	Co	> 90	1.69	1.29	Fossatello Creek irrelevant	3
3.3	2	3	PC	34	4.48	1.12		3
4.1	4.6	4	PC	23	2.45	1.3	Ripuglie and Rivalcale Creeks irrelevant	3

Channel and floodplain evolution

Channel widths of the three reference years considered in this study (1883, 1954, 2012) at the 10 sampling transects were analyzed. It is evident that the Paglia river has suffered significant channel narrowing 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). These changes represent a well known type of channel adjustment along most of the alluvial rivers in Italy, together with bed incision. The causes of these changes are a combination of land use changes (*i.e*., afforestation) at catchment scale with intensive sediment mining (Surian *et al*., 2009; Scorpio & Rosskopf, 2016).

Geomorphic characterization and interpretation of sampling transects

A sequence of recent 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 on 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 on the aerial photos of 1954; recent terrace (T4), formed after 1954, corresponding to the modern floodplain recognized on 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 on 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 also after (but before 2012). For each transect, a profile representing the distribution, lateral extension and elevation of the different MUs was obtained.

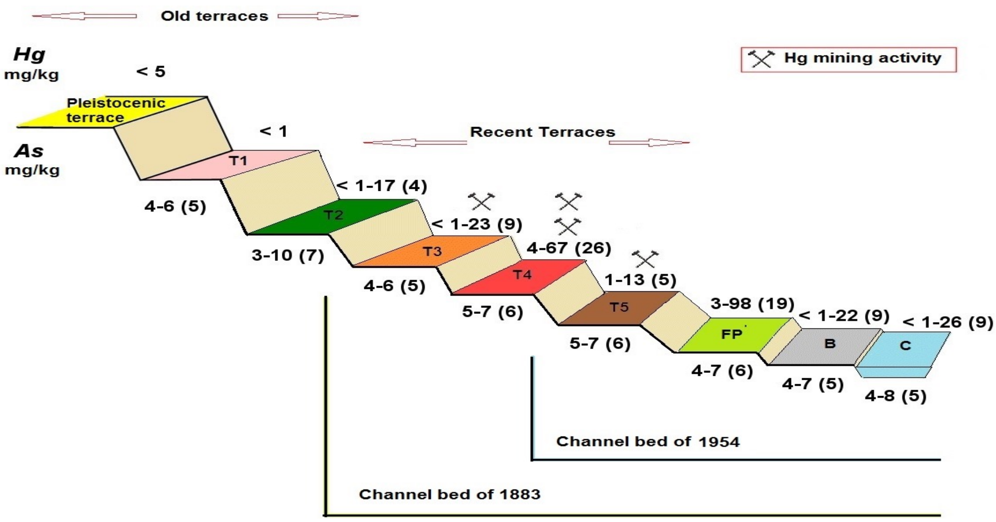

Fig. 2 - Range and mean values of Hg and As concentrations (mg/kg) in the different MUS along the Paglia river.

Geochemical result

The analyzes were conducted on 82 samples from the transects along the Paglia river, 7 samples from the Siele transect, and 13 samples from pre-mining activity deposits (5 samples from T1 Centeno terrace and 8 samples from Pleistocenic terrace) formed outside the studied transects, to establish a further comparison between pre- and post-industrial mining activity (Fig. 2). The Centeno T1 (Hg < 1 mg/kg), the Pleistocenic (Hg < 5 mg/kg) and T1 terraces along transect 3.2 (Hg 0.8 mg/kg) are characterized by Hg concentrations comparable with the background estimate of the Amiata area (2-6 mg/kg; Rimondi, 2013). The MUs C, T2 and T3 of the transects along the Paglia river are largely above the Hg limit of 1 mg/kg (Italian Legislative Decree 152/2006), whereas all samples taken from FP, T4 and T5 are consistently above this threshold. 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 (79-79.4, mean value 79.2 mg/kg), FP (182-185.5, mean value 183.7 mg/kg) and T4 (90-94, mean value 92 mg/kg). The concentration of As is consistently below the limit of 20 mg/kg (Italian Legislative Decree 152/2006). Arsenic shows no particular changes both at the level of the various MUs present in the individual transects and among the various transects. Fig. 3 reports the Hg concentration in the MUs in the transects along the Paglia river. These values have trends with notable asymmetries. In particular, the high values of Hg concentration are shown in the following transects: 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 major flood event of February 2016

At the end of February 2016, a major flood event along the Paglia river caused the deposition of Hg overbank deposits on top of pre-existing MUs. The overbanks deposits have a range value of 5-40 mg/kg (stars in Fig. 3) and a mean value of 21 mg/kg. The latter mean value is similar to that of the FP (19 mg/kg). Comparing these data with those collected from the major flood of November 2012 (Hg range: 2-40 mg/kg; Hg mean value: 15 mg/kg - Pattelli *et al.*, 2014; circles in Fig. 3), it becomes evident that large quantities of Hg-contaminated sediments have been transported during major flood events. The Hg concentration values are, in almost all cases, above the limits set by Italian law. Particularly, the Hg concentration in transect 2.2 is about four times higher in the 2016 event compared to that of 2012.

The Hg and As bulks

The volumes of river sediments accumulated in the reaches were calculated and then, through Hg and As concentrations, the bulk of contaminants was determined. The total bulk values are 63 ton of Hg and 22 ton of As (Colica *et al*., 2015, 2016). In the following MUs the total bulk values are: T3: 4 and 3 ton of Hg and As, respectively; T4: 39 and 13 ton of Hg and As, respectively; T5: 1 and 2 ton of Hg and As, respectively; FP: 19 and 4 ton of Hg and As, respectively. The highest Hg and As contents are found in T4, followed by FP, T3 and T5.

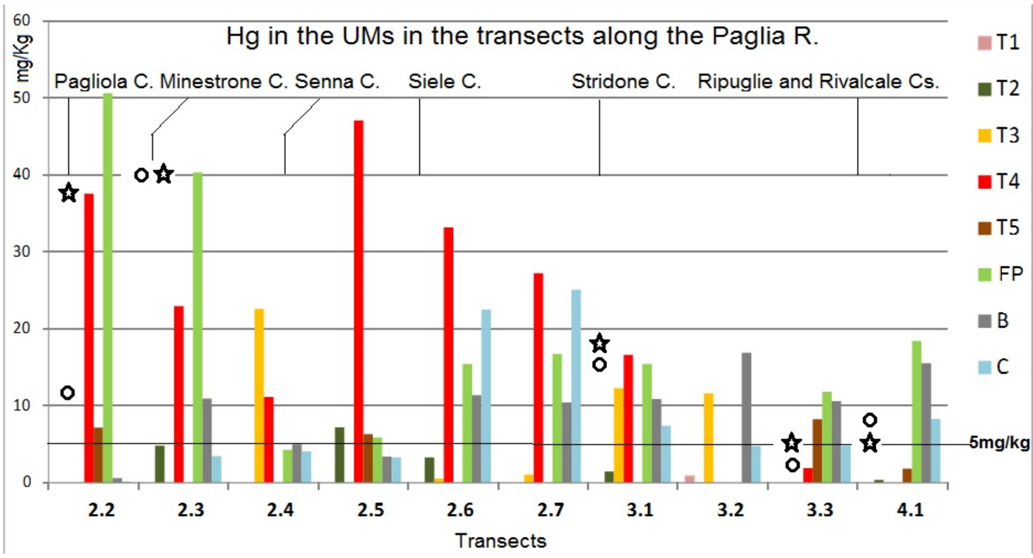

Fig. 3 - Hg concentrations in MUs along the transects of the Paglia river with the locations of the tributaries. Due to graphic limitations, only the value of the legal limit (5 mg/kg) of Hg (Italian Legislative Decree 152/2006) is here reported. The values are the mean of the Hg concentration in the two banks. Hg concentrations in the overbank deposits after the major flood events of February 2016 (stars) and November 2012 (circles).

In order to identify the most dangerous reaches in terms of mass of contaminants and potential environmental hazards, the mass of Hg and As was calculated for each stretch. Reach 3.1 is the location with the largest amount of Hg (25 ton) and As (10 ton), followed by reaches 2.3 (Hg = 12 ton, As = 3 ton) and 2.5 (Hg = 10 ton, As = 2 ton) and reaches 2.6, 2.7 and 4.1 (each containing 4 ton of Hg and 2 ton of As). It should be noted that very recently (post-2012) local and partial enlargement of reaches 2.3, 2.6, 3.1 and 4.1 of the Paglia river were observed. This phenomenon was also described by Bollati *et al*. (2014) and Nardi & Rinaldi (2015) in other italian rivers. This phenomenon of partial enlarging of the reach may reduce water stream flow velocity by creating favorable conditions for particulate deposition, as observed in the modern FP reaches (reache 2.3: Hg = 7 ton, As = 1 ton; reache 2.6: Hg = 4 ton, As = 2 ton; reach 3.1: Hg = 3 ton, As = 1 ton; reache 4.1: Hg = 4 ton).

DISCUSSION

On the basis of the geomorphologic-geochemical analysis, it can be stated that current and recent MUs are sometimes heavily contaminated by Hg and As within the Paglia river basin. In particular, the contaminated MUs are the following (from the most to the least contaminated MUs): T4) this MU contain the highest Hg and As content. It were formed during the peak of the MAMD production period for Hg and, as consequence, also of As; FPs) theses MUs contain high Hg and As values. This could be due both to the last flood events, which deposited abundant amounts of sediment and contaminated materials along the river banks, and to recent local and partial enlargement of some reaches of the Paglia river; T3) this MU formed between the beginning of the MAMD mining activity and immediately prior to the peak activity period. In this MU Hg and As content are both less than the two previous cases but the total Hg bulk is about 4 times higher than in T5; T5) this MU formed after 1954 and before 2012. The sediment accumulated during this period seems to have low Hg and As content, which is probably a result of the closure of the mining activities around the '80s.

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 reclamation or securing of these MUs areas must take into 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: 1) the Pagliola creek drains the mining area of Abbadia San Salvatore and, despite the fact that this area has been secured underground, it carries high Hg concentrations in fluvial sediments during flood events (*e.g.*, FP of transect 2.2 contains 98 mg/kg Hg). Examples are the deposits of the baseflow channel (C) and bar (B) sampled during a period without intense floods (2013-2014), in which Hg is 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; 2) 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.

CONCLUSIONS

Based on the above geomorphologic-geochemical approach, variable and sometimes elevated Hg concentrations in the Paglia river sediments, belonging to the various geomorphic units (MUs), were found in both the transects and along the watercourse. Arsenic concentration is instead more constant (< 10 mg/kg). The bulk of Hg and As in the various MUs also varies considerably. This variability is not casual, but is conditioned both by past and current fluvial dynamics and MAMD activity (about 100 years of activity which ended in the 1980s), whose effects are still affecting the fluvial environment at some 40 years after the mining activity ended. It is estimated that the total mass of contaminated material in MUs of the analysed stretch of the Paglia river (43 km) is 63 ton of Hg and 22 ton of As. During the 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: *i*) the Pagliola creek, which drains the mining area of Abbadia San Salvatore continues to release Hg-contaminated material, as evidenced by the FP and by the sediments deposited during major flood events; *ii*) the Siele creek, which drains the reclaimed Siele-Carpine mining area, carries sediments with the highest concentrations of Hg in all current flow conditions (see Siele transect, MUs: C, B, FP). The course of the Paglia river has undergone and is undergoing strong fluvial dynamics; particularly, since 1883 there has been a gradual incision as a consequence of this phenomenon. The most recent MUs can be eroded and thus become secondary sources of contaminants. However, a reversal trend has been currently and locally observed. Where this last phenomenon occurs, there are favorable conditions for 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, such as reaches 2.3, 2.5 and 3.1 and MUs with more contaminated content, such as the T4 (formed during the period of major mining activity) and the FPs. The survey methodology that interconnects the geomorphologic and geochemical aspects is at the moment the most effective tool for identifying these MUs, understanding current and potential environmental hazards and conducting future monitoring that may have relevance to studies on the restoration of various environmental matrices.

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