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From point source to diffuse source of contaminants: The example of mercury dispersion in the Paglia River (Central Italy)

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ABSTRACT

Fluvial sediments of the Paglia River, a tributary of Tiber River (Central Italy), are contaminated by mercury (Hg) as a consequence of past mining activity (1846–1981, with main production 1900–1970) in the Monte Amiata district (the 3rd largest Hg producer worldwide). In this study, we combine a geomorphological analysis with geochemical data to try and understand the influence of fluvial dynamics on the spatial distribution of Hg in fluvial sediments over a 43 km segment of the river.

By considering the evolution of the river course between 1883 and 2013, eight different geomorphic units (GUs) were recognised, including the active channel bed (baseflow channel and bar), the floodplain, and five orders of terraces. The distribution of Hg in sediments of these GUs reflects the timing of their formation with respect to evolution of the mining activity. In GUs formed before the main peak of mining activity, or after mine closure, sediments show mean Hg contents comparable to, or slightly higher than, the local background, estimated at 2–6 mg/kg; in GUs formed during the peak production, Hg mean contents are definitely higher (up to 26 mg/kg). The current floodplain also shows high contents (mean 19 mg/kg), because of continuous reworking and transport of older contaminated sediments during major flood events. Therefore, the point contaminant sources represented by mining centres evolved into a diffuse source spread over several tens of kilometres.

By combining geochemical data with calculated sediment volumes, we estimate that not less than 63 tonnes of Hg are currently contained in the sediments of the investigated river stretch. Such amount of Hg will probably limit for the near future a full land use along the Paglia–Tiber course.

1. Introduction

In recent decades, human civilization and a concomitant increase in industrial activity have gradually redistributed many potentially toxic metals from the Earth's crust to the environment, increasing the possibility of human exposure. Contaminated sediments generated by industrial and other anthropogenic activities may enter in fluvial systems and be deposited on stream banks, floodplains, and within channel during normal transport and large flood events. As stressed by Lafhaj et al. (2008), international, especially European, laws became more stringent, and in many areas of the world stream sediments have to be treated as waste material. In many European countries, former point sources of pollution (e.g., waste heaps) were progressively distributed along rivers by runoff, becoming diffuse sources (Pattelli et al., 2014; Hurley et al., 2017). As a consequence, stream sediment management has become an environmental and economical concern for a large number of countries (Lafhaj et al., 2008).

This large-scale contamination has been documented in several studies (e.g., Martin and Maybeck, 1979; Salomons and Forstner, 1984; Lewin and Macklin, 1987; Miller, 1997; Owens et al., 2005; see also a recent special issue of Journal of Soils and Sediments, vol. 17(11), November 2017). The important role of geomorphological fluvial processes and dynamics in controlling mining waste transport and storage in river systems has been widely demonstrated in a number of papers (e.g., Lewin and Macklin, 1987; Graf, 1990; Graf et al., 1991; Macklin, 1992, 1996; Miller, 1997; Lecce and Pavlowsky, 1997; Miller et al., 1999; Macklin et al., 2003; Cáceres et al., 2013; Grygar et al., 2016). For example, interactions between channel change and historic mining

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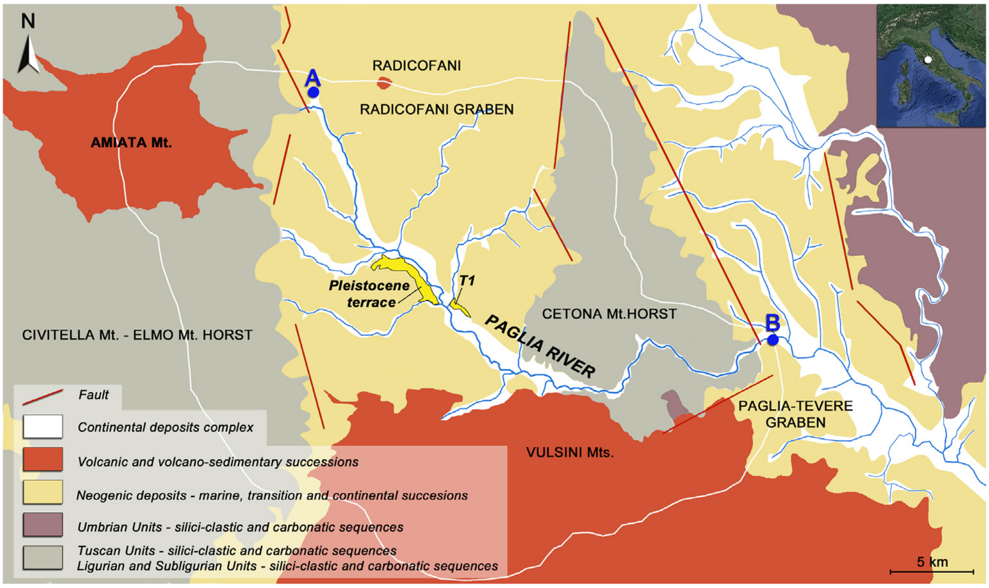

Fig. 1. Geological sketch of the study area (modified from Carta geologica d'Italia, sheets 129 and 130, and Mancini et al., 2004). The white contour delimits the Paglia R. catchment; A and B points define the studied stretch of the river. The Pleistocenic terrace of Podere Bolognino and T1 terrace of Centeno are also shown (§ 4.4).

sediments, quantification of bank erosion, and sediment budgets are important aspects for understanding and assessing metal contamination in fluvial sediments (e.g., Lewin et al., 1977; Macklin, 1996; Rhoades et al., 2009; Grygar et al., 2017).

Macklin et al. (2006) provided a review on sediment-associated metal dispersion processes in river systems, and emphasized how a geomorphological approach based on an understanding of these processes, and the space and timescales over which they operate, is fundamental to support river basin management and mitigate the effects of current and historical metal mining.

Among the various potentially toxic metals, mercury (Hg) 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 quantity. Globally, approximately one million metric tons (t) of Hg have been extracted from various deposits in the world (Hylander and Meili, 2003), most notably in the Mediterranean region (Baldi and D'Amato, 1986; Barghigiani and Ristori, 1995; Cossa and Coquery, 2005; Rajar et al., 2007), which hosts about 65% of the world's cinnabar (HgS) deposits (Bargagli et al., 1986; Rytuba, 2003).

High concentrations of Hg deposited in fluvial sediments were documented by various studies e.g. Rhoades et al. (2009, VA, USA), including the widespread Hg contamination following two thousand years of mining activity in Almadén (Spain, Berzas Nevado et al., 2003; García-Ordiales et al., 2014, 2016) and five hundred years in Idrija (Slovenia, Gosar et al., 1997; Biester et al., 2000; Žibret and Gosar, 2006; Gosar, 2008; Gosar and Žibret, 2011; see more in § 5.1).

Between the 1860s and 1980s, the Monte Amiata Mining District (MAMD), located in southern Tuscany (Italy), produced about 102,000 t of Hg. A large amount (at least 30,000 t, and possibly as much as 44,000 t, Bombace et al., 1973; Benvenuti and Costagliola, 2016) was dispersed into the environment, notably into the hydrographic basin of the Paglia River (R.), a tributary of the Tiber River (the third longest river in Italy, flowing through the capital city of Rome). Rimondi et al. (2012) showed that, > 30 years after the mining activity came to a complete halt, Hg-rich processing residues and abandoned mine structures still constitute an environmental pollution problem. Gray et al. (2014) and Lattanzi et al. (2017) documented the long-distance transport of Hg along the Tiber River downstream from the MAMD. Pattelli et al. (2014) compared stream sediment contamination of the Paglia and Tiber rivers before and after a large flood event (November 2012) to assess its effects on total Hg contents. Although many aspects related to the contamination deriving from the MAMD have been analysed, an overall study considering the distribution of contaminant in the fluvial system and its links with geomorphological features and past channel changes was not adequately addressed.

In this paper, an integrated geomorphological and geochemical approach combining various data sources, observations and analyses is used to support an interpretation and understanding of the contaminant distribution in the upper catchment of the Paglia R. The contamination from the MAMD to the sediments of the upper Paglia R. catchment is used as a case study, aiming to: (i) describe and discuss the overall methodological framework for analysing the contaminant amount and distribution in the fluvial system; (ii) illustrate and discuss the spatial variability of contaminants along the analysed portion of the catchment; (iii) document an example of the evolution from point source to diffuse source of contamination.

2. Study area

2.1. General setting of the upper part of Paglia R. catchment

The upper part of the hydrographic basin of the Paglia R. extends over an area of about 720 km^2, straddling southern Tuscany, northern Latium, and central Umbria. The shape of the basin and the hydrographic net are mainly defined by the structural setting of two grabens: Radicofani to NNW (Liotta, 1994a, 1994b, 1996; Liotta and Salvatorini, 1994; Barchi et al., 1998), and Paglia-Tiber to SSE (Funiciello et al., 1981 - Fig. 1). The hydrographic basin is also morphologically influenced to the N by the volcanic structure of Radicofani, to N and E by the Horst of Monte Cetona (Bertini et al., 1991; Brogi et al., 2000); to NW by the volcanic structure of Monte Amiata; to W by the Horst of Monte Civitella - Monte Elmo; to the S by the presence of the Vulsini volcanic complex, and to SE by the Monte Peglia (east of the limits of Figs. 1 and 2).

The geological structure of this area is related to the Tertiary Apenninic orogeny and subsequent post-collision events (Brogi, 2008; Molli, 2008). These events led to the genesis of extensive magmatic and hydrothermal phenomena, with formation of the Monte Amiata volcano and the associated geothermal zone. As a result of this geodynamic history, the area is characterised by a stack of units over the western edge of the Adria tectonic plate: from bottom to top, these units are composed by Tuscan and Umbrian Units, detached from the Adria plate; Ligurian and Subligurian Units, consisting of fragments of oceanic basin and its oceanic-continental transition (Marroni et al., 2015 - Fig. 1). These units, mainly constituted by siliciclastic and carbonatic sequences, represent the pre-Neogenic substrate.

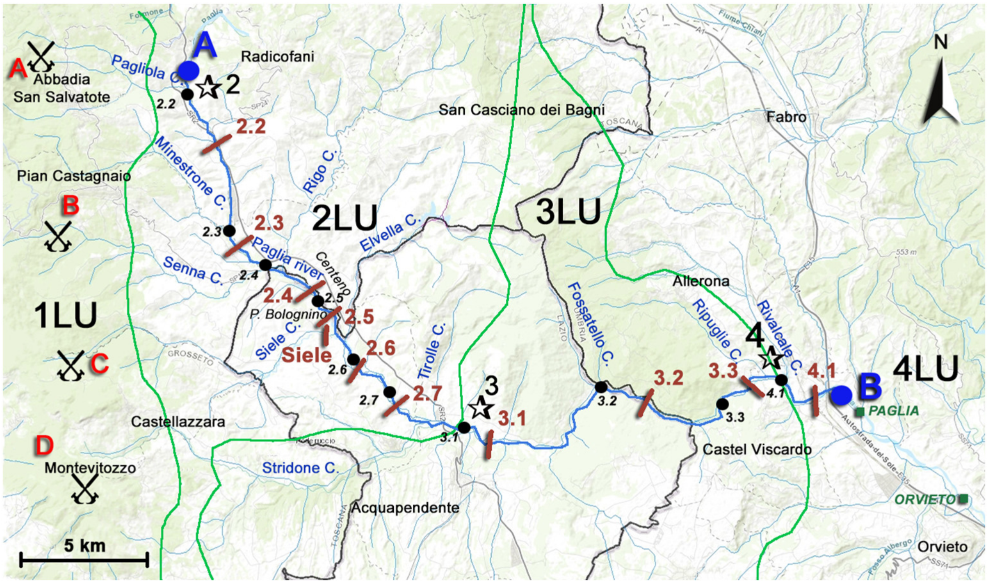

Fig. 2. Location of sampling sites along the studied stretch of the Paglia R. (between points **A** and **B**). The figure also shows the relevant spatial units (landscape units, segments, and reaches, as defined in § 4.1), the mining areas drained by the tributaries, and the two additional sampling points ("Paglia" and "Orvieto") located downstream of the studied stretch (§ 4.5). The stars (*.n) indicate the beginning of segments (§ 4.1), **n.n** (black dots) the beginning of the reaches, **n.n** (red bars) transects along the Paglia R., **Siele** (red font) the transect along the Siele C.
Landscape Units: **1LU** - Mountain area, **2LU** - Hilly areas, **3LU** - Mainly hilly areas, **4LU** - Intermontane plain unit.
Mining areas: **A** - Abbadia San Salvatore (drained by Pagliola C.), **B** - Case di Paolo - Senna mine (drained by Senna C.) - Cerro del Tasca (drained by Minestrone C.), **C** - Siele - Carpine (drained by Siele C.), **D** - Cornacchino (drained by Stridolone C.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

This substrate is overlain by a) Neogenic deposits (marine, transition and continental successions – Liotta, 1996; Marroni et al., 2015); b) Quaternary volcanic and volcano-sedimentary successions - Monte Amiata (Marroni et al., 2015) and Radicofani complexes (Conticelli et al., 2011) in the northern part, Vulsini complex to the south; c) continental deposits complex (Quaternary). The latter is characterised by: (1) Holocenic fluvial deposits: these are present along the Paglia R. valleys and its main tributaries, consisting mainly of sandy-silty beds and pebbles. The Paglia R. cuts through its alluvial deposits, locally 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 elevation (from 5 to 20 m) compared to the current course of the Paglia R. (e.g. Pleistocene terrace in Fig. 1).

2.2. The Paglia River

The studied stretch of the Paglia R. extends for about 43 km from the river starting point (marked by the confluence of the Pagliola and Cacarello creeks, about 4 km W of Abbadia San Salvatore - point A in Figs. 1 and 2; 388 m asl), to Allerona Scalo (point B in Figs. 1 and 2; 156 m asl). The area of specific interest has an average width of 500 m, for a total extension of approximately 18.5 km^2, and is characterised by present-day alluvial deposits and various orders of fluvial terraces.

The Paglia R. sediments lie for 53% of the length of the examined stretch over Neogenic sediments within the Radicofani Graben, for 36% over the pre-Neogenic substrate in the area of Cetona Horst and Quaternary volcanites of the Vulsini complex, and for the remaining 11% over the Neogenic sediments of the Paglia-Tiber Graben.

The course of the Paglia R. follows largely the NNW-SSE direction of Radicofani Graben, then it turns toward WNW-ESE, in the southern part of the Radicofani Graben. This change of direction is probably conditioned by the uprise of the area related to the emplacement of the Vulsini volcanic apparatus. Then the river assumes variable directions (SW-NE, NW-SE, WSW-ENE) when crossing the Cetona Horst, and in the final part it runs along the NNW-SSE direction of the Paglia-Tiber Graben.

2.3. Overview of mining activity and contamination problems

In the MAMD, the genesis of Hg deposits has been associated to the hydrothermal systems present in southern Tuscany during Pliocene-Quaternary, possibly with secondary enrichment during Pleistocene (Tanelli, 1983; Klemm and Neumann, 1984; Brogi and Fabbrini, 2009; Morteani et al., 2011; Gasparrini et al., 2013; Rimondi et al., 2015). Cinnabar was by far the prevalent mineral, while metacinnabar and native Hg were subordinate; accessory As sulfides (realgar and orpiment) were quite common.

Although the Monte Amiata area has been known since the antiquity for the presence of cinnabar, the Hg mining activity went on essentially from the mid-1800s to 1980 (Bombace et al., 1973; Strappa, 1977). In 1948, there were 42 mines in activity and several prospects. The run-of-the-mine had a Hg content of 0.6 to 2% (Klemm and Neumann, 1984; Morteani et al., 2011). The main mines of relevance for the Paglia R. were Abbadia San Salvatore, Siele - Carpine, Case di Paolo – Senna mine - Cerro del Tasca, and Cornacchino (Table 1 and Fig. 2); Abbadia San Salvatore was by far the most important.

The Hg contamination problems in the Paglia R. basin (Table S1) are mainly related with the presence of mining residues, including calcines (e.g. in Abbadia San Salvatore these materials cover an area of about 120,000 m^2). The presence of Hg in calcines can be attributed to an incomplete retorting process. This leads to the presence of residual cinnabar that was not converted into gases, and to formation of secondary Hg compounds (Gray et al., 2004; Esbri et al., 2010; Gray et al., 2010; Teršič et al., 2011a, 2011b, 2014; Rimondi et al., 2012, 2014a, 2014b; Smith et al., 2014).

The occurrence of Hg contamination in soils of the mining district of

Table 1
List of the mines, the main periods of mining activity, and the areas of the underlying hydrographic sub-basins of the Paglia R. watershed (according to www.mindat.org, 2018, Mascaro et al., 1991 and www.parcoamiata.com, 2018).

Hg mining areas	Period of main activity	Hydrographic basin(s)
Abbadia San Salvatore	1901–1981	Pagliola Creek (about 27 km^2)
Cerro del Tasca	1846–1855 1876–1971	Minestrone Creek (about 24 km^2)
Case di Paolo Senna mine	1846–1855 1876–1971	Senna Creek (about 35 km^2)
Siele Carpine	1846–1949 retorting active until 1981	Siele Creek (about 24 km^2)
Cornacchino	1872–1921	Stridolone Creek (about 98 km^2)

Abbadia San Salvatore and fluvial sediments along the Paglia R. and along the fluvial terraces of the Pagliola Creek is reported by several authors (Bombace et al., 1973; Fantozzi et al., 2013; Rimondi et al., 2012; Rimondi, 2013; Gray et al., 2014). The values of Hg concentration (Table S1) in both soils and fluvial sediments are usually beyond the threshold value of Italian laws (D. Lgs. 152/2006, 2006) for soils of public, private and residential use (1 mg/kg) - and locally also beyond the limit value of 5 mg/kg for commercial and industrial sites. Because of the presence of arsenic minerals in the ores, some dispersion of this element in the environment may occur. For this reason, As was analysed along with Hg in samples of this study, even if the previous work by Gray et al. (2014) did not find in fluvial sediments and water of the Paglia-Tiber system any value exceeding the regulatory thresholds.

3. Methods and data collection

An integrated geomorphological and geochemical approach combining various data sources, observations and analyses was used to analyse the contaminants distribution. The Paglia is a relatively high-energy, dynamic river characterised by a sequence of channel adjustments during the period of mining activity and during the last decades. Therefore, a geomorphological approach is fundamental for placing the mining activity and its consequences in an appropriate spatio-temporal, evolutionary context.

3.1. Delineation and characterization of spatial units

A multi-scale, hierarchical framework provided an appropriate spatio-temporal background for the metal contamination problem. We used the multi-scale approach developed by Rinaldi et al. (2013, 2015) and by Gurnell et al. (2016).

The delineation process consists in defining boundaries between spatial units from larger to smaller scales (Gurnell et al., 2016). The largest spatial unit in our study is the sub-catchment of the investigated portion of the Paglia R. Within this sub-catchment, a series of physiographic (or landscape) units are established on the basis of the catchment scale controls such as geology and physiographic characteristics. Then, segments are defined as sections of the river controlled by similar valley-scale influences and river energy conditions. Segments are at first delineated by accounting for the intersection of the main river with the physiographic units, as well as by considering a number of additional factors (e.g. major changes in valley gradient, catchment area, confluences of major tributaries, and lateral confinement).

Within each segment, one to several different reaches are identified along which boundary conditions are relatively uniform, displaying a near consistent internal set of process-form interactions (Brierley and Fryirs, 2005; Rinaldi et al., 2013, 2015; Gurnell et al., 2016). Reaches are thus delineated on the basis of: (a) valley setting, in terms of confinement; (b) channel morphology (e.g. sinuous, meandering, etc.); (c) presence of other discontinuities, such as presence of tributaries.

The lower hierarchical spatial order is that of the geomorphic units (GUs - Belletti et al., 2016), i.e. areas within the channel or in the floodplain containing a landform created by erosion or deposition of sediment, locally in association with vegetation. Once the spatial units are delineated, their properties are characterised using existing data and information.

The delineation and characterization of spatial units were performed on the basis of the following materials and methods:

1. Physiographic units were defined by using GIS data (layers), i.e. maps on catchment geology and digital elevation models (DEM).
2. Segments were delineated on GIS, and by using images from Google Earth.
3. Reaches were delineated by using images from Google Earth and orthophotos of 2012, from which parameters characterising river morphology (e.g. sinuosity, confinement) were calculated (according to Rinaldi et al., 2016).
4. Geomorphic units were checked during a field survey (2013), including sampling of transects (§ 3.3).

3.2. Multi-temporal analysis of channel changes

A multi-temporal analysis of the main channel changes occurred during the time interval from the start of the mining activity up to present time was performed, aiming at: (i) an overall interpretation and understanding of the evolution of channel and floodplain; (ii) interpretation and relative dating of recent terraces and modern floodplain.

A detailed reconstruction of the trajectory of channel changes is beyond the scopes of this paper, so in this study the analysis was restricted to the following three sources, corresponding to key years for mining activity and its consequences:

1. First topographic maps produced by the IGM (Istituto Geografico Militare, Italy) dated 1883 (scale 1:50,000), coinciding with the initial period of the MAMD mining activity;
2. Aerial photos of 1954 (IGM, scale 1:33,000), corresponding to one of peak periods of production of the MAMD;
3. Orthophotos of 2012 (Italian Environmental Ministry, scale 1:10,000), corresponding to the most recent and best resolution available aerial photos.

Maps and aerial photos were processed by a GIS analysis, consisting of orthorectification and georeferencing of each image, digitalization of channel margins, and measurement of channel width. Orthorectification was performed by using ArcGis 9.3, where maps and aerial photos were coregistered by using a series of Ground-Control Points.

Limitations and errors related to georectification and digitizing of channel morphological features have been widely discussed by various authors (e.g., Winterbottom, 2000; Hughes et al., 2006). According to previous similar analyses using the same methodologies (e.g., Winterbottom, 2000; Surian et al., 2009; Bollati et al., 2014), a maximum error of 10 and 7 m, respectively, was estimated for our measurements of channel width on the historical map and aerial photographs.

Multitemporal analysis of channel changes was then used to support interpretation and classification of the geomorphic units (baseflow channel, bar, floodplain and recent terraces) related to the channel evolution occurred during the investigated period (see next section).

3.3. Geomorphological field characterization of sampling transects

Following the delineation phase, a sampling transect was identified for each reach, based on accessibility of the field site and on representativeness of the typical assemblage of geomorphic units observed within the reach. A total of 11 sampling transects were selected (10 along the Paglia R., and 1 along the Siele Creek; Fig. 2). For each selected site, a delineation and classification of the geomorphic units along the transect was carried out by applying the GUS (geomorphic units survey and classification system, Belletti et al., 2016), that is embedded into a multiscale, hierarchical framework for the analysis of river hydromorphological conditions. Following this method, geomorphic units are classified within two broad spatial domains, bankfull channel and floodplain.

In this study, bankfull channel units predominantly comprise the baseflow channel and various types of depositional bars. Floodplain units are strongly influenced by the recent channel dynamics. In fact, channel incision and narrowing of the Paglia R., that occurred during about the last 150 years (§ 4.2), have determined the formation of a series of 'recent terraces', i.e. former historical levels of floodplain that became terraces because of bed incision. 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', according to the GUS (Belletti et al., 2016). In addition to field survey, GIS analysis of channel changes provided supplementary information to support the interpretation and classification of the various recent terraces. Following the delineation and classification, the length of each geomorphic unit along each transect was measured.

In order to get an estimation of the volumes of overbank fine sediments accumulated within the channel of 1883, the thickness of the overbank fine sediments overlying the gravel-bed deposits in proximity of the geochemical sampling sites was estimated by a hand borer. Then, the area of each polygon of the different floodplain units deposited after 1883 was measured by GIS, and the volume of fine sediment was calculated as product of area and thickness. The volume of fine sediment accumulated within the channel bed of 1883 was calculated for each reach, and was then used to get an estimation of the volumes of contaminants stocked within the floodplain (§ 4.4.2).

3.4. Geochemical sampling and analysis

The main sampling campaign was conducted in 2013 picking up a composite sample of about 1 kg of sediment, made up by mixing five sub-samples taken within a square of 5 m side around the selected sampling point. Sampling of floodplains and terraces was conducted with a hand borer taking the sediment from the surface down to the underlying gravel bed (that represents the channel bed or bar on which these sediments were deposited); the less thick C and B deposits were sampled with a shovel. Based on evidence from 2012 and 2016 floods (§ 4.5), we believe that the terraces are not affected by subsequent flood events.

Overall, a total of 102 samples were collected: 82 from the transects along Paglia R., 7 from the Siele transect, 5 from T1 terraces at Centeno (on the left bank of Paglia R., Fig. 1), and 8 taken from the Pleistocene terrace of Podere Bolognino (located on the right bank of Paglia R., Fig. 1). The Centeno and Podere Bolognino terraces were formed before 1883. They lie outside of the studied transects, and were sampled to establish a further comparison between situations pre-dating and post-dating mining activity. An additional set of eleven samples was collected in February 2016 to document the effect of a flood event occurred in those days (§ 4.5).

Each sample was air dried in the laboratory of the Department of Earth Sciences, University of Florence. Samples were then sieved, and the $< 250\,\mu m$ fraction was subsequently pulverized with specific agate mortars; all analyses were carried out on this fraction. This operational approach is based on the commonly reported finding that Hg is effectively concentrated in the fine fraction of river sediments (e.g., Žibret and Gosar, 2006; Rimondi et al., 2012).

However, to ascertain whether this approach is correct, 12 samples (two for each GU) were selected on the basis of geomorphic units (GUs) recognised within the 1883 riverbed (C - baseflow channel, B - bar, FP - modern floodplain, and recent terraces: T5, T4, T3; § 4.3). For these specific samples, the Hg content was determined both in the $< 250\,\mu m$ fraction, and in the total $< 2\,mm$ fraction. It turned out that the content of Hg in the fraction $< 250\,\mu m$ indeed represents ~100% of the total Hg of the sample (assuming that no Hg is contained in the $> 2\,mm$ fraction; Table S2). A similar behavior was assumed also for As.

The concentrations of the two elements were determined by ICP-OES following attack by aqua regia in a microwave oven of 0.5 to 1 g of material.

The accuracy and analytical precision were verified for each analytical batch, consisting of a total of 12 vials including 9 samples, one blank, one duplicate, and one certified standard: Montana Soil 2711 (Hg 6.25 mg/kg, As 0.1 mg/kg); in alternative, one of the following internal standards: MARS1 (Hg 2.4 mg/kg, As 2.6 mg/kg), TRSE (Hg 0.14 mg/kg, As 110.4 mg/kg), STSD-1 (Hg 0.11 mg/kg, As 17 mg/kg), previously tested by ACME - Analytical Laboratories Ltd. (USA), and periodically tested in our labs.

The chosen standard materials approach the Hg limit values in residential (1 mg/kg) and industrial (5 mg/kg) soil, as dictated by D. Lgs 152/06.

The lower limit of determination for Hg was 0.01 mg/kg. The results remained within confidence limits of 95% of the recommended values for the certified materials; the reproducibility of duplicate analyses was within 5% for both Hg and As.

To calculate the total mass of sediments in the GUs of interest (§ 4.4.2), it was necessary to have an estimate of the density. To this end, the density of five random samples from each GU was determined by means of a pycnometer. The measurements were carried out using small blocks cut from dried sediment cores. Therefore, measured densities should be considered as dry bulk densities. We believe that they are a reasonable approximation of the actual behavior in the field.

4. Results

4.1. Segmentation of the sub-catchment in spatial units

Based on criteria described in § 3.1, Landscape Units (LUs), segments and reaches of the Paglia R. were delineated (Fig. 2). Four LUs were defined:

1. Mountain areas (1LU), from 600 up to 1738 m a.s.l., occupying the upper portion of the catchment, characterised by volcanic and volcano-sedimentary sequences of the Monte Amiata and Radicofani edifices, and by Ligurian and Subligurian Units;
2. Hilly areas (2LU), below 600 m a.s.l., characterised by prevailing Neogene sedimentary deposits located in the Radicofani Graben;
3. Predominantly hilly areas (3LU), below 600 m a.s.l., characterised by Ligurian and Subligurian Units and volcanic and volcano-sedimentary sequences, located on the Monte Cetona Horst and along the Vulsini;
4. Intermontane plain unit (4LU), comprising a relatively high plain and including some low hilly portions, situated along the Paglia main stem, mainly characterised by Neogene sedimentary deposits located in the Paglia-Tiber Graben.

By intersecting the main streams with the LU, three segments were identified; these are shown as ***.n** in Fig. 2. On the basis of criteria exposed in § 3.1, a total of 10 reaches were then defined (**n.n** in Fig. 2) along the studied stretch of the Paglia river. Of these 10 reaches, seven lie on a Pliocene substrate (six in the Radicofani Graben: reaches 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, and one in the Paglia-Tiber Graben: reach 4.1), and three on the pre-Pliocenic substrate along the Monte Cetona Horst and on Quaternary volcanic rocks (reaches 3.1, 3.2, 3.3) (Table S3). The transects were defined within these reaches, and described with the same reference numbers (**n.n** - red bars in Fig. 2).

The Siele transect is along the tributary of the same name, and is located a few meters from the confluence of Siele Creek with Paglia R. (17 km from Abbadia San Salvatore and 13 km from the Siele Mine). This tributary develops mainly on the Pliocene substrate (within the Radicofani Graben) in the hilly unit (2 LU - Fig. 2).

4.2. Channel and floodplain evolution

Channel widths measured along the 10 sampling transects from maps/photos of the three reference years considered in this study (1883, 1954, 2012) are reported in Fig. 3. Because of this restriction to three periods only, the data do not allow for a detailed reconstruction of the evolutionary trajectory of the river. However, they provide a meaningful insight on the major channel adjustments from the start of the mining activity to the present. From these data, it is evident that the Paglia R. experienced a significant channel narrowing through time, with an average reduction of channel width of about 64% from 1883 to

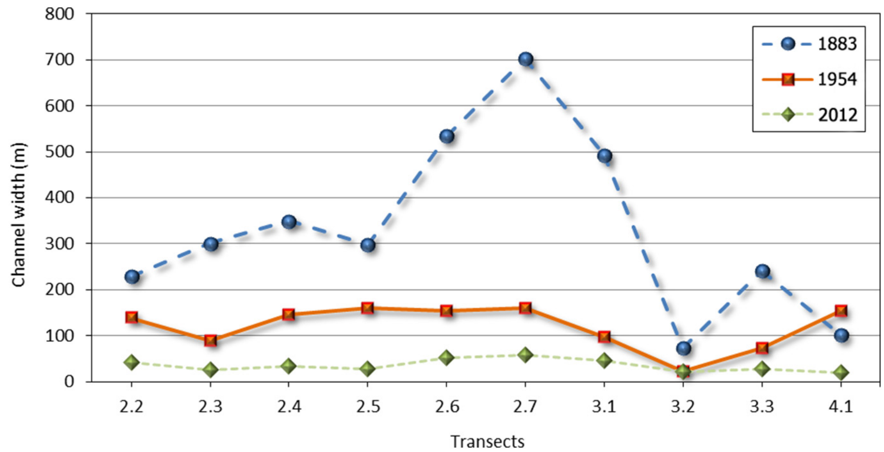

Fig. 3. Changes in channel width of the Paglia R. based on maps (1883) and aerial photos analysis (1954–2012).

1954, and a further reduction of about 70% from 1954 to 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 are consistent with those observed along the medium and lower alluvial portions of the Paglia R. (Cencetti et al., 2017), and, together with bed incision, represent a well known type of channel adjustment along most alluvial rivers in Italy and Europe (e.g. Liébault and Piégay, 2002; Surian and Rinaldi, 2003; Rinaldi, 2003; Rinaldi et al., 2009; Surian et al., 2009; Bollati et al., 2014; Scorpio et al., 2015; Scorpio and Rosskopf, 2016).

In the case of the Paglia R., bed incision was recognised by several evidences observed during the geomorphological field characterization. The two main evidences were: (i) differences in elevation between homologous geomorphic surfaces, i.e. modern floodplain vs. recent terraces corresponding to the floodplains of 1883 and 1954 (Rinaldi, 2003; Liébault et al., 2013); (ii) differences in elevation between top of gravel deposits exposed in bank scarps above current bed level, corresponding to the pre-incision bed elevation, and top of gravel deposits in the present channel bed. The causes of bed incision and narrowing, according to the existing literature on channel evolution of Italian rivers (e.g. Surian and Rinaldi, 2003; Rinaldi, 2003; Surian et al., 2009; Scorpio et al., 2015), are a combination of land use changes (i.e. afforestation) at catchment scale with intensive sediment mining. These disturbances have also affected the Paglia R. catchment (Cencetti et al., 2017), and therefore are interpreted as the causes of the observed channel adjustments in the study area. An additional cause of bed incision and narrowing could be a decrease of sediment supply consequent to mine closure.

The evaluation of channel adjustments (incision and narrowing) was fundamental for characterising the assemblage of geomorphic units in present conditions, and therefore for supporting the interpretation of the spatial distribution of metal contaminants. In fact, a sequence of recent terraces was generated by bed incision and narrowing, corresponding to former levels of floodplain and channel bed. This recognition allowed a correct interpretation of the different surfaces during the phase of geomorphological field characterization of the sampling transects (see next section).

On the other hand, a very recent (post 2012) local and partial widening of some reaches of the Paglia R. was observed; this phenomenon is also described by Bollati et al. (2014) and Nardi and Rinaldi (2015) in other rivers in Italy. According to these authors, the causes of this phenomenon that occurred from the 21st century could be attributed to a renewed sediment supply (mainly for bank erosion), greater mobility of these sediments due to a series of flood events, and a late morphological response to the cessation of intense exploitation of the materials in the riverbed (which took place between 1950 and early 1990s).

Finally, it should be noted that at the end of February 2016, a major flood event along the Paglia R. caused the deposition of overbank deposits above pre-existing GUs; samples of these sediments were collected to make a comparison with samples of the GUs taken before the event.

4.3. Geomorphological characterization and interpretation of sampling transects

As previously noted, the floodplain units are characterised by a series of recent terraces and a modern floodplain as a consequence of the channel adjustments occurred during the last 150 years. The following orders of terraces and lower surfaces have been identified (Fig. 4):

1. Old terrace (T1) (i.e. formed before the last 150 years), corresponding to an alluvial surface that is already recognised on the maps of 1883 as higher than the floodplain of that year;
2. 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;

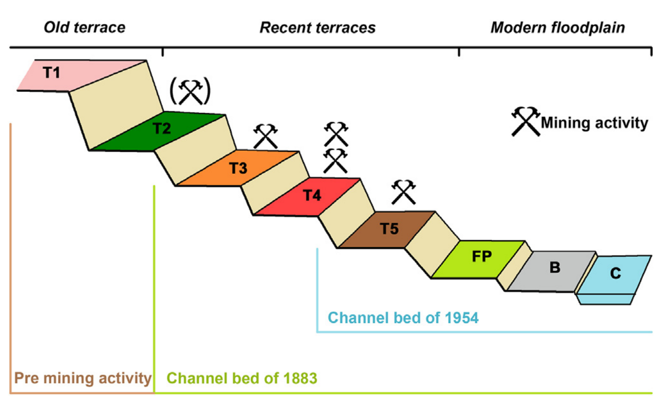

Fig. 4. Sketch of terraces, floodplain, channel bar and baseflow channel of the Paglia R.
T1 - Old terrace formed before the last 150 years, i.e. before the beginning of the mining activity; T2 - Recent terrace interpreted as the modern floodplain in the maps of 1883; T3 - Recent terrace formed between 1883 and 1954; T4 - Recent terrace formed after 1954, corresponding to the modern floodplain recognised in the aerial photos of 1954; T5 - Recent terrace formed between 1954 and 2012; FP - Modern floodplain, corresponding to the lowest flat and vegetated surface adjacent to the river bed; B - Channel bars, i.e. various types of depositional bars; C - Baseflow channel corresponding to the submerged portion of the channel bed.

3. Recent terrace (T3) formed after 1883 and before 1954, corresponding to a flat surface at an intermediate elevation between T2 and T4, that has been interpreted as a recent terrace on the recent terraces on the aerial photos of 1954;
4. Recent terrace (T4) formed after 1954 and before 2012, corresponding to the modern floodplain recognised on the aerial photos of 1954;
5. Recent terrace (T5), formed after T4, but before 2012, corresponding to a flat surface at an intermediate elevation between T4 and the modern floodplain, coinciding with portions of the channel bed of 1954;
6. Modern floodplain (FP), corresponding to the lowest flat and vegetated surface adjacent to the river bed, created by lateral and vertical accretion under the present river flow and sediment regime (recognised in the aerial photos of 2012 and during the field survey);
7. Channel bars (B), i.e. various types of depositional bars (recognised in the aerial photos of 2012 and during the field survey);
8. Baseflow channel (C), corresponding to the submerged portion of the channel bed (recognised in the aerial photos of 2012 and during the field survey).

As can be seen in Fig. 4, some GUs that are present within the 1883 channel bed were formed during mining activity of MAMD: T2 at the very beginning, T3 during the initial phase, T4 during the maximum period of activity (years 1950–60s), T5 during the final and closing stages (years 1980s), and possibly after (but before 2012). This concept will be further elaborated in the following Discussion.

For each transect, a sketch representing the distribution, lateral extension and elevation of the different geomorphic units was obtained (an example of transect is reported in Fig. 5). Past channel adjustments (i.e. incision and narrowing) caused changes in the distribution and extension of the different geomorphic units through time (see Table 2 for an example referred to the transect of Fig. 5).

4.4. Geochemical results

A summary of the analyses carried out in the 102 collected samples is reported in Table 3. It appears that the concentrations of Hg of all samples taken from GUs FP, T5 and T4 of the transects along Paglia R. are largely above the Italian legal limit (1 mg/kg) for residential soils; also most samples from C, T2 and T3 are above this threshold. For all GUs, the mean Hg values are always higher than 3 mg/kg, and the median values are higher than 2 mg/kg.

In the Paglia R., the highest mean and median Hg concentration values are observed in recent T4 terraces (26.4 mg/kg and 17 mg/kg, respectively), but the highest values of this study (up to 185 mg/kg) occur along the Siele transect, for GUs C, B, FP, and T4. On the other hand, the GU T1 along transect 3.2 shows a value of Hg of 0.8 mg/kg, consistent with the values found in Centeno for the same GU, and at Podere Bolognino for a Pleistocene terrace. These Hg concentrations are comparable with, or lower than, the local background for the Amiata area (estimated at 2 to 6 mg/kg; Rimondi, 2013).

Table 2
Temporal evolution of channel bars and baseflow channel widths, and relative percent values of the narrowing (with respect to 1883 width) as a consequence of the bed incision in the transect 2.2.

Period	GUs along the 2.2 transect								C + B	% of narrowing
2013	T4	T5	FP	C	B	FP	T5	T4	41.7 m	81.71
1954	FP	C	B	B	B	B	B	FP	138 m	60.53
1883	B	C	C	C	C	C	C	C	228 m	–

Fig. 6 is a graphic portray of Hg concentrations (mean values between the two banks of the river) in the GUs in transects along the Paglia R. The distribution of Hg shows evident asymmetries. In particular, the highest values occur in the following units and transects:

– T4 along the transects 2.2, 2.5 and 2.6 (> 30 mg/kg)
– FP along the transects 2.2, 2.3 (> 30 mg/kg)
– C along the transects 2.6 and 2.7 (> 20 mg/kg).

4.4.1. Arsenic

Arsenic concentrations fall within the local baseline values (11 mg/kg after Gray et al., 2014), and are always below the limit prescribed by the Italian law for soils for civil use (20 mg/kg - D.Lgs 152/2006, 2006). The presence of As in these concentrations is presumably of little environmental concern, and will be not further discussed in this paper.

4.4.2. Estimates of total Hg mass in the sediments

In this section we attempt a quantification of the total Hg masses contained in selected GUs. Sediments belonging to GUs outside the 1883 channel bed were not taken into account, because they were mostly accumulated before the beginning of mining activity (§ 4.3 and Discussion). The volumes of river sediments accumulated in the reaches were calculated based on the extension of the GUs and their thickness (§ 3.3), and the corresponding masses were then calculated by using the average density (§ 3.4). Following the assumption that all Hg is contained only in the < 250 μm fraction (§ 3.4), the GU masses were reduced proportionally to the relative amount of this granulometric fraction. From these reduced masses, considering the Hg concentrations, we calculated the Hg masses contained in GUs for each specific transect, and then we summed up the Hg masses for each GU. Table 4 summarizes the results of the calculations; because of the above mentioned assumption, the Hg masses shown represent only minimum estimates.

Table 4 shows that the highest contents of Hg are found in T4 deposits, followed by deposits of FP, T3 and T5. In order to identify the most dangerous reaches in terms of mass of contaminants and potential environmental hazards, the mass of Hg was calculated for each reach (Table S4). The reach 3.1 is the one with the largest amount of Hg (25 t), and therefore with the highest environmental risk, followed by reaches 2.3 (12 t) and 2.5 (10 t).

The comparatively high mass of Hg associated with FP in some reaches (2.3, 7 t; 2.6 and 4.1, 4 t each; 3.1, 3 t) may be explained with the very recent (post 2012) local and partial enlargement of the Paglia

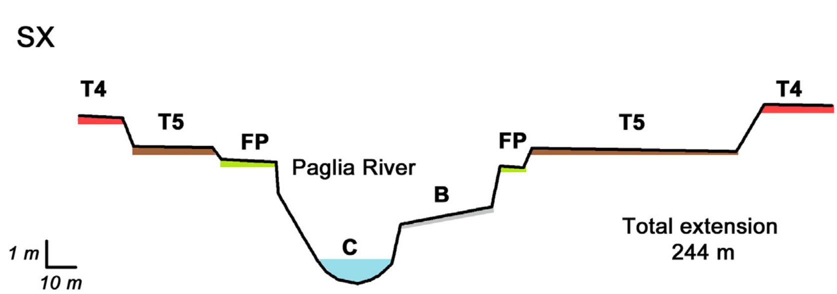

Fig. 5. Example of 2.2 transect with the corresponding post-1954 geomorphic surfaces.

Table 3
Intervals, mean and median values of Hg and As concentrations in GUs along the Paglia R. and Siele C. transects. All values in mg/kg.

Morphological units		Hg range	Hg mean	Hg median	As range	As mean	As median
Paglia R.	C	0.2 ↔ 27.5	8.9	4.8	4.1 ↔ 8.2	5.2	5.0
	B	0.6 ↔ 22.4	9.4	8.8	4.1 ↔ 6.6	5.2	5.1
	FP	2.6 ↔ 97.9	19.1	13.0	3.8 ↔ 6.6	5.6	5.6
	T5	1.3 ↔ 13	5.4	4.0	5.1 ↔ 6.7	5.6	5.3
	T4	44 ↔ 66.9	26.4	17.0	4.9 ↔ 7.1	6.0	6.0
	T3	0.4 ↔ 22.6	9.4	11.0	3.8 ↔ 6.5	5.4	5.6
	T2	0.1 ↔ 17.3	3.7	2.0	3.2 ↔ 10.1	6.9	6.7
	T1 (pre 1883)	0.8	–	–	4.5	–	–
Siele C.	C	29.4	–	–	4.9	4.9	4.9
	B	79 ↔ 79.4	79.2	79.2	6.0	6.0	6.0
	FP	182 ↔ 185.5	183.7	183.7	5.2↔5.4	5.3	5.3
	T4	90 ↔ 94	92.0	92.0	4.4↔4.6	4.5	4.5
Centeno	T1 (pre 1883)	< 0.05 (D.L.) ↔ 1.1	0.3*	0.2*	n.a.	–	–
Pod. Bolognino	Pleistocenic Terrace	< 0.05 (D.L.) ↔ 5.4	0.6*	0.6*	n.a.	–	–

n.a. = not analysed.
*Calculated assuming a nominal concentration of 0.05 mg/kg for samples below detection limit (D.L.)

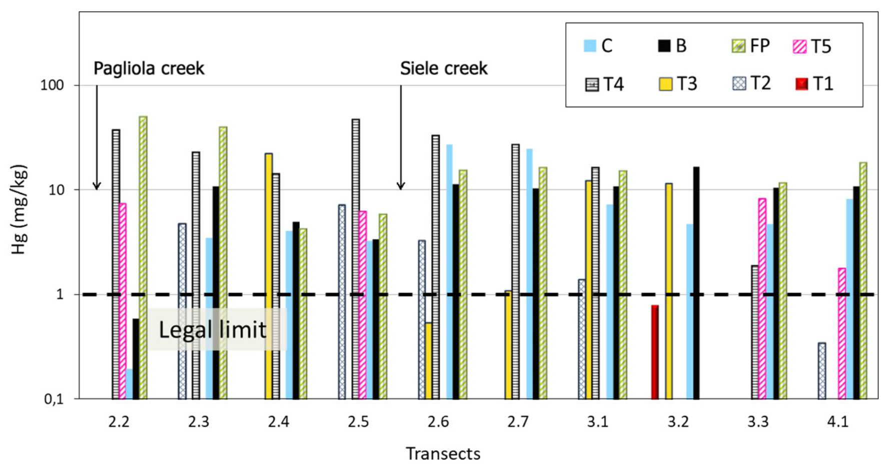

Fig. 6. Hg concentrations (mean values between the two banks of the river) in MUs along the transects of Paglia R. The Italian Hg limit (D.Lgs 152/2006, 2006) of 1 mg/kg in soil for public, private and residential use is shown. The position of Pagliola and Siele creeks confluence is shown by arrows.

Table 4
Thicknesses, volumes and masses of sediments of selected GUs along the Paglia R. transects.

	FP	T5	T4	T3
Range (cm)	5 ÷ 100	15 ÷ 125	15 ÷ 130	15 ÷ 150
Mean (cm)	35	63	52	54
Median (cm)	22	30	45	25
Volume (m^3)	814,371	435,873	2,155,897	636,175
Density (kg/m^3)	2130	1915	1663	1730
Mass (t)	1,734,612	834,697	3,585,256	1,100,583
Hg mass (t)	19	1	39	4

R. channel (§ 4.2). This partial enlargement probably reduced the speed of the stream water, creating favorable conditions for deposition of Hg-bearing particulate.

4.5. The flood event of February 2016

As previously noted, a major flood event occurred along the Paglia R. in February 2016. A comparison was made between the Hg concentrations of the overbank deposits of this event, and the deposits of baseflow channel, bar, and floodplain (Table 5), to ascertain whether this event caused an important remobilization of Hg-contaminated sediments, as demonstrated by Pattelli et al. (2014) for the November 2012 event.

In most cases, the Hg concentrations of 2016 overbank flood

Table 5
Hg concentration values of baseflow channel (C), bar (B) and floodplain (FP) collected in 2013, and of the overbank deposits of the February 2016 flood.

Transects	C Hg (mg/kg)	B Hg (mg/kg)	FP Hg (mg/kg)	Flood sediments February 2016 Hg (mg/kg)	Flood sediments, November 2012° Hg (mg/kg)
2.2	0.2	0.6	50.6*	38.2	10 (P08)
2.3	3.5	10.9	40.3	39.6	40 (P07)
2.4	4.1	5.0	4.3*	4.4	–
2.5	3.3	3.4*	5.9*	5.6	–
2.6	27.5	11.4*	15.5*	19.4	–
2.7	25.1	10.4*	15.6	12.1	–
3.1	7.4	10.9*	15.4*	17.2	16 (P06)
3.3	4.8	10.6	11.8	7.1	2 (PAG1)
4.1	8.3	10.9*	18.4*	5.0	Mean 8.5 (PAG2)
Paglia**	–	–	–	6.7	3 (PAG3)
Orvieto**	–	–	–	3	0.05 (PAG4)

– No data.
°(After Pattelli et al., 2014; in parentheses, their sample label is reported).
* = mean value between the two banks.
**These samples lie outside the river segment investigated in this study, and were taken only for comparison with the previous data of Pattelli et al. (2014).

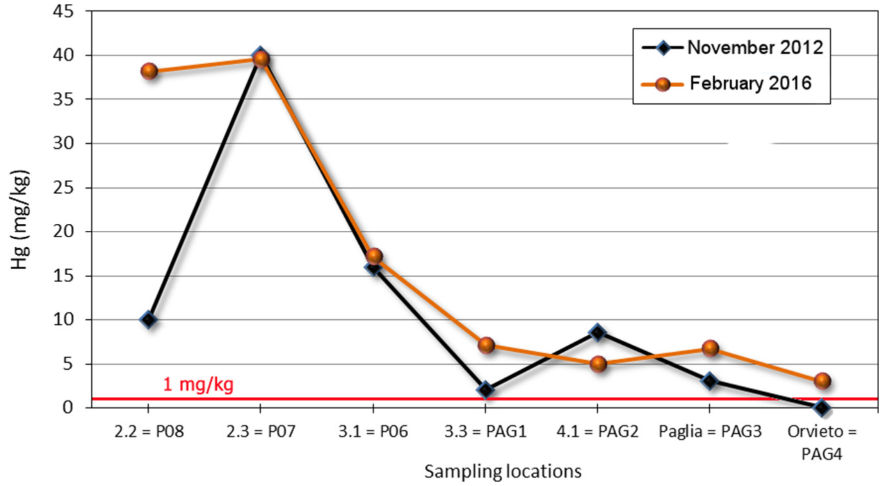

Fig. 7. Hg contents in overbank sediments of the flood events of February 2016 and November 2012 (data for the latter from Pattelli et al., 2014). For each sampling site, the first label is the one used in this work, the second is that of Pattelli et al. (2014).

deposits are higher than in deposits of C and B. A significant exception are C deposits downstream of Siele C. (transects 2.6 and 2.7), where Hg concentrations are higher (Fig. 6), showing that this tributary currently discharges, under “normal” conditions, sediments with > 20 mg/kg Hg into the Paglia R.

Downstream of Pagliola C. (transects 2.2 and 2.3), very high (> 30 mg/kg) contents of Hg are recorded both in FP deposits and in 2016 overbank deposits. As shown by Table 5, the general trend of concentrations of Hg in deposits attributed to the flood of February 2016 is similar to that of the FP (i.e., they decrease from transects 2.2–2.3 to 2.4, then sharply increase in transect 2.6–2.7 after the confluence of Siele C.).

Some of the 2016 flood deposits were collected at the same sites of the previous sampling by Pattelli et al. (2014) following the 2012 flood event (samples P08, P07, P06, PAG1, PAG2 – Table 5 and Fig. 7). To strengthen the comparison between the effects of the two events, two additional overbank sediment samples (Paglia and Orvieto in Fig. 2 and Fig. 7) along the Paglia R. were obtained south of the study area, in the sites corresponding to samples PAG3 and PAG4 of Pattelli et al. (2014). The results of the analyses are reported in Table 5, and graphically portrayed in Fig. 7.

From comparison of these data, it is noted that in every major flood event large quantities of Hg- contaminated sediments are transported (the concentration values are in almost all cases above the limits set by the Italian law for residential soils of 1 mg/kg). Except for transect 2.2, Hg concentrations at each specific location are similar in the two flood events (the differences are of the same order of the analytical error). In transect 2.2, the value of Hg concentration is about four times higher in the overbank deposits of 2016 compared to those of 2012, indicating that in the 2016 event the Pagliola C., located upstream of Section 2.2, discharged heavily Hg-contaminated sediments.

5. Discussion

This study confirms and expands the results by Rimondi et al. (2012) and Gray et al. (2014) about dispersion of Hg-contaminated sediments in the Paglia R. basin. Moreover, combination of geomorphologic features and geochemical analysis allows a more precise picture of Hg distribution, and a first attempt to quantify the masses stored in the different GUs of the Paglia R. (see Table 4).

The oldest GUs considered in this study (T1) were formed before 1883, and therefore received little input from the mining activity, except possibly in the occasion of large flood events causing inundation and overbank deposition over these surfaces. Although we have few samples of these GUs, they consistently show comparatively low Hg concentrations, in the order of, or even lower than, the estimated local background (Rimondi, 2013). Therefore, the Hg concentration encountered in T1 could represent a local background value for Hg, reflecting the pre-mining concentration but indeed the presence of a diffuse Hg anomaly (with respect to the average Hg value of European soils – e.g., Table 4 in Teršič et al., 2014) in the Paglia drainage basin.

The T2 terraces represent an evolution of the 1883 FP. These terraces may have been inundated during ordinary flood events, therefore overbank deposition of contaminated sediments from ongoing mining activities possibly occurred. However, in the first decades (1850–1883) of activity the production was modest (< 2% of the cumulate of the district; Strappa, 1977). Accordingly, the impact of mining on this GU was marginal, with some concentration values that can be considered anomalous with respect to the local background, but with mean values not exceeding this background.

The first GUs that clearly show anomalously high Hg values are T3. These were formed between 1883 and 1954, i.e. in a time span fully coincident with mine activities. However, the extent of the anomaly is only moderate (Table 3), suggesting that these units might predate the peak of mining production (occurring in the 20th century: Strappa, 1977).

The GUs containing the highest average concentrations and the largest Hg total mass (39 t) are the recent terraces T4. These GUs were formed as an evolution of the 1954 FP, i.e. they received the influence of the peak production period in the MAMD. This period corresponds to the phase of maximum release of pollutants that have been accumulated in the river sediments.

The T5 GUs were also formed after 1954 and before 2012, but are younger than T4. Indeed the comparatively low Hg contents suggest that they were only marginally affected by mining activities, i.e. they were formed shortly before, or after, the closure in the 1980s.

The current floodplains (FPs) may show quite high Hg concentrations, and contain significant masses (19 t) of the metal. This large Hg input is somewhat surprising, and could be due both to the last flood events, that have deposited abundant amounts of sediment and contaminated materials on this GU, and to the recent local and partial enlargement of some reaches of the Paglia R. (§ 4.2).

It is important to highlight how the erosion of some GUs can result in a high environmental risk for the large mass of contaminants present. It should also be noted that any eventual remediation plan of these GUs must take into account that in every major flood event large quantities of locally heavily Hg-contaminated sediments are transported downstream, and may be re-deposited onto the pre-existing GUs.

In this context, the influence of the Paglia R. tributaries appears to be fundamental in the supply of Hg-contaminated sediments (Fig. 6):

1) Pagliola C. drains the mining area of Abbadia San Salvatore; despite that this area has been subject to decommissioning and is undergoing reclamation, during flood events the drainage carries high concentrations of Hg in fluvial sediments, as evidenced in the FP (where Hg concentration may reach 97.9 mg/kg - Table 3, and transect 2.2, Fig. 6). The effect of the input from the Pagliola C. is also evident in T4 terraces in transect 2.2 (Fig. 6). On the other hand, the deposits of baseflow channel (C) and bar (B), sampled during a period without intense floods (2013–2014), showed Hg concentrations < 1 mg/kg (Fig. 6 - transect 2.2).
2) Siele C. drains the Siele - Carpine mining area, where reclamation was completed in 2001. However, along this creek we find the samples with the highest Hg concentrations in all GUs (C, B, FP and T4 samples taken from the transect Siele - see Table 3). Hence, Siele C. is still contributing sediments with high Hg concentrations to current deposits of Paglia R. (GUs C and B - transect 2.6 in Fig. 6). This phenomenon also occurred during the formation of FPs. Likewise, Siele C. may have contributed Hg to the FP of 1954 (now transformed by fluvial engraving in T4 - transect 2.6 in Fig. 6).

A high concentration of Hg in T4 is recorded also in transect 2.5 (Fig. 6). Such a high concentration may be interpreted by making reference to the morphological evolution of the river, namely to the existence, in 1954, of an extended FP (Fig. 8), where a slowdown of the stream speed could have favored the deposition of Hg-contaminated sediments from mine runoff.

5.1. Comparison with Idrija Hg district

In this section, we establish a comparison between the here described fluvial sediment contamination and that occurring in another major Hg mining district discharging into the Mediterranean Sea: Idrija (Slovenia; Gosar, 2008; Gosar and Žibret, 2011; Bavec et al., 2014; Gosar and Teršič, 2015; Baptista Salazar et al., 2017), the second most important in the world.

Idrija is an area where a naturally elevated (2 mg/kg, Gosar et al., 1997) Hg concentration is technologically enhanced due to 500-year long Hg mining. In this area detailed investigations on Hg distribution in different environmental compartments such as calcine, mine tailings, soil, atmosphere, stream sediments, river suspended matter, road sediments and attic dusts were conducted (Biester et al., 2000; Gosar and Čar, 2006; Gosar, 2008; Teršič et al., 2011a, 2011b, 2014; Bavec et al., 2014; Gosar and Teršič, 2015; Baptista Salazar et al., 2017).

The Idrijca river drains the district before becoming an affluent of Soča-Isonzo R., which flows directly into the Sea (see Covelli et al., 2001).

Table 6 shows the comparative characteristics of the two rivers draining the mining districts, the Hg production of the two districts, the amount of Hg dispersed in the environment, the Hg concentrations in floodplains, terraces and actual sediments, the volume of contaminated sediments, the masses of Hg in the fluvial sediments, and the fraction of total Hg dispersed accumulated in the river sediments.

As it appears from the comparison, the productions and the total amounts of the Hg dispersed in the environment are similar for both districts. On the other hand, the estimated mass of metal accumulated in the fluvial sediments is much higher (30 times) at Idrija. This difference is primarily the result of a much higher average Hg concentration mainly in the floodplain and in first order terraces at Idrija. The volumes of sediments involved are also twice higher for Idrija, but we notice that in this district the sediment thickness was calculated with respect to the current bed of the river, regardless of the time of accumulation (see Žibret and Gosar, 2006). On the contrary, in the case of Paglia R., the thickness of contaminated sediments is calculated with respect to the effective riverbed at the moment of the deposition (§ 3.3). We therefore suggest that the volumes (and consequently the total Hg mass) of contaminated sediments at Idrija may be overestimated. On the other hand, in the calculation of the Hg mass in the Paglia sediments we assumed that all Hg is contained in the < 250 μm fraction, and that the coarser fraction does not contain Hg. Moreover, only the GUs deposited after 1883 (T3, T4, T5, and FP) were considered, but

Table 6
Comparative features of rivers draining the two mining districts of Monte Amiata and Idrija.

	MAMD	Hg mining district of Idrija (Slovenia)
Length of the river	Paglia R. - 43 km	Idrijca R - 60 km
Hg production period	1870–1981	1490–1995 (Žibret and Gosar, 2006)
Hg yield	102,000 t (Gray et al., 2014)	107,000 t (Žibret and Gosar, 2006) > 140,000 t (Mlakar, 1974; Miklavčič, 1999; Dizdarevič, 2001)
Hg dispersed in the environment	44,000 t (Bombace et al., 1973)	> 35,000 t (Mlakar, 1974; Miklavčič, 1999; Dizdarevič, 2001) 45,500 (Gosar, 2008)
Mean Hg concentration floodplains and terraces (mg/kg)	Floodplains (FP): 19.1 Recent terraces (T3 to T5): 5.4 to 26.4 (fraction < 0.250 mm)	Floodplain: 342.3 1st order terraces: 145.3 2nd order terraces: 7.8 (Žibret and Gosar, 2006 fraction < 0.063 mm)
Range of Hg concentration in actual fluvial sediments (mg/kg)	Channel sediments (C): 0.2–27.5 Bar sediments (B): 0.6–22.4 (fraction < 0.250 mm)	Stream sediments: 2.3–9.5 (fraction < 0.04 mm) Stream sediments: 14–27 (fraction < 0.125 mm) (from Table 1 in Gosar and Teršič, 2015)
Volumes of contaminated sediments	Floodplains (FP): 0.81×10^6 m^3 Recent terraces (T3 to T5): 3.23×10^6 m^3	Floodplains: 4×10^6 m^3 1st order terraces: 2.3×10^6 m^3 2nd order terraces: 2.3×10^6 m^3 (Žibret and Gosar, 2006)
Mass of Hg in the fluvial sediments	63 t	2029 t (Žibret and Gosar, 2006)
Fraction of total Hg dispersed accumulated in river sediments	0.2%	5%

Fig. 8. View of the extended FP in 1954 (a) that became a T4 terrace as a consequence of fluvial engrave (b - current situation) along the transect 2.5.

from the collected data it would appear that part of the sediments belonging to T2 (located off the 1883 riverbed) could have been contaminated by Hg derived by the mining areas present in the basins of the tributaries, and/or by deposition of contaminated sediments resulting from post-1883 major floods – see previous Discussion. The here reported value of 63 t Hg for Paglia R. is therefore a minimum estimate.

The recent reclaiming of some areas where the mining wastes were discharged (e.g., Abbadia San Salvatore, or the Siele-Carpine mining area), that may be considered as point sources of pollution, conceivably reduced the feed of contaminants in the superficial fluvial network. However, our results indicate that the effects of the diffuse sources, now represented by the stream sediment of the Paglia R., will affect the environmental quality of the surficial drainage system for a long time, also at a considerable distances from the MAMD mining district (Gray et al., 2014). Assuming that the transport of Hg by the Paglia R. is constant, the flux estimate of about 11 kg/y (Rimondi et al., 2014b) implies that the removal of about 63 t of Hg will take a time lapse in the order of 10^3 years.

6. Conclusions

The geomorphologic-geochemical approach adopted in this study shows that the sediments of the Paglia R. belonging to the various geomorphic units (GUs) exhibit variable, locally elevated Hg concentrations, both in the transects and along the course. This variability is not casual, but it is conditioned by both past and current fluvial dynamics, and by the mining activity in the Monte Amiata District, the impact of which can still be perceived over 30 years from the end of mining.

The course of Paglia R. has undergone, and is undergoing, a strong fluvial dynamics; in particular, since 1883 there has been a gradual incision. As a consequence, the most recent GUs can be eroded, and thus become secondary sources of contaminants. On the other hand, currently a trend reversal is locally observed; where this last phenomenon occurs, there are favorable conditions for a greater accumulation of contaminated sediments.

The estimate of the total mass of Hg in contaminated sediments in the GUs of the analysed stretch (43 km) of the Paglia R. is 63 t. This mass can be mobilized and redistributed during major flood events and conceivably will affect the environmental quality of the river for the next future.

The Paglia R. tributaries contribute to this process, in particular:

– Pagliola C., which drains the partly remediated mining area of Abbadia San Salvatore, continues to supply Hg contaminated materials, as evidenced by sediments accumulated in the current floodplain (FP) or deposited during major flood events;
– Siele C., that drains the reclaimed Siele-Carpine mining area, carries, in all current flow conditions, sediments with the highest Hg concentrations documented in this study.

Knowledge of the river dynamics of Paglia R. and of its current and past GUs is crucial for identifying the areas with the highest environmental risk. The approach of this study, combining geomorphologic and geochemical aspects, appears quite effective for identifying the actual and potential environmental hazards and for planning future monitoring. Full remediation of a diffuse pollution source like that represented by stream sediments in a large river system (like Paglia-Tiber) may be complex and expensive. It may be necessary a long term (years, or even decades) limitation of land and natural resource use (primarily fishing) along the river courses. Moreover, it seems advisable monitoring all the activities carried out along the rivers, in order to minimise the effects on human health.

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Conflict of interests

The authors declared no conflict of interests.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2018.08.043.

References

Baldi, F., D'Amato, M.L., 1986. Mercury pollution in marine sediment cores near cinnabar deposits and a chlor-alkali plant. Sci. Total Environ. 57, 111–120.
Baptista Salazar, C., Richard, J.H., Horf, M., Rejc, M., Gosar, M., Biester, H., 2017. Grain-size dependence of mercury speciation in river suspended matter, sediments and soils in mercury mining area at varying hydrological conditions. Appl. Geochem. 81, 132–142.
Barchi, M., Minelli, G., Pialli, G., 1998. The CROP 03 profile: a synthesis of results on deep structures of the northern Apennines. Mem. Soc. Geol. Ital. 52, 383–400.
Bargagli, R., Barghigiani, C., Maserti, B.E., 1986. Mercury in vegetation of the Mount Amiata area (Italy). Chemosphere 15, 1035–1042.
Barghigiani, C., Ristori, T., 1995. Preliminary study on mercury uptake by *Rosmarinus officinalis* L. (Rosemary) in a mining area (Mount Amiata, Italy). Bull. Environ. Contam. Toxicol. 54, 519–525.
Bavec, Š., Biester, H., Gosar, M., 2014. Urban sediment contamination in a former Hg mining district. Idrija, Slovenia. Environ. Geochem. Health 36, 427–439.
Belletti, B., Rinaldi, M., Bussettini, M., Comiti, F., Gurnell, A.M., Mao, L., Nardi, L., Vezza, P., 2016. Characterising physical habitats and fluvial hydromorphology: a new system for the survey and classification of river geomorphic units. Geomorphology 283, 143–157.
Benvenuti, M., Costagliola, P., 2016. Il distretto mercurifero del comprensorio amiatino: nuovi dati sull'impatto ambientale nel sistema fluviale Paglia-Tevere. Geol. Ambient. XXIV (4), 2–5.
Bertini, G., Cameli, G.M., Costantini, A., De Candia, F.A., Di Filippo, M., Dini, I., Elter, F.M., Lazzarotto, A., Liotta, D., Pandeli, E., Sandrelli, F., Toro, B., 1991. Struttura geologica fra i monti di Campiglia e Rapolano Terme (Toscana Meridionale): stato attuale delle conoscenze e problematiche. Studi Geol. Camerti 1, 155–178.
Berzas Nevado, J.J., García Bermejo, L.F., Rodríguez Martin-Doimeadios, R.C., 2003. Distribution of mercury in the aquatic environment at Almadén, Spain. Environ. Pollut. 122, 261–271.
Biester, H., Gosar, M., Covelli, S., 2000. Mercury speciation in sediments affected by dumped mining residues in the drainage area of Idrija mercury mine, Slovenia. Environ. Sci. Technol. 34, 330–336.
Bollati, I.M., Pellegrini, L., Rinaldi, M., Duci, G., Pelfini, M., 2014. Reach-scale morphological adjustments and stages of channel evolution: the case of the Trebbia River (Northern Italy). Geomorphology 221, 176–186.
Bombace, M.A., Cigna Rossi, L., Clemente, G.F., Zuccaro Labellarte, G., Allegrini, M., Lanzola, E., Gatti, L., 1973. Ricerca ecologica sulle zone mercurifere del Monte Amiata. Rivista Igiene e Sanità Pubblica 29, 191–237.
Brierley, G.J., Fryirs, K.A., 2005. Geomorphology and River Management: Applications of the River Styles Framework. Blackwell.
Brogi, A., 2008. The structure of the Monte Amiata volcano-geothermal area (Northern Apennines, Italy): Neogene-Quaternary compression versus extension. Int. J Earth Sci (Geol Rundsch) 97, 677–703.
Brogi, A., Fabbrini, L., 2009. Extensional and strike-slip tectonics across the Monte Amiata-Monte Cetona transect (Northern Apennines, Italy) and seismotectonic implications. Tectonophysics 476, 195–209.
Brogi, A., Cornamusini, G., Costantini, A., Di Vincenzo, G., Lazzarotto, A., 2000. Cretaceous volcanism of the Southern Tuscany: record of volcanic bodies from Tuscan succession of Rapolano Terme. Mem. Soc. Geol. Ital. 55, 329–337.
Cáceres, L.M., Olías, M., De Andrés, J.R., Rodríguez-Vidal, J., Clemente, L., Galván, L., Medina, B., 2013. Geochemistry of Quaternary sediments in terraces of the Tinto River (SW Spain): Palaeoenviromental implications. Catena 101, 1–10.
Cencetti, C., De Rosa, P., Fredduzzi, A., 2017. Geoinformatics in morphological study of River Paglia, Tiber River basin, Central Italy. Environ. Earth Sci. 76, 128.
Conticelli, S., Avanzinelli, R., Marchionni, S., Tommasini, S., Melluso, L., 2011. Sr-Nb-Pb isotopes from the Radicofani Volcano, Central Italy: constraints on eterogeneities in a veined mantle responsible for the shift from ultrapotassic shoshonite to basaltic andesite magmas in a post- collisional setting. Mineral. Petrol. 103, 123–148.
Cossa, D., Coquery, M., 2005. The Mediterranean Mercury Anomaly, a Geochemical or a Biological Issue. In the Mediterranean Sea. Springer, Berlin, Germany, pp. 177–208.

Covelli, S., Faganeli, J., Horvat, M., Brambati, A., 2001. Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic Sea). Appl. Geochem. 16, 541–558.
D. Lgs. 152/2006, 14 April 2006. Decreto Legislativo n. 152 “Norme in materia ambientale.”. 88 Gazzetta Ufficiale Repubblica Italiana.
Dizdarevič, T., 2001. The influence of mercury production in Idrija mine on the environment in the Idrija region and over a board area. RMZ-Mater. Geoenviron. 48 (1), 56.
Esbri, J.M., Bernaus, A., Ávila, M., Kocman, D., García-Noguero, E.M., Guerrero, B., Gaona, X., Álvarez, R., Perez-Gonzales, G., Valiente, M., Higueras, P., Horvat, M., Loredo, J., 2010. XANES speciation of mercury in three mining districts – Almadén, Asturias (Spain), Idria (Slovenia). J. Synchrotron Radiat. 17, 179–186.
Fantozzi, L., Ferrara, R., Dini, F., Tamburello, L., Pirrone, N., Sprovieri, F., 2013. Study of the reduction of atmospheric mercury emissions from mine waste enriched soils through native grass cover in the Mt. Amiata region of Italy. Environ. Res. 125, 69–74.
Funiciello, R., Parotto, M., Praturlon, A., 1981. Carta tettonica d'Italia, scala 1:500.000: Schema preliminare. CNR, Roma.
García-Ordiales, E., Loredo, J., Esbrí, J.M., Lominchar, M.A., Milán, R., Higueras, P.L., 2014. Stream bottom sediments as a mean to assess metal contamination in the historic mining district of Almadén (Spain). Int. J. Min. Reclam. Environ. 28 (6), 377–388.
García-Ordiales, E., Esbrí, J.M., Covelli, S., López-Berdoneces, M.A., Higueras, P.L., Loredo, J., 2016. Heavy metal contamination in sediments of an artificial reservoir impacted by long- term miming activity in the Almadén mercury district (Spain). Environ. Sci. Pollut. Res. 23, 6024–6638.
Gasparrini, M., Ruggieri, G., Brogi, A., 2013. Diagenesis versus hydrothermalism and fluid–rock interaction within the Tuscan Nappe of the Monte Amiata CO_2-rich geothermal area (Italy). Geofluids 13, 159–179.
Gosar, M., 2008. Mercury in river sediments, floodplains and plants growing thereon in drainage area of Idrija mine, Slovenia. Pol. J. Environ. Stud. 17, 227–236.
Gosar, M., Čar, J., 2006. Influence of mercury ore roasting sites from sixteenth and seventeenth century on the mercury dispersion in surroundings of Idrija. Geologija 49, 91–101.
Gosar, M., Teršič, T., 2015. Contaminated sediment loads from ancient mercury ore roasting sites, Idrija area, Slovenia. J. Geochem. Explor. 149, 97–105.
Gosar, M., Žibret, G., 2011. Mercury contents in vertical profiles through alluvial sediments as reflection of mining in Idrija (Slovenia). J. Geochem. Explor. 110, 81–91.
Gosar, M., Pirc, S., Bidovec, M., 1997. Mercury in the Idrijca River sediments as a reflection of mining and smelting activities of the mercury mine Idrija. J. Geochem. Explor. 58, 125–131.
Graf, W.L., 1990. Fluvial dynamics of thorium-230 in the Church Rock event, Puerco River, New Mexico. Assoc. Am. Geogr. Ann. 80, 327–342.
Graf, W.L., Clark, S.A., Kammerer, M.T., Lehman, T.W., Randall, K., Schroeder, R., 1991. Geomorphology of heavy metals in the sediments of Queen Creek,Arizona, USA. Catena 18, 567–582.
Gray, J.E., Hines, M., Higueras, P.L., Adatto, I., Lasorsa, B., 2004. Mercury speciation and microbial transformations in mine wastes, stream sediments, and surface waters at the Almaden Mining District, Spain. Environ. Sci. Technol. 38, 4285–4292.
Gray, J.E., Plumlee, G.S., Morman, S.A., Higueras, P.L., Crock, J.G., Lowers, H.A., Witten, M.L., 2010. In vitro studies evaluating leaching of mercury from mine waste calcine using simulated human body fluids. Environ. Sci. Technol. 44, 4782–4788.
Gray, J.E., Rimondi, V., Costagliola, P., Vaselli, O., Lattanzi, P., 2014. Long-distance transport of Hg, Sb, and As from a mined area, conversion of Hg to methyl-Hg, and uptake of Hg by fish on the Tiber River basin, west-central Italy. Environ. Geochem. Health 36, 145–157.
Grygar, T.M., Elznicová, J., Kiss, T., Smith, H.G., 2016. Using sedimentary archives to reconstruct pollution history and sediment provenance: the Ohře River, Czech Republic. Catena 144, 109–129.
Grygar, T.M., Elznicová, J., Lelková, T., Kiss, T., Balogh, M., Strnad, L., Navrátil, T., 2017. Sedimentary archive of contamination in the confined channel of the Ohře River, Czech Republic. J. Soils Sed. 17, 2596–2609.
Gurnell, A.M., Belletti, B., Bizzi, S., Blamauer, B., Braca, G., Buijse, A.D., Bussettini, M., Camenen, B., Comiti, F., Demarchi, L., García De Jalón, D., González Del Tánago, M., Grabowski, R.C., Gunn, I.D.M., Habersack, H., Hendriks, D., Henshaw, A., Klösch, M., Lastoria, B., Latapie, A., Marcinkowski, P., Martínez-Fernández, V., Mosselman, E., Mountford, J.O., Nardi, L., Okruszko, T., O'Hare, M.T., Palma, M., Percopo, C., Rinaldi, M., Surian, N., Van de Bund, W., Weissteiner, C., Ziliani, L., 2016. A multiscale hierarchical framework for developing understanding of river behaviour. Aquat. Sci. 78, 1–16.
Hughes, M.L., McDowell, P.F., Marcus, W.A., 2006. Accuracy assessment of georectified aerial photographs: implications for measuring lateral channel movement in a GIS. Geomorphology 74, 1–16.
Hurley, R.R., Rothwell, J.J., Woodward, J.C., 2017. Metal contamination of bed sediments in the Irwell and Upper Mersey catchments, northwest England: exploring the legacy of industry and urban growth. J. Soils Sediments 17, 2648–2665.
Hylander, L.D., Meili, M., 2003. 500 years of mercury production: global annual inventory by region until 2000 and associated emissions. Sci. Total Environ. 304, 13–27.
Klemm, D.D., Neumann, N., 1984. Ore-controlling factors in the Hg-Sb province of southern Tuscany, Italy. In: Syngenesis and Epigenesis in the Formation of Mineral Deposits. Springer, pp. 482–503.
Lafhaj, Z., Samara, M., Agostini, F., Boucard, L., Skoczylas, F., Depelsenaire, G., 2008. Polluted river sediments from the North region of France: treatment with Novosol® process and valorization in clay bricks. Constr. Build. Mater. 22, 755–762.
Lattanzi, P., Rimondi, V., Chiarantini, L., Colica, A., Benvenuti, M., Costagliola, P., Ruggieri, G., 2017. Mercury dispersion through streams draining the Mt. Amiata district, southern Tuscany, Italy. Procedia Earth Planet. Sci. 17, 468–471.
Lecce, S.A., Pavlowsky, R.T., 1997. Storage of mining-related zinc in floodplain sediments, Blue River, Wisconsin. Phys. Geogr. 18, 424–439.
Lewin, J., Macklin, M.G., 1987. Metal mining and floodplain sedimentation in Britain. In: Gardiner, V. (Ed.), International Geomorphology 1986 Part I. John Wiley & Sons Ltd, pp. 1009–1027.
Lewin, J., Davies, B.E., Wolfenden, P.J., 1977. Interactions between channel change and historic mining sediments. In: Gregory, K.J. (Ed.), River Channel Changes. Wiley, Chichester, pp. 353–367.
Liébault, F., Piégay, H., 2002. Causes of 20th century channel narrowing in Mountain and Piedmont Rivers of southeastern France. Earth Surf. Proc. Landf. 27, 425–444.
Liébault, F., Lallias-Tacon, S., Cassel, M., Talaska, N., 2013. Long profile responses of alpine braided rivers in SE France. River Res. Appl. 29 (10), 1253–1266.
Liotta, D., 1994a. Carta Geologica del Settore Centro-Meridionale del bacino di Radicofani (provincia di Siena). Dipartimento Sci. Terra UNISI (Geological Map (1:25.000)).
Liotta, D., 1994b. Structural features of the Radicofani basin along the Piancastagnaio (M.Amiata). San Casciano dei Bagni (Monte Cetona) cross section. Mem. Soc. Geol. Ital. 48, 401–408.
Liotta, D., 1996. Analisi del settore centro-meridionale del Bacino pliocenico di Radicofani. Boll. Soc. Geol. Ital. 115, 115–143.
Liotta, D., Salvatorini, G.F., 1994. Evoluzione sedimentaria e tettonica della parte centro meridionale del Bacino pliocenico di Radicofani. Studi Geol. Camerti 1, 65–77.
Macklin, M.G., 1992. Metal contaminated soils and sediment: a geographical perspective. In: Newson, M.D. (Ed.), Managing the Human Impact on the Natural Environment: Patterns and Processes. Belhaven Press, London, pp. 174–195.
Macklin, M.G., 1996. Fluxes and storage of sediment-associated heavy metals in floodplain systems: assessment and river basin management issues at a time of rapid environmental change. In: Anderson, M.G., Walling, D.E., Bates, P.D. (Eds.), Floodplain Processes. Wiley, Chichester, pp. 441–460.
Macklin, M.G., Brewer, P.A., Balteanu, D., Coulthard, T.J., Driga, B., Howard, A.J., Zaharia, S., 2003. The long term fate and environmental significance of contaminant metals released by the January and March 2000 mining tailings dam failures in Maramureş County, upper Tisa Basin, Romania. Appl. Geochem. 18, 241–257.
Macklin, M.G., Brewer, P.A., Hudson-Edwards, K.A., Bird, G., Coulthard, T.J., Dennis, I.A., Lechler, P.J., Miller, J.R., Turner, J.N., 2006. A geomorphological approach to the management of rivers contaminated by metal mining. Geomorphology 79, 423–447.
Mancini, M., Girotto, O., Cavinato, G.P., 2004. Il Pliocene e il Quaternario della media valle del Tevere (Appennino Centrale). Geol. Romana 37, 175–236.
Marroni, M., Moratti, G., Costantini, A., Conticelli, S., Benvenuti, M.G., Pandolfi, L., Bonini, M., Cornamusini, G., Laurenzi, M.A., 2015. Geology of the Monte Amiata region, Southern Tuscany, Central Italy. Ital. J. Geosci. 134, 171–199.
Martin, J.M., Maybeck, M., 1979. Elemental mass balance of material carried by major world rivers. Mar. Chem. 7, 173–206.
Mascaro, I., Guideri, S., Benvenuti, M., 1991. Inventario del patrimonio minerario e mineralogico in Toscana. Aspetti naturalistici e storico-archeologici. Edizioni della Giunta Regionale Toscana, 2, I–II. (240 pp).
Miklavčič, V., 1999. Mercury in the town of Idrija (Slovenia) after 500 years of mining and smelting. In: Ebinghaus, R., Turner, R.R., Lacedra, L.D., Vasiljev, O., Salomons, W. (Eds.), Mercury Contaminated Sites. Springer-Verlag, Berlin, pp. 70–259.
Miller, J.R., 1997. The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites. J. Geochem. Explor. 58, 101–118.
Miller, J., Barr, R., Grow, D., Lechler, P., Richardson, D., Waltman, K., Warwick, J., 1999. Effects of the 1997 flood on the transport and storage of sediment and mercury within the Carson River valley, West-Central Nevada. J. Geol. 107, 313–327.
Mlakar, I., 1974. An outline of production of the Idrija mercury mine trough the century. Idrijski razgledi 19, 1–40.
Molli, G., 2008. Northern Apennine-Corsica orogenic system: an updated review. Geol. Soc. Lond. Spec. Publ. 298, 413–442.
Morteani, G., Ruggieri, G., Möller, P., Preinfalk, C., 2011. Geothermal mineralized scales in the pipe system of the geothermal Piancastagnaio power plant (Mt. Amiata geothermal area): a key to understand the stibnite, cinnabarite and gold mineralization of Tuscany (central Italy). Mineral. Deposita 46, 197–210.
Nardi, L., Rinaldi, M., 2015. Spatio-temporal patterns of channel changes in response to a major flood event: the case of the Magra River (central-northern Italy). Earth Surf. Process. Landf. 40, 326–339.
Owens, P.N., Batalla, R.J., Collins, A.J., Gomez, B., Hicks, D.M., Horowitz, A.J., Kondolf, G.M., Marden, M., Page, M.J., Peacock, D.H., Petticrew, E.L., Salomons, W., Trustrum, N.A., 2005. Fine-grained sediment in river systems: environmental significance and management issues. River Res. Appl. 21, 693–717.
Pattelli, G., Rimondi, V., Benvenuti, M., Chiarantini, L., Colica, A., Costagliola, P., Di Benedetto, F., Lattanzi, P., Paolieri, M., Rinaldi, M., 2014. Effects of the November 2012 flood event on the mobilization of Hg from the Mount Amiata Mining District to the sediments of the Paglia River Basin. Fortschr. Mineral. 4, 241–256.
Rajar, R., Cetina, M., Horvat, M., Žagar, D., 2007. Mass balance of mercury in the Mediterranean Sea. Mar. Chem. 107, 89–102.
Rhoades, E.L., O'Neal, M.A., Pizzuto, J.E., 2009. Quantifying bank erosion on the South River from 1937 to 2005, and its importance in assessing Hg contamination. Appl. Geogr. 29, 125–134.
Rimondi, V., 2013. Distribution of Mercury and Other Trace Elements in the Mt. Amiata Region (Southern Tuscany, Italy). Ph.D. Thesis. Università di Firenze, pp. 179.
Rimondi, V., Gray, J.E., Costagliola, P., Vaselli, O., Lattanzi, P., 2012. Concentration, distribution, and translocation of mercury and methylmercury in mine-waste, sediment, soil, water, and fish collected near the Abbadia San Salvatore mercury mine,

Monte Amiata district, Italy. Sci. Total Environ. 414, 318–327.
Rimondi, V., Bardelli, F., Benvenuti, M., Costagliola, P., Gray, J.E., Lattanzi, P., 2014a. Mercury speciation in the Mt. Amiata mining district (Italy): interplay between urban activities and mercury contamination. Chem. Geol. 328, 110–118.
Rimondi, V., Costagliola, P., Gray, J.E., Lattanzi, P., Nannucci, M., Paolieri, M., Salvadori, A., 2014b. Mass loads of dissolved and particulate mercury and other trace elements in the Mt. Amiata mining district, southern Tuscany (Italy). Environ. Sci. Pollut. Res. 21, 5575–5585.
Rimondi, V., Chiarantini, L., Lattanzi, P., Benvenuti, M., Beutel, M., Colica, A., Costagliola, P., Di Benedetto, F., Gabbani, G., Gray, J.E., Pandeli, E., Pattelli, G., Paolieri, M., Ruggieri, G., 2015. Metallogeny, exploitation and environmental impact of Mt. Amiata mercury ore district (Southern Tuscany, Italy). Ital. J. Geosci. 134, 323–336.
Rinaldi, M., 2003. Recent channel adjustments in alluvial rivers of Tuscany, Central Italy. Earth Surf. Process. Landf. 28 (6), 587–608.
Rinaldi, M., Simoncini, C., Piégay, H., 2009. Scientific design strategy for promoting sustainable sediment management: the case of the Magra river (Central-Northern Italy). River Res. Appl. 25, 607–625.
Rinaldi, M., Surian, N., Comiti, F., Bussettini, M., 2013. A method for the assessment and analysis of the hydromorphological condition of Italian streams: the morphological quality index (MQI). Geomorphology 180-181, 96–108.
Rinaldi, M., Surian, N., Comiti, F., Bussettini, M., 2015. A methodological framework for hydromorphological assessment, analysis and monitoring (IDRAIM) aimed at promoting integrated river management. Geomorphology 251, 122–136.
Rinaldi, M., Gurnell, A.M., Gonzalez del Tanago, M., Bussettini, M., Hendriks, D., 2016. Classification of river morphology and hydrology to support management and restoration. Aquat. Sci. 78, 17–33.
Rytuba, J.J., 2003. Mercury from mineral deposits and potential environmental impact. Environ. Geol. 43, 326–338.
Salomons, W., Forstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag, Berlin, Germany.
Scorpio, V., Rosskopf, C.M., 2016. Channel adjustments in a Mediterranean river over the last 150 years in the context of anthropic and natural controls. Geomorphology 275, 90–104.
Scorpio, V., Aucelli, P.P.C., Giano, I., Pisano, L., Robustelli, G., Rosskopf, C.M., Schiattarella, M., 2015. River channel adjustment in southern Italy over the past 150 years and implications for channel recovery. Geomorphology 251, 77–90.
Smith, R.S., Wiederhold, J.G., Jew, A.D., Brown Jr., G.E., Bourdon, B., Kretzschmar, R., 2014. Small-scale studies of roasted ore waste reveal extreme ranges of stable mercury isotope signatures. Geochim. Cosmochim. Acta 137, 1–17.
Strappa, O., 1977. Storia delle miniere di mercurio del Monte Amiata. L'Industria Mineraria XXVIII. 4. pp. 252–259 (5, pp. 336–348; 6, 433–439).
Surian, N., Rinaldi, M., 2003. Morphological response to river engineering and management in alluvial channels in Italy. Geomorphology 50, 307–326.
Surian, N., Rinaldi, M., Pellegrini, L., Audisio, C., Maraga, F., Teruggi, L., Turitto, O., Ziliani, L., 2009. Channel adjustments in northern and central Italy over the last 200 years. Geol. Soc. Am. Spec. Pap. 451, 83–95.
Tanelli, G., 1983. Mineralizzazioni metallifere e minerogenesi della Toscana. Mem. Soc. Geol. Ital. 25, 91–109.
Teršič, T., Gosar, M., Biester, H., 2011a. Environmental impact of ancient small-scale mercury ore processing at Pšenk on soil (Idrija, Slovenia). Appl. Geochem. 3, 1–10.
Teršič, T., Gosar, M., Biester, H., 2011b. Distribution and speciation of mercury ore processing in soil in the ancient mercury ore roasting site, Frbejžene trate (Idrija area, Slovenia). J. Geochem. Explor. 110, 136–145.
Teršič, T., Gosar, M., Biester, H., 2014. Leaching of mercury from soil at extremely contaminated historical roasting sites (Idrija area, Slovenia). Geoderma 226 (227), 213–222.
Winterbottom, S.J., 2000. Medium and short-term channel planform changes on the Rivers Tay and Tummel, Scotland. Geomorphology 34, 195–208.
www.mindat.org. Accessed Jan. 2, 2018.
www.parcoamiata.com. Accessed Jan. 2, 2018.
Žibret, G., Gosar, M., 2006. Calculation of mercury accumulation in the Idrijca River alluvial plain sediments. Sci. Total Environ. 368, 291–297.